Synthesis of Heterobimetallic Lanthanide Complexes Towards Functionalized Cerium(III) and Cerium(IV) Complexes and a Study of Their Redox Properties

Jee Eon Kim, Patrick J. Carroll and Eric J. Schelter*

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

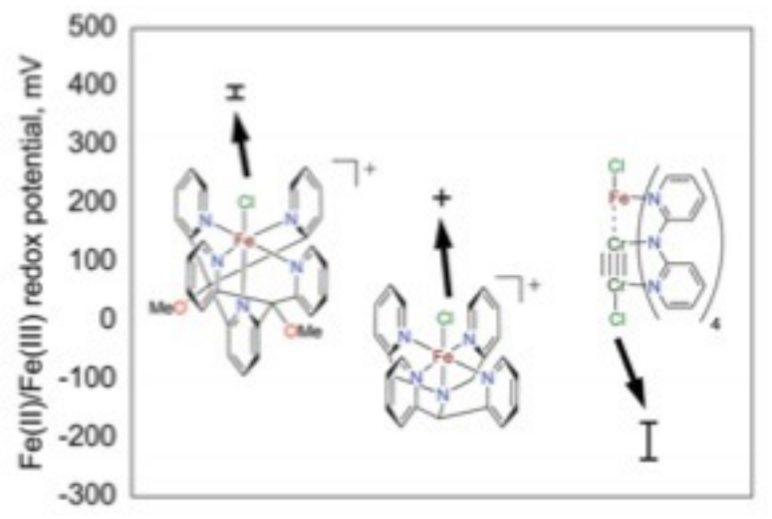
Abstract

The preparation of functionalized cerium(IV) complexes is an important goal because of the desirable properties of that ion for catalysis and for materials synthesis. The development of general and predictive oxidative functionalization chemistry for cerium(III) complexes has proven challenging and ligand reorganization has been suggested as a major determinant in these reactions. We have prepared a heterobimetallic lanthanide complexes, $Ce(OTf)(bdmmp)_3M$ (bdmmp = bis(dimethylamino)methyl-4-phenoxide; M = Na, K; OTf = SO_3CF_3) and evaluated its redox behavior. Investigation of functionalized cerium complexes with different alkali metals and the redox properties of the complexes will be presented.

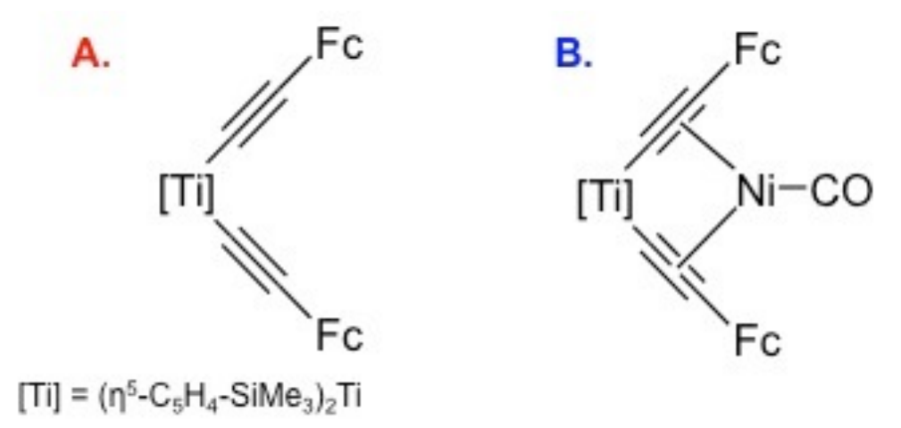
Robinson, J.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2012**, manuscript accepted

