

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/279853894>

Luminescent Ce(III) Complexes as Stoichiometric and Catalytic Photo-reductants for Halogen Atom Abstraction Reactions

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JULY 2015

Impact Factor: 12.11 · DOI: 10.1021/jacs.5b05411

READS

28

4 AUTHORS, INCLUDING:



Haolin Yin

University of Pennsylvania

14 PUBLICATIONS 64 CITATIONS

SEE PROFILE



Eric J Schelter

University of Pennsylvania

104 PUBLICATIONS 1,877 CITATIONS

SEE PROFILE

Communication

Luminescent Ce(III) Complexes as Stoichiometric and Catalytic Photo-reductants for Halogen Atom Abstraction Reactions

Haolin Yin, Patrick J. Carroll, Jessica M. Anna, and Eric J. Schelter

J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 07 Jul 2015

Downloaded from <http://pubs.acs.org> on July 7, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Publications
High quality. High impact.

Luminescent Ce(III) Complexes as Stoichiometric and Catalytic Photo-reductants for Halogen Atom Abstraction Reactions

Haolin Yin, Patrick J. Carroll, Jessica M. Anna* and Eric J. Schelter*

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34 Street, Philadelphia, Pennsylvania 19104, United States

Supporting Information Placeholder

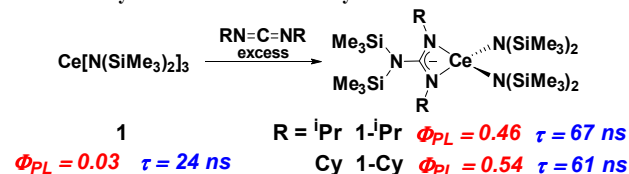
ABSTRACT: Luminescent Ce(III) complexes, $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ (**1**) and $[(\text{Me}_3\text{Si})_2\text{NC}(\text{RN})_2]\text{Ce}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{R} = {}^i\text{Pr}$, **1- ^iPr** ; $\text{R} = \text{Cy}$, **1-Cy**), with C_{3v} and C_{2v} solution symmetries display absorptive $4f \rightarrow 5d$ electronic transitions in the visible region. Emission bands are observed at 553, 518 and 523 nm for **1**, **1- ^iPr** and **1-Cy** with lifetimes of 24, 67 and 61 ns, respectively. Time-dependent density functional theory (TD-DFT) studies on **1** and **1- ^iPr** revealed the ${}^2\text{A}_1$ excited states corresponded to singly occupied $5d^2$ orbitals. The strongly reducing metalloradical character of **1**, **1- ^iPr** and **1-Cy** in their ${}^2\text{A}_1$ excited states afforded photochemical halogen atom abstraction reactions from sp^3 and sp^2 C–X ($\text{X} = \text{Cl}$, Br , I) bonds for the first time with a lanthanide cation. The dehalogenation reactions could be turned over with catalytic amounts of photosensitizers by coupling salt metathesis and reduction to the photo-promoted atom abstraction reactions.

In photoredox chemistry the energy of visible light, especially of high energy blue light (440 nm, 2.8 eV), is absorbed by photosensitizers and converted into redox power for reactivity. Current molecular photosensitizers including $\text{Ru}^{\text{II}}(\text{bpy})^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine),¹ $\text{fac-Ir}^{\text{IV}}(\text{ppy})^+$ ($\text{ppy} = 2,2'$ -phenylpyridine),² tungsten(0) isocyanides,³ $\text{Cu}(\text{I})$ complexes⁴ and organic dyes,⁵ accomplish photoredox reactions exclusively through outer sphere electron transfer processes. Photoreductants activate substrates under mild conditions and have drawn interests in catalysis.⁶ For example, in catalytic oxidative quenching cycles,^{6d} electrons are transferred from excited-state photosensitizers to acceptors to effect chemical changes. Anti-bonding orbitals of C–X ($\text{X} = \text{Cl}$, Br , I) bonds are one such target, leading to reductive C–X bond cleavage. In such cases, the scope of accessible substrates containing C–X bonds depends solely on the excited state reduction potential of the photosensitizer.⁷

