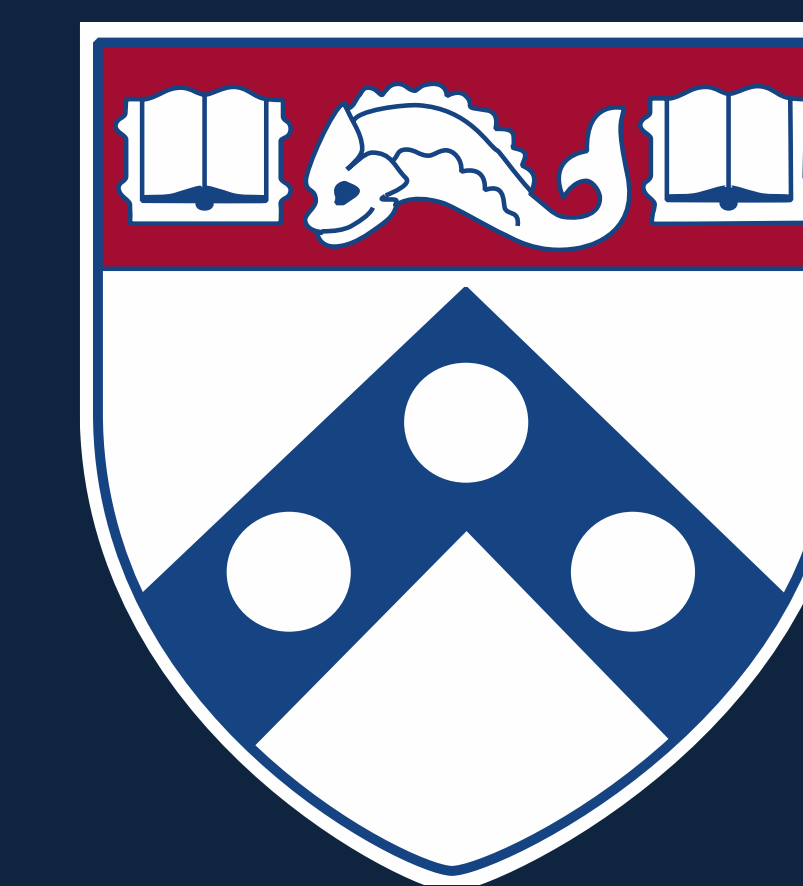


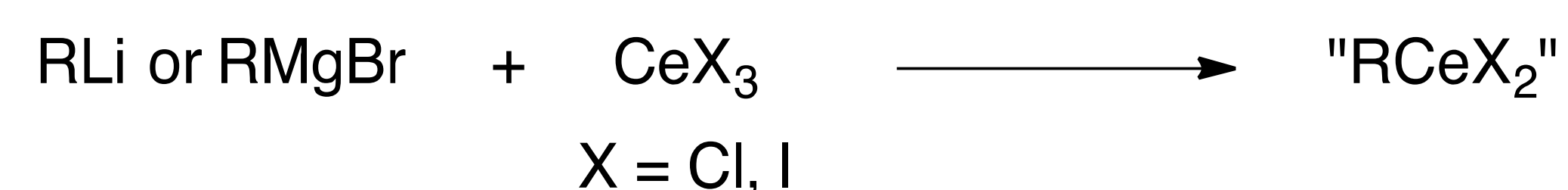
# Isolation of a Terminal Trivalent Organocerium Acetylide Complex and its Reactivity with Highly Enolizable Ketones