Motivation

Heterobimetallic Complexes in Transition Metal Chemistry

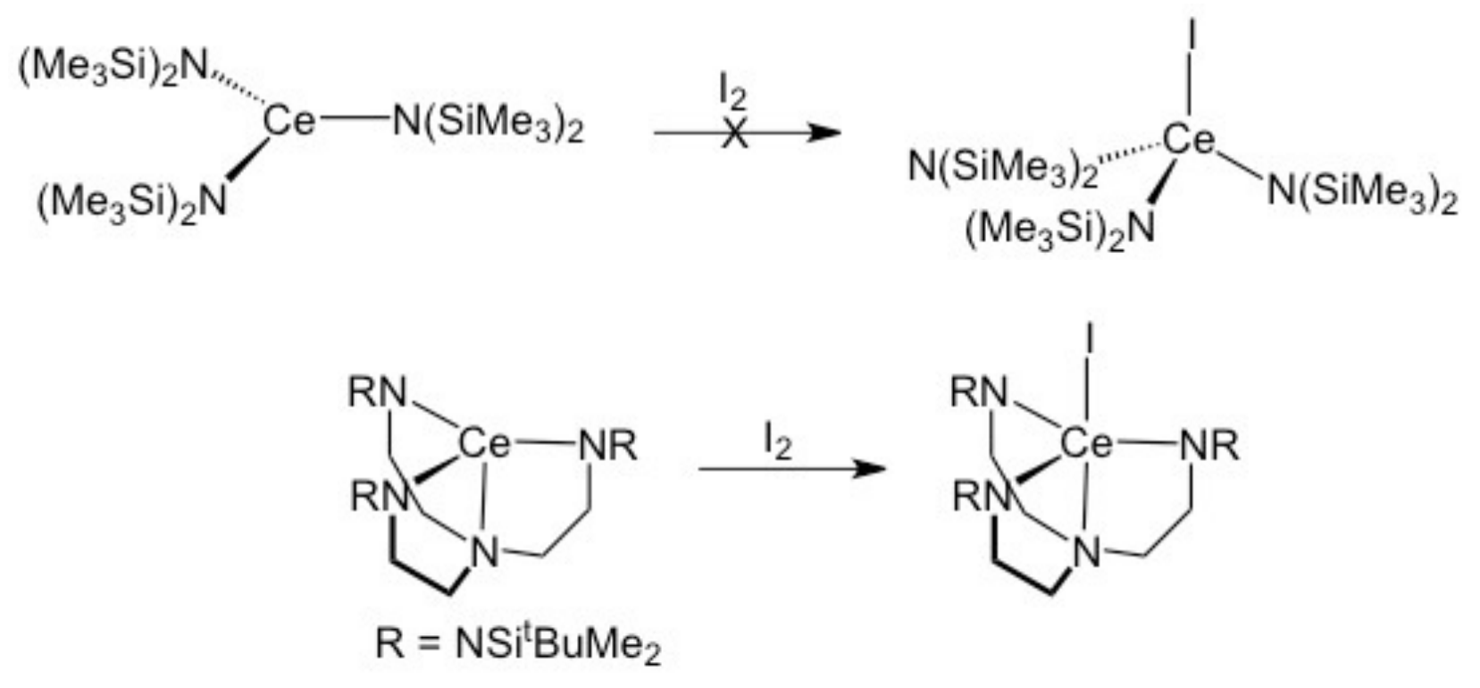


Left	Middle	Right
~400 mV	~200 mV	avg. –200 mV



	A	B
$Ti^{IV/III}$	–1.28 V	–1.83 V
E_{pc}	73 mV	84 mV
	2055 cm	1876 cm

Oxidation Chemistry of Ce(III)



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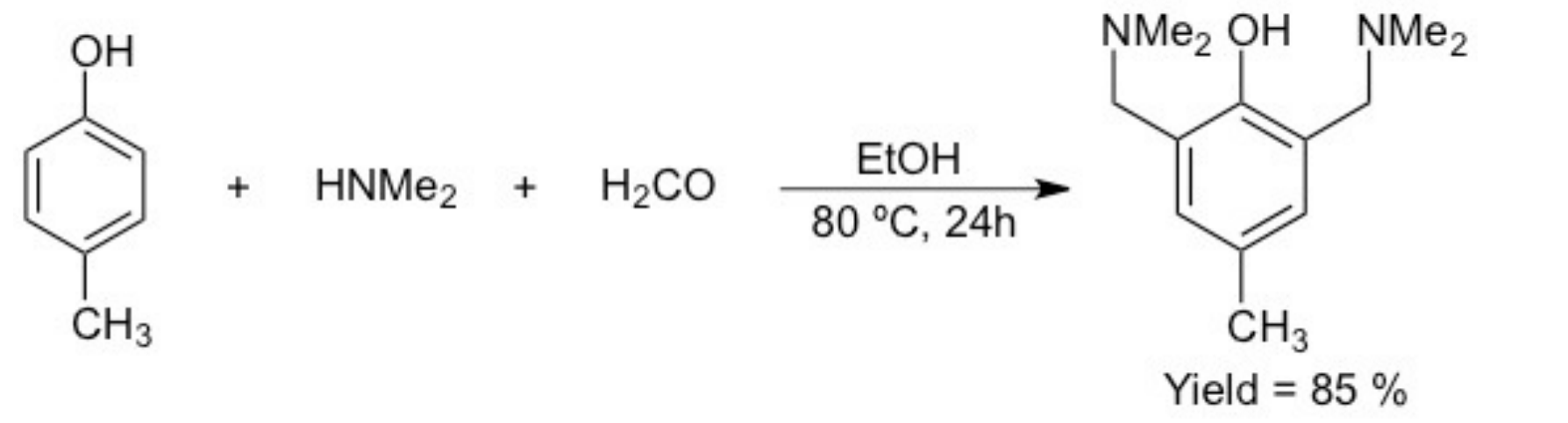
Ligand Synthesis