In contrast to outer sphere processes, we hypothesized that favourable M–X bond formation enthalpies could be coupled with metal redox power in an inner sphere electron transfer process, providing additional driving force for the activation of substrates. An inner sphere photosensitizer would require the association of C–X bonds to a metal cation in its excited state. As such, highly electrophilic f-block cations are excellent candidates for such reactivity. Herein, we report the use of luminescent Ce(III) complexes as inner sphere photoreductants for C–X bond activation. Cerium(III) is a redox active cation.⁸ With its single 4f electron, Ce(III) complexes have simple, well-defined electronic structures featuring ${}^2\text{F}_{5/2}$ ground states. In fact, reported luminescence of

Ce^{3+} cations originates from $5d \rightarrow 4f$ transitions,⁹ distinct from most other Ln^{3+} cations where $4f \rightarrow 4f$ transitions underlie optical properties. The inter-configurational transition shows greater emission intensity but shorter lifetimes compared to other lanthanide cations; the $5d \rightarrow 4f$ transition is allowed both by parity and spin selection rules.¹⁰

Scheme 1. Synthesis of **1- ^iPr** and **1-Cy** from **1**



We noted that the common Ce(III) protonolysis reagent, $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ (**1**), emitted yellow light weakly under UV irradiation (365 nm). However, treatment of **1** with excess carbodiimides, $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ ($\text{R} = {}^i\text{Pr}$, Cy) afforded isolation of their mono-insertion products, **1- ^iPr** and **1-Cy** (Scheme 1), which were found to be bright green emitters. X-ray studies confirmed the yellow compounds **1- ^iPr** and **1-Cy** as the mono-guanidinate insertion products (Figure S3–S4). No further insertion was observed for **1- ^iPr** or **1-Cy** with excess carbodiimide to 80 °C.

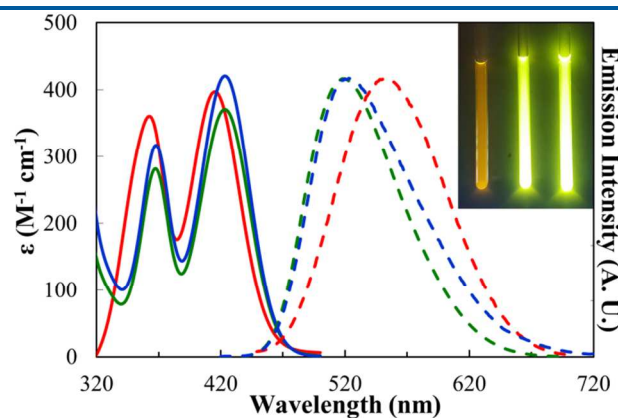


Figure 1. UV-vis electronic absorption spectra (solid lines) and normalized emission spectra (dashed lines) of **1** (red), **1- ^iPr** (green), **1-Cy** (blue) recorded in toluene. Pictures of C_6H_6 solution containing **1** (left), **1- ^iPr** (middle) and **1-Cy** (right) in Pyrex NMR tubes (1.0 mM) under UV irradiation (365 nm) (inset).