Bis(dimethylamino)methyl-4-phenol
(bdmmpH)

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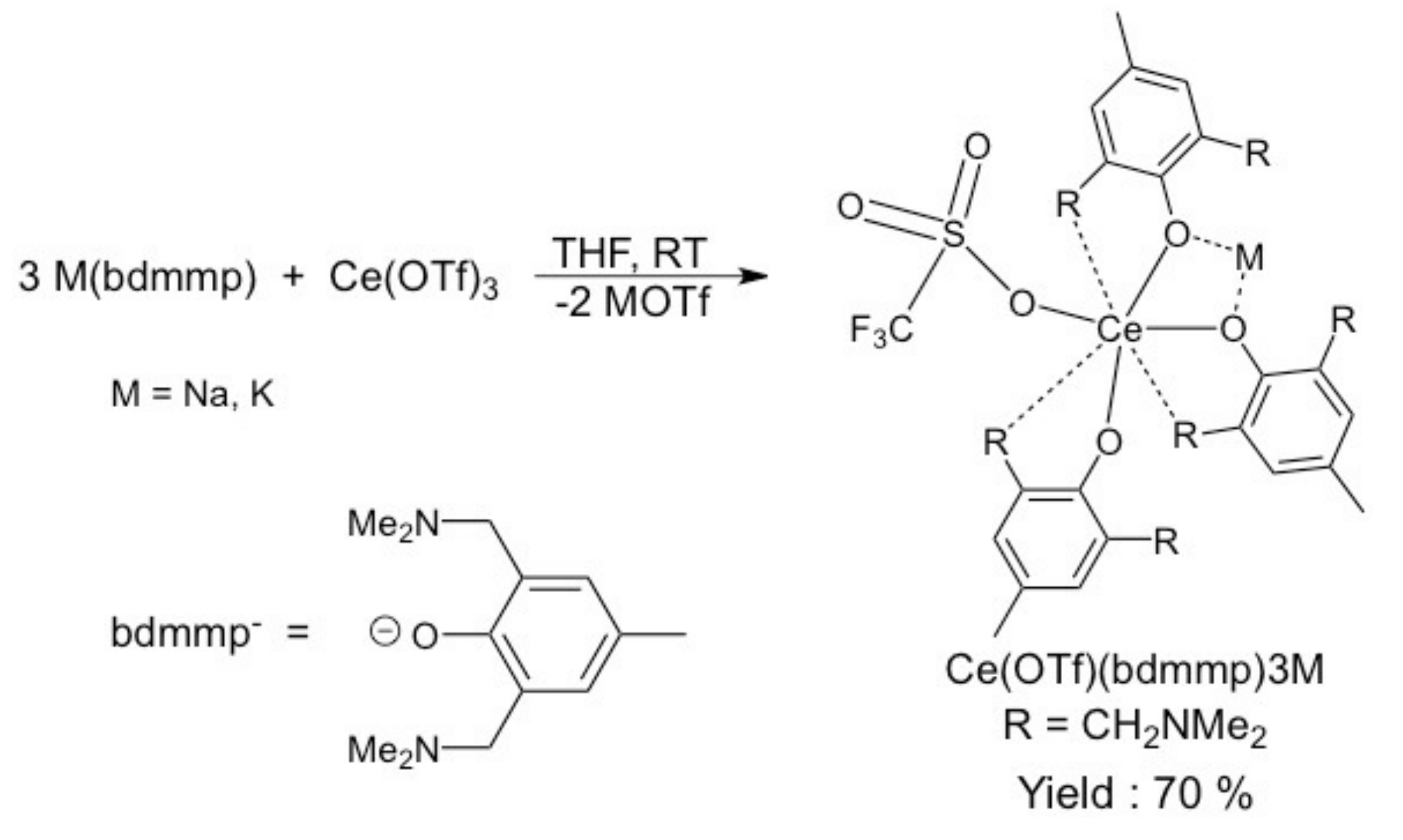
Synthesis of $Ce(OTf)(bdmmp)_3M$