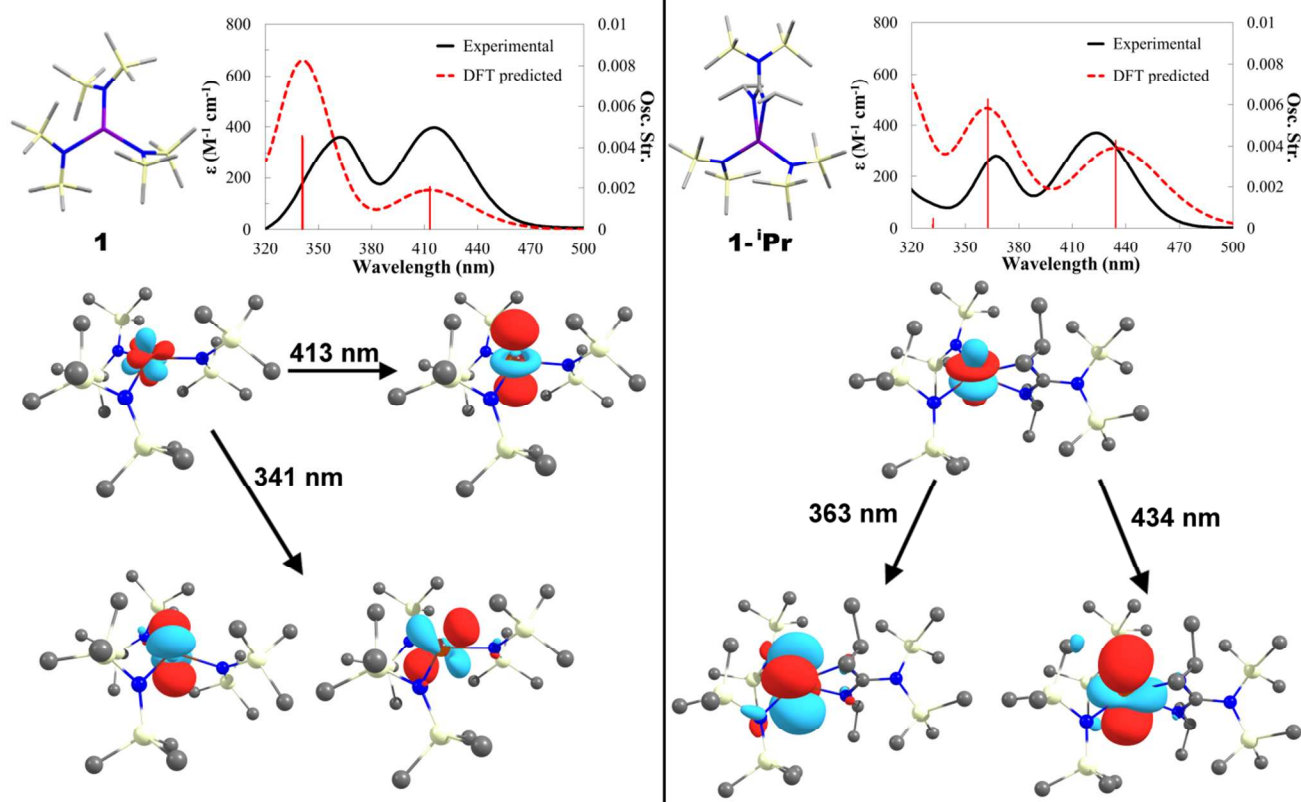


Figure 2. Experimental (black solid lines) and TD-DFT predicted (red dashed lines) absorption spectra of **1** (left) and **1-Pr** (right). The predicted spectra were rendered with FWHM 3000 cm^{-1} . Oscillator strengths for the electronic transitions are shown as red vertical lines. Stick representations of the crystal structures of **1** and **1-Pr** are shown to the left of the spectra. Natural transition orbitals (NTOs) are shown for the donor/acceptor orbitals of each transition.