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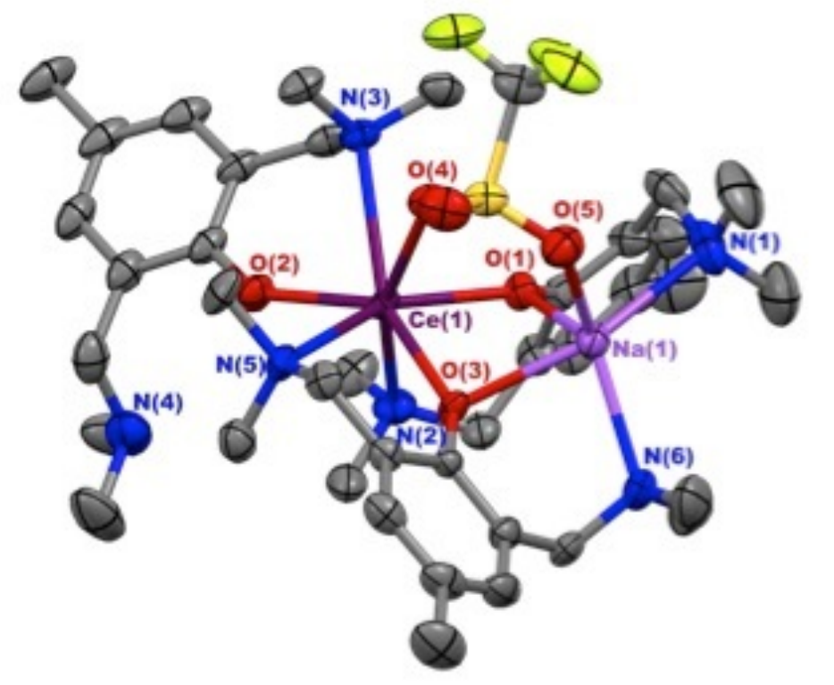
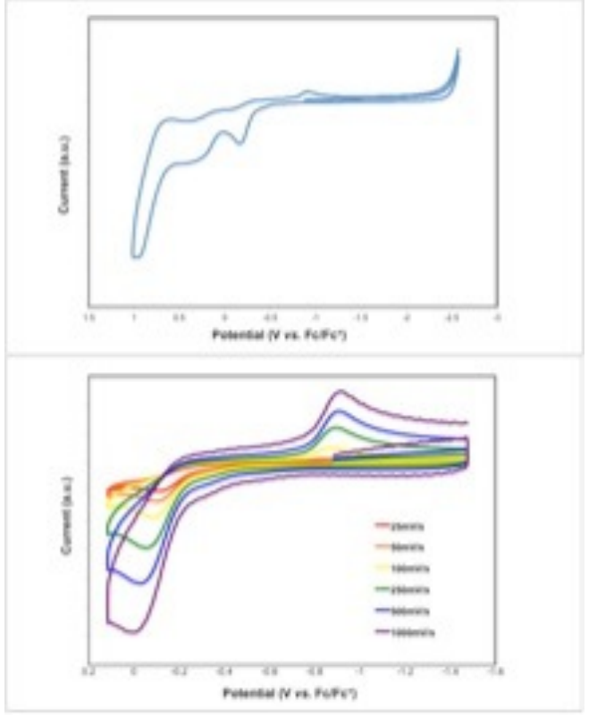
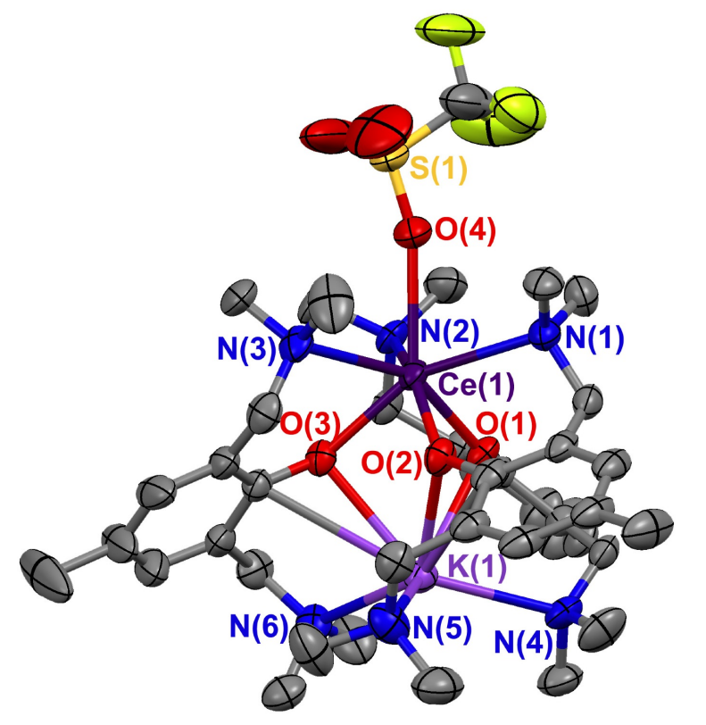


$Ce(OTf)(bdmmp)_3Na$

- Ce(1)-O(1) 2.310(3) Å
- Ce(1)-O(2) 2.280(3) Å
- Ce(1)-O(3) 2.316(3) Å
- Ce(1)-O_{OTf}(4) 2.571(4) Å
- Ce(1)-N(1) 2.703(3) Å
- Ce(1)-N(2) 2.715(4) Å
- Ce(1)-N(3) 2.729(3) Å





$Ce(OTf)(bdmmp)_3K$

- Ce(1)-O(1) 2.285(3) Å
- Ce(1)-O(2) 2.288(3) Å
- Ce(1)-O(3) 2.302(3) Å
- Ce(1)-O_{OTf}(4) 2.576(3) Å
- Ce(1)-N(1) 2.707(4) Å
- Ce(1)-N(2) 2.728(4) Å
- Ce(1)-N(3) 2.731(4) Å

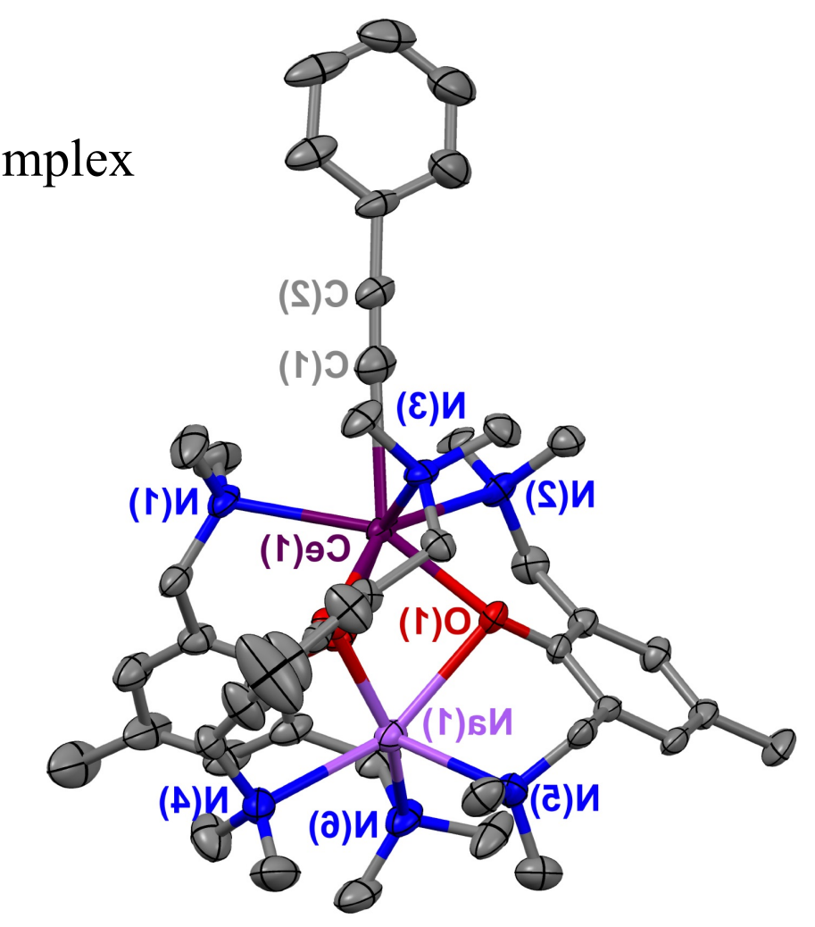
Functionalization of $Ce(OTf)(bdmmp)_3M$