Electronic absorption spectra of **1-Pr**, **1-Cy** resembled the spectrum of **1**, displaying two bands with $\epsilon \sim 300\text{--}400 \text{ M}^{-1} \text{ cm}^{-1}$ in the visible range attributed to $4f \rightarrow 5d$ transitions (Figure 1). The emission energies of **1-Pr** and **1-Cy** were blue shifted by *ca.* 30 nm compared to **1**, resulting in green luminescence. The guanidinate complexes **1-Pr** and **1-Cy** exhibited relatively high photoluminescence quantum yields: $\Phi_{\text{PL}} = 0.46$ and 0.54 for **1-Pr** and **1-Cy**, respectively, compared to **1**: $\Phi_{\text{PL}} = 0.03$. Consistent with the observation of low quantum yield is the short measured lifetime for **1** (24 ns) compared to **1-Pr** (67 ns) and **1-Cy** (61 ns). No variance of the lifetime was observed across the emission profiles for all complexes, suggesting the emissions originated from a single excited electronic state.^{10c} All emission spectra were deconvoluted into pairs of overlapping Gaussian bands (Figure S48–S50), consistent with the transitions from their emissive states to the ^2F ground manifold. The ^2F ground manifold is split by spin-orbital coupling into the $J = 5/2$ ground state and $J = 7/2$ excited states.^{9b} Excitation spectra collected at the emission maxima for **1**, **1-Pr**, **1-Cy** showed intense, overlapping bands with their lowest energy $4f \rightarrow 5d$ absorption bands at *ca.* 420 nm (Figure S45–S47), supporting the associated excited state as the long-lived emissive state.

In an effort to identify the frontier orbitals involved in the electronic transitions of **1**, **1-Pr** and **1-Cy**, time-dependent density functional theory (TD-DFT) calculations were performed for complexes **1** and **1-Pr**. The predicted vertical excitations and intensities were in reasonably good agreement with the experimental data, indicating two metal based $4f \rightarrow 5d$ transitions (Figure 2). Natural transition orbitals (NTOs)¹¹ analyses revealed the lowest energy transitions at *ca.* 420 nm for **1** and **1-Pr** were both

from ground states of primarily $4f$ character to $5d^2$ orbital-based excited states: $^2\text{A}_1$ in both the C_{3v} and C_{2v} point groups. The results are readily rationalized as the $5d^2$ orbitals are essentially non-bonding in both cases and therefore of the lowest in energy within the $5d$ -manifold.¹² The acceptor orbitals of the transition at 341 nm were found to be a degenerate set of $5d_{xz}$ and $5d_{yz}$ orbitals for **1**; such degeneracy is lost for the lower symmetry complex, **1-Pr**. The $^2\text{A}_1$ states were therefore assigned as the long-lived excited states for all three complexes. Additionally, a ligand-to-metal charge transfer (LMCT) absorption tail located below 320 nm for **1-Pr** was attributed by the TD-DFT result to a guanidinate non-bonding π_n orbital to $4f$ -orbital CT transition (Figure S78).

To evaluate the reduction potential of the Ce(III) upon photo-excitation, the excited state potentials ($E^*_{1/2}$) for the $^2\text{A}_1$ states were approximated using the ground state potentials ($E_{1/2}$) and emission band energies following the Rehn-Weller formalism:¹³