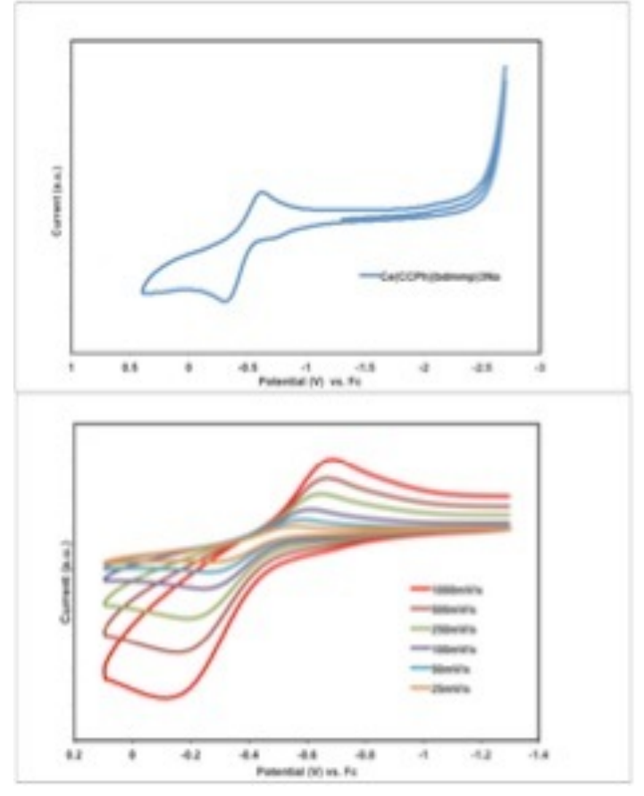
$$Ce(OTf)(bdmmp)_3Na + NaCCPh \xrightarrow[–Na(OTf)]{THF} Ce(CCPh)(bdmmp)_3Na$$

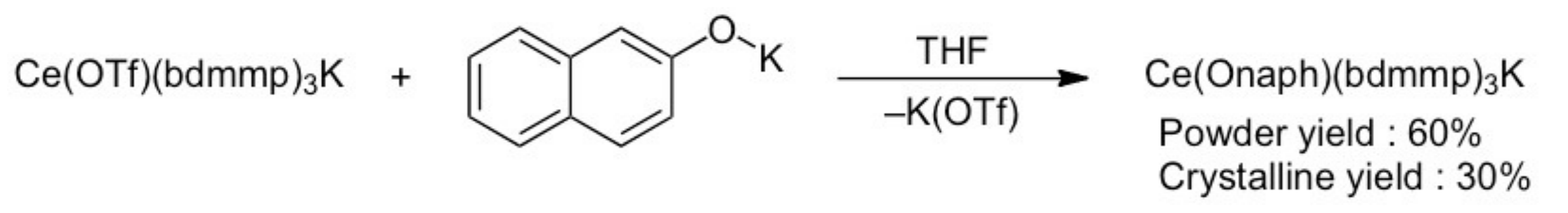
Powder yield : 60%
Crystalline yield : 20%

First cerium acetylide complex

- Ce(1)-O(1) 2.329(5) Å
- Ce(1)-O(2) 2.304(5) Å
- Ce(1)-O(3) 2.332(5) Å
- Ce(1)-C(1) 2.652(9) Å
- Ce(1)-N(1) 2.719(6) Å
- Ce(1)-N(2) 2.732(6) Å
- Ce(1)-N(3) 2.748(6) Å
- C(1)-C(2)   1.212(12) Å

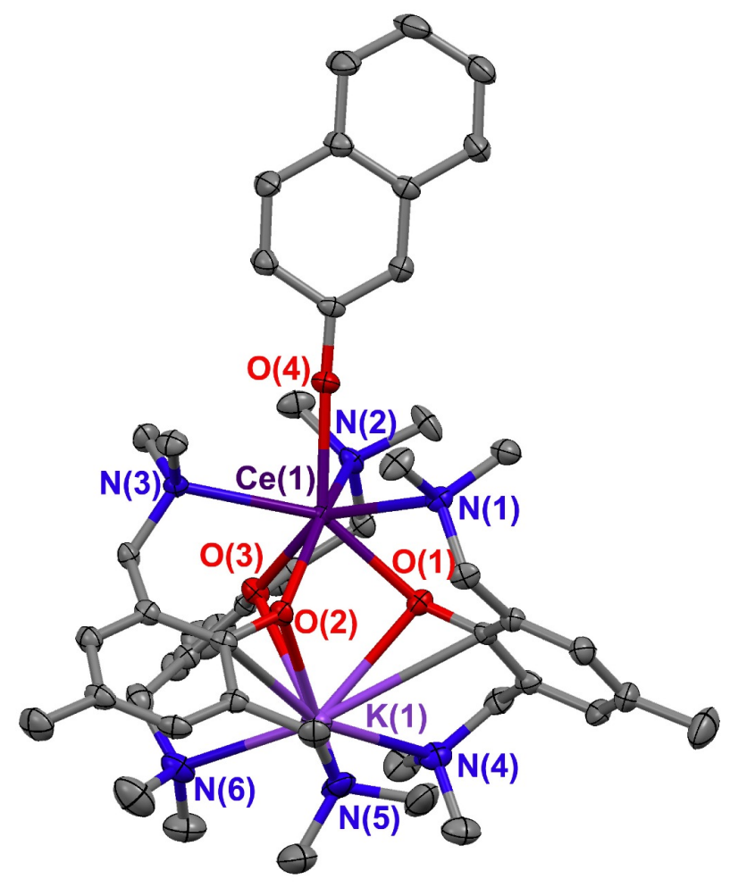


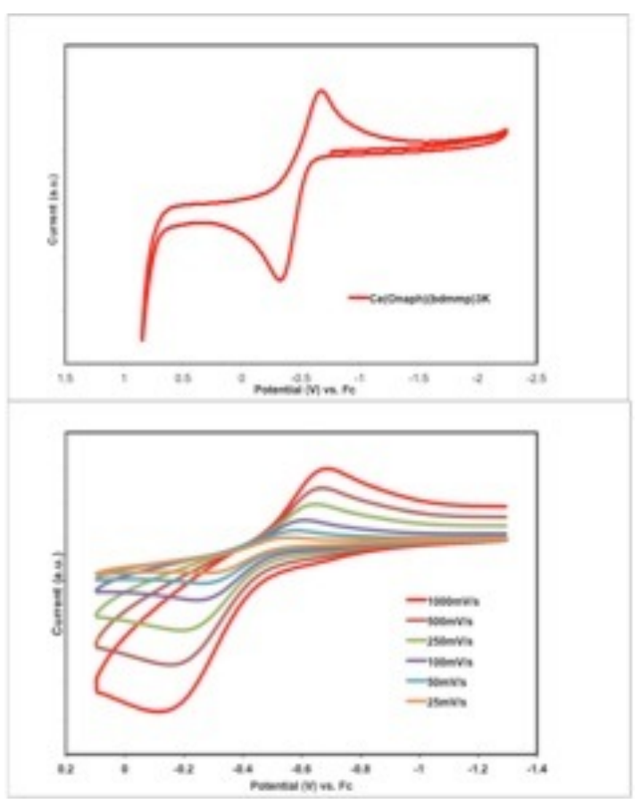




Powder yield : 60%
Crystalline yield : 30%

- Ce(1)-O(1) 2.3445(10) Å
- Ce(1)-O(2) 2.3501(10) Å
- Ce(1)-O(3) 2.3561(11) Å
- Ce(1)-O(4) 2.3275(11) Å
- Ce(1)-N(1) 2.7008(13) Å
- Ce(1)-N(2) 2.7093(13) Å
- Ce(1)-N(3) 2.7263(13) Å





Electrochemical Analysis of $Ce(X)(bdmmp)_3M$

Compound	E	E	(E	E	k
Ce(OTf) (bdmmp)	–0.085	–0.85	0.76	–0.46	3.3
Ce(CCPh) (bdmmp)	–0.25	–0.61	0.37	–0.43	5.6
Ce(Onaph) (bdmmp)	–0.31	–0.66	0.35	–0.49	8.0

$$k_s = 2.18\left(\frac{D_{ox}\cdot\alpha\cdot n\cdot F\cdot v}{RT}\right)^{1/2}\exp\left[-\frac{\alpha^2\cdot n\cdot F}{RT}(E_{pa}-E_{pc})\right]$$

k_s : heterogeneous electron transfer rate constant
D_{ox} : diffusion constant
α : electrochemical transfer coefficient
n : number electrons transferred
F : Farraday constant
v : sweep rate