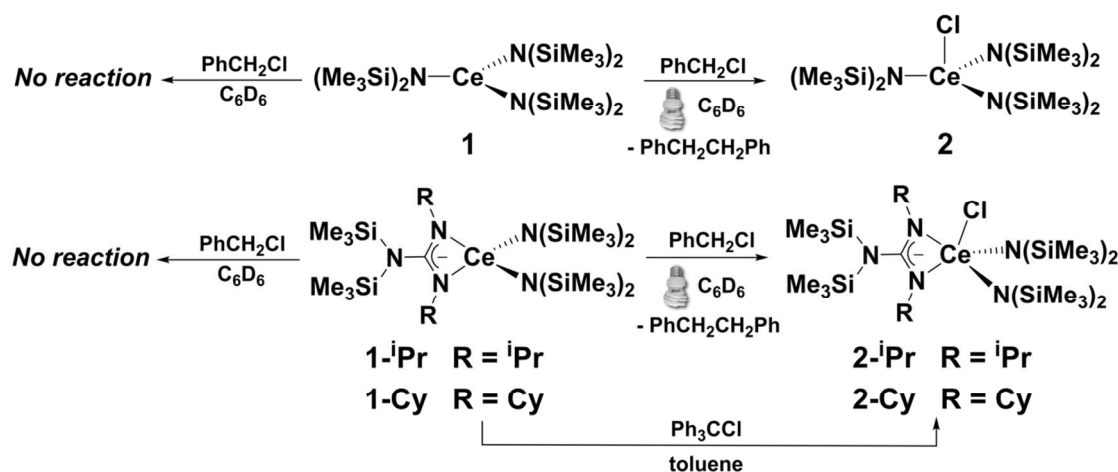
$$E^*_{1/2} = E_{1/2} - E_{0,0}$$

Cyclic voltammetry experiments on **1-Pr** and **1-Cy** in CH_2Cl_2 with 0.1 M $[\text{Pr}_4\text{N}][\text{BAR}^{\text{F}}_4]$ as supporting electrolyte revealed quasi-reversible $\text{Ce}^{\text{IV/III}}$ couples with $E_{1/2} = +0.03 \text{ V}$ and $+0.13 \text{ V}$ versus $\text{Cp}_2\text{Fe}^{+/0}$, respectively (Figure S54–S55). The electrochemical data of **1** in THF ($E_{1/2} = +0.35 \text{ V}$)¹⁴ was applied for its estimate of the excited state reduction potential because no feature

Table 1. Estimation of reduction potential for $\text{Ce(III)} \ ^2\text{A}_1$ excited states

	$E_{1/2}^a$ /eV	$E_{0,0}$ /eV	$E^*_{1/2}$ /eV
1	+ 0.35 ^b	+ 2.24	– 1.89
1-Pr	+ 0.03	+ 2.39	– 2.36
1-Cy	+ 0.13	+ 2.37	– 2.24

^aCyclic voltammetry in 0.1 M $[\text{Pr}_4\text{N}][\text{BAR}^{\text{F}}_4]/\text{CH}_2\text{Cl}_2$. ^bIn THF.

Scheme 2. Photo-induced oxidation of **1**, **1-ⁱPr** and **1-Cy** with PhCH₂Cl

was observed for **1** in CH₂Cl₂. The $E_{1/2}^*$ values were estimated to be -1.89, -2.36 and -2.24 V versus Cp₂Fe⁺⁰ for **1**, **1-ⁱPr** and **1-Cy**, respectively (Table 1), providing opportunities for accessing photo-reduction chemistry with Ce(III) complexes.

Based on the spectroscopic and electrochemical data, we hypothesized that combining the reducing power of the ²A₁ excited state and Ce(III)-X bond enthalpy would allow us to activate challenging C-X bonds photo-chemically through an inner sphere atom abstraction pathway. We choose PhCH₂Cl as a first target for activation since the cathodic reduction wave of PhCH₂Cl was reported at $E_{pc} = -2.66$ V versus Cp₂Fe⁺⁰ in DMF,¹⁵ lower than the -1.89 V estimated reduction potential for **1**^{*}. Thus, an outer sphere electron transfer process would not be expected to occur between **1**^{*} and PhCH₂Cl on thermodynamic grounds. Combinations of **1** and PhCH₂Cl showed no reaction in the absence of light. Irradiation of a C₆D₆ solution containing **1** with excess of PhCH₂Cl in a photoreactor equipped with 420 nm narrow band lamps led to a color change of the solution from yellow to dark red/purple within 5 min. The reaction also proceeded with commercially available compact fluorescent lamps (CFLs) as light sources. An ¹H NMR experiment showed the formation of Ce^{IV}Cl[N(SiMe₃)₂]₃ (**2**), concomitant with the generation of PhCH₂CH₂Ph (Scheme 2) through radical homo-coupling.