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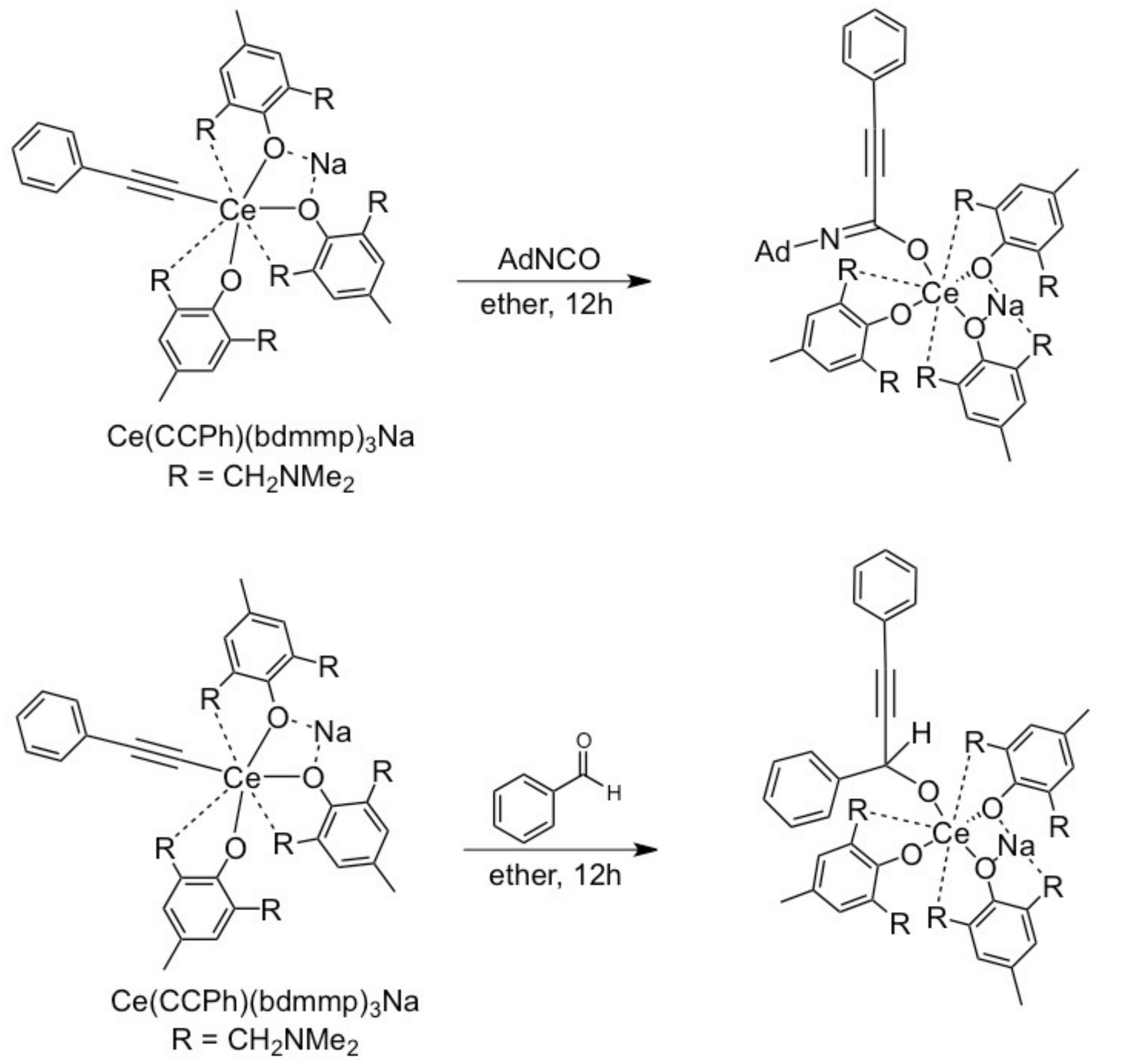
Insertion Reactions of $Ce(CCPh)(bdmmp)_3Na$



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Conclusions and Future Work

Heterobimetallic cerium complexes with bis(diaminomethyl)-4-methyl phenoxide ligands were synthesized.
The complexes were tuned by simple metathesis with alkali metal salts, and first cerium acetylide complex was isolated. Cyclic voltammograms were measured for each complex and all complexes showed a $Ce^{IV/III}$ wave that was shifted at least 2.9 V vs. Fc in methylene chloride solution. Depending on the type of substituents, the separation of oxidation/reduction waves was largest for the triflate ion, followed by acetylide and 2-naphthoxide. From the electron transfer rate analysis, the complex with 2-naphthoxide was fastest, followed by acetylide and triflate. The chemical oxidation of these complexes is under way. The insertion reactions of $Ce(CCPh)(bdmmp)_3Na$ are also under way.

Acknowledgements

NSF CHE–0840438
Schelter group