Similarly, photo-reactions of **1-ⁱPr** (or **1-Cy**) with excess PhCH₂Cl led to color changes from yellow to black (Scheme 2) and the production of PhCH₂CH₂Ph was confirmed by ¹H NMR spectroscopy. Also noted in the solution ¹H NMR spectra were sets of resonances for the Ce(IV)-Cl products, **2-ⁱPr** (or **2-Cy**). To confirm the assessments of the oxidation products, **2-ⁱPr** and **2-Cy**, were independently prepared from reactions of Ph₃C-Cl with **1-ⁱPr** and **1-Cy**. X-ray crystallography studies confirmed their identities as the Ce(IV)-Cl products (Figure S5-6). The black complexes **2-ⁱPr** and **2-Cy** are the first examples of κ²-guanidinate moieties coordinated to Ce(IV) cations; related cerium(III/IV) amidates and formamidinates have been reported.¹⁶ The black appearances of **2-ⁱPr** and **2-Cy** were evident in their UV-vis spectra, where both compounds were found to absorb evenly in the visible range, 400-800 nm (3.1-1.5 eV, Figure S42). TD-DFT calculations performed on **2-ⁱPr** afforded assignment of bands in the visible region as LMCT (Figure S89). The computed HOMO→LUMO excitation at 725 nm (1.71 eV) corresponded to a guanidinate non-bonding π orbital (π_n) to a 4f-orbital.

In all cases, the Ce(IV)-Cl products, **2**, **2-ⁱPr** and **2-Cy** were stronger absorbers than their Ce(III) congeners. As such, the Ce(IV) products in the reaction mixture inhibited the absorption of light by Ce(III) species and resulted in incomplete reactions. To avoid accumulation of Ce(IV) species we found NaN(SiMe₃)₂ could effectively reduce the Ce(IV)-Cl products to Ce(III) species with precipitation of NaCl and formation of aminyl radical: •N(SiMe₃)₂. However, under catalytic conditions with stoichiometric NaN(SiMe₃)₂, only a low yield (22% in Et₂O) of PhCH₂CH₂Ph was achieved, due to side-reactions of the aminyl radical with the starting material, PhCH₂Cl. Byproducts, including PhCH₂N(SiMe₃)₂ and PhCH₂CHClPh, were identified by ¹H NMR spectroscopy and GC-MS (See Figure S22, S30-34). To address these problems, Zn or Ce metal powders were introduced to the reaction mixtures as additives to quench the aminyl radical and afforded bibenzyl products in reasonable yields; control experiments showed slow background reactions of the metal powders with PhCH₂Cl (Scheme 3 and Table S1). Further controls demonstrated the metal powders reacted slowly with **2**; direction reaction of NaN(SiMe₃)₂ with **2** proceeded instantaneously.

The dehalogenation of PhCH₂Cl proceeded much slower with **1-ⁱPr** and **1-Cy** despite their longer lifetimes than **1**. This difference was attributed to steric congestion from the guanidinate ligands which disfavored coordination at the Ce(III) cation.

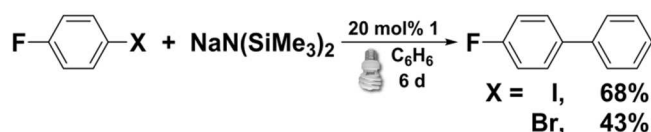
Scheme 3. PhCH₂Cl coupling reactions with Ce-metal as external reductant

$\text{Ph}-\text{CH}_2-\text{Cl} + \text{NaN}(\text{SiMe}_3)_2 \xrightarrow[\text{solvent, 48 h}]{10 \text{ mol\% } [\text{Ce}^{\text{III}}], 0.33 \text{ eq Ce}^0} \text{Ph}-\text{CH}_2-\text{CH}_2-\text{Ph}$			
Entry	[Ce ^{III}]	Solvent	Yield ^a /%
1	1	Et ₂ O	68
2	1-ⁱPr	Et ₂ O	17
3	1-Cy	Et ₂ O	10
4	-	Et ₂ O	5
5	1	C ₆ H ₆	45
6	1	TMS ₂ O	23
7	1	CPME	44
8	1	<i>n</i> -pentane	12
9	1	1,4-dioxane	19

a. Determined by ¹H NMR integration against internal standard CH₂Br₂.

We also reasoned that the aminyl radical could be harnessed for hydrogen atom abstraction reactions. This objective was achieved using more challenging substrates containing C(sp²)-X bonds. Irradiation of a 20 mol% solution of **1** with 4-F-C₆H₄X (X = I, Br) and NaN(SiMe₃)₂ in benzene at room temperature for 6 d afforded 1-(4-fluorophenyl)benzene in 68% and 43% isolated yields for X = I and Br, respectively (Scheme 4), while no reaction was observed for X = Cl (Figure S27). The identity of the biphenyl product was also confirmed by ¹⁹F NMR spectroscopy as well as high resolution mass spectroscopy (HRMS). The origin of the phenyl group was confirmed with the use of deuterobenzene as the reaction solvent; the molecular mass corresponding to 1-(4-fluorophenyl)-2,3,4,5,6-deuterobenzene was detected by HRMS (see Figure S29). Direct C(sp²)-H and C(sp²)-X coupling in the presence of catalytic 1,10-phenanthroline derivatives at elevated temperatures was reported recently by Shi and Hayashi,¹⁷ and were proposed to proceed through a single electron transfer (SET) mechanism. In our case, NMR-scale reactions of **1** with excess 4-F-C₆H₄Br in C₆D₆ revealed the formation of Ce^{IV}Br[N(SiMe₃)₂]₃.¹⁸ Therefore, the catalytic generation of the biphenyl products was rationalized through an S_{RN}1-type mechanism comprising: 1) photo-induced halogen abstraction from 4-F-C₆H₄Br by **1** leading to Ce^{IV}Br[N(SiMe₃)₂]₃ and 4-F-C₆H₄•; 2) addition of 4-F-C₆H₄• to benzene forming the radical adduct; 3) salt-metathesis and reduction of Ce^{IV}Br[N(SiMe₃)₂]₃ with NaN(SiMe₃)₂ to regenerate **1** and form •N(SiMe₃)₂; 4) hydrogen atom abstraction of the radical adduct by •N(SiMe₃)₂ to give the biphenyl product (See Scheme S2 for proposed catalytic cycle). These reactions were catalytic in **1** and demonstrated for the first time that an f-block complex could serve as an effective molecular photoredox catalyst.

Scheme 4. Catalytic arylations of benzene with ArX (X = I, Br)



Through combined spectroscopic and computational studies, we demonstrated luminescent Ce(III) complexes **1**, **1-ⁱPr** and **1-Cy** possess singly occupied 5d² orbitals in their long lived excited states. The metalloradical nature of the excited states allowed electrophilic cerium(III) complexes to act as photosensitizers that activated challenging substrates through inner sphere processes, taking advantage of the enthalpy gain in the formation of Ce(IV)-X bonds. A drawback in the current system is the relatively low absorptivity of Ce(III) complexes, which limits the catalytic turnover rates. Development of new sensitized cerium(III) photo-redox catalysts, expanded reactivity studies and physicochemical studies on cerium(III) luminescence characteristics are currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF), electrochemical data, electronic absorption data, excitation and emission data, computational details and optimization data for catalysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*jmananna@sas.upenn.edu, *schelter@sas.upenn.edu

ACKNOWLEDGMENT

We gratefully acknowledge the University of Pennsylvania and the National Science Foundation (CHE-1362854) for financial support. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by U.S. NSF grant number OCI-1053575. We thank the E. J. Petersson and S. J. Park groups at UPenn for use of their fluorimeters.

REFERENCES

- (1) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
- (2) Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Encinas, S.; Barigelli, F. *Chem. Soc. Rev.* **2000**, *29*, 385.
- (3) a) Sattler, W.; Ener, M. E.; Blakemore, J. D.; Rachford, A. A.; LaBeaume, P. J.; Thackeray, J. W.; Cameron, J. F.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2013**, *135*, 10614; b) Sattler, W.; Henling, L. M.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2015**, *137*, 1198.
- (4) a) Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 546; b) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030.
- (5) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. *Science* **2014**, *346*, 725.
- (6) a) Zeitler, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9785; b) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527; c) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102; d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322; e) Xi, Y.; Yi, H.; Lei, A. *Org. Biomol. Chem.* **2013**, *11*, 2387; f) Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433.
- (7) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4*, 854.
- (8) Piro, N. A.; Robinson, J. R.; Walsh, P. J.; Schelter, E. J. *Coord. Chem. Rev.* **2014**, *260*, 21.
- (9) a) Aspinall, H. C. *Chemistry of the f-Block Elements*; CRC Press, 2001, p 34; b) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley and Sons: West Sussex, U. K., 2006, p 61-77.
- (10) a) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Weeks, J. A.; Hunter, W. E.; Brittain, H. G. *Organometallics* **1986**, *5*, 1281; b) Hazin, P. N.; Bruno, J. W.; Brittain, H. G. *Organometallics* **1987**, *6*, 913; c) Hazin, P. N.; Lakshminarayan, C.; Brinen, L. S.; Kneé, J. L.; Bruno, J. W.; Streib, W. E.; Folting, K. *Inorg. Chem.* **1988**, *27*, 1393; d) Zheng, X.-L.; Liu, Y.; Pan, M.; Lü, X.-Q.; Zhang, J.-Y.; Zhao, C.-Y.; Tong, Y.-X.; Su, C.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 7399.
- (11) a) Tretiak, S.; Saxena, A.; Martin, R. L.; Bishop, A. R. *Chem. Phys. Lett.* **2000**, *331*, 561; b) Martin, R. L. *J. Chem. Phys.* **2003**, *118*, 4775.
- (12) a) Fieser, M. E.; MacDonald, M. R.; Krull, B. T.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2015**, *137*, 369; b) MacDonald, M. R.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2013**, *135*, 9857; c) Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *Chem. Sci.* **2015**, *6*, 517; d) MacDonald, M. R.; Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2013**, *135*, 13310.
- (13) a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259; b) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617.
- (14) Williams, U. J.; Robinson, J. R.; Lewis, A. J.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J. *Inorg. Chem.* **2014**, *53*, 27.
- (15) Grimshaw, J. *Electrochemical reactions and mechanisms in organic chemistry*; Elsevier Science B. V., 2000, p 99.
- (16) a) Dröse, P.; Hrib, C. G.; Edelmann, F. T. *J. Organomet. Chem.* **2010**, *695*, 1953; b) Dröse, P.; Crozier, A. R.; Lashkari, S.; Gottfriedsen, J.; Blaurock, S.; Hrib, C. G.; Maichle-Mössmer, C.; Schädle, C.; Anwänder, R.; Edelmann, F. T. *J. Am. Chem. Soc.* **2010**, *132*, 14046; c) Werner, D.; Deacon, G. B.; Junk, P. C.; Anwänder, R. *Chem. – Eur. J.* **2014**, *20*, 4426.
- (17) a) Shirakawa, E.; Itoh, K.-i.; Higashino, T.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 15537; b) Sun, C.-L.; Li, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2*, 1044; c) Li, H.; Sun, C.-L.; Yu, M.; Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Chem. – Eur. J.* **2011**, *17*, 3593; d) Sun, C.-L.; Gu, Y.-F.; Huang, W.-P.; Shi, Z.-J. *Chem. Commun.* **2011**, 47, 9813.
- (18) Williams, U. J.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2014**, *53*, 6338.

TOC