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

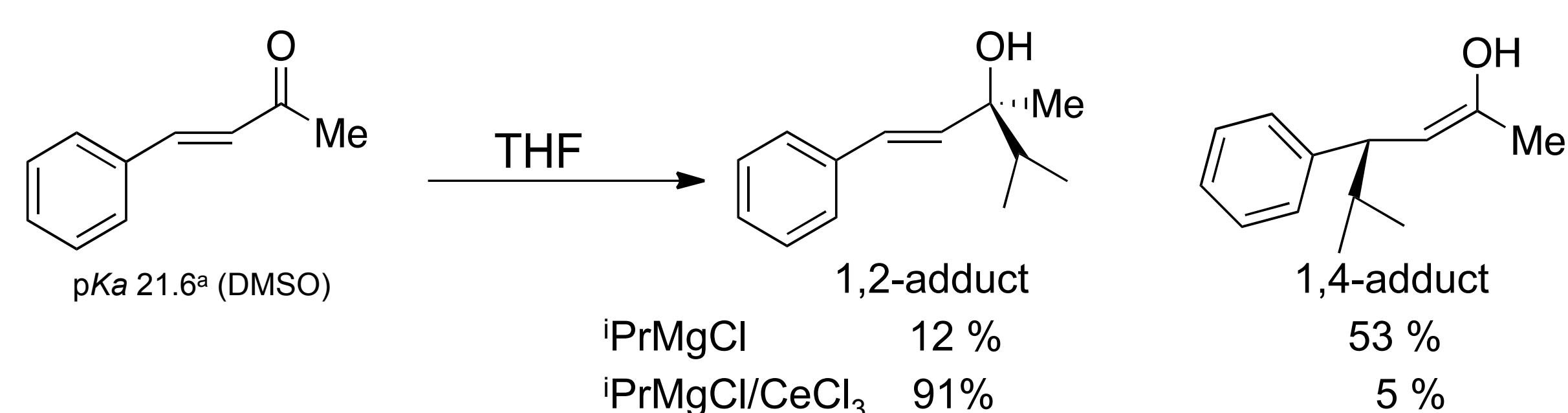
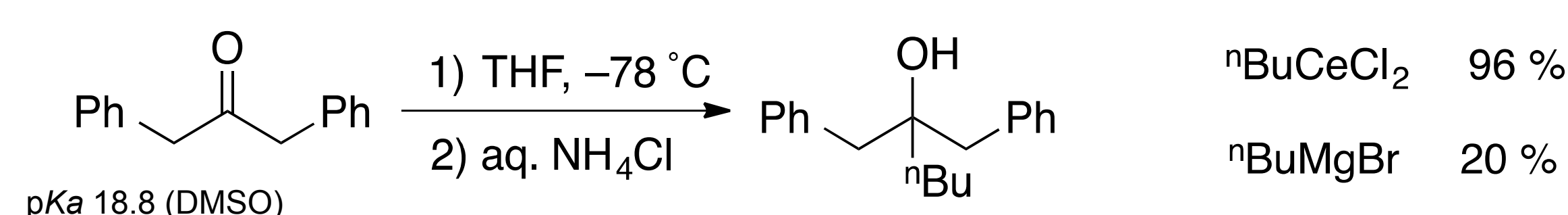
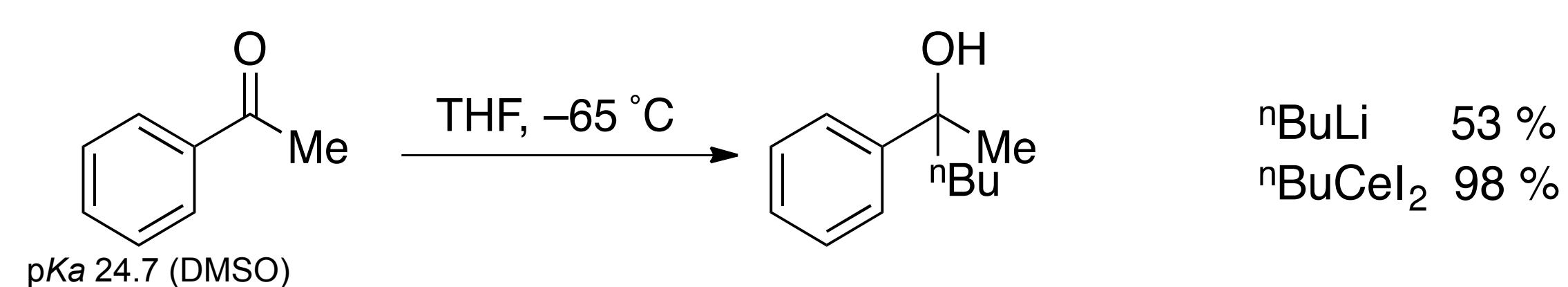
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## Motivation



RCeX<sub>2</sub> react "in-situ" with ketones in carbonyl addition reactions, without formation of enolates. The reagents are highly selective to 1,2-additions.



Imamoto, T., *Pure & Appl. Chem.*, **1990**, 62, 747-752  
Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y.: *J. Am. Chem. Soc.* **1989**, 111, 4392-4398



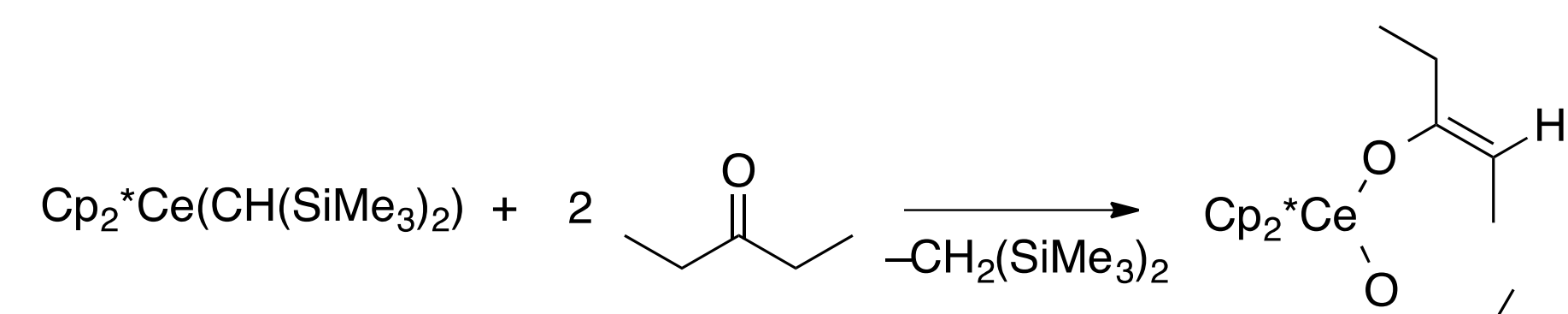
"Little is known of the structure of these organoceriums, or the exact nature of the reactive species."

Molander, G. A.: *Chem. Rev.* **1992**, 92, 29-68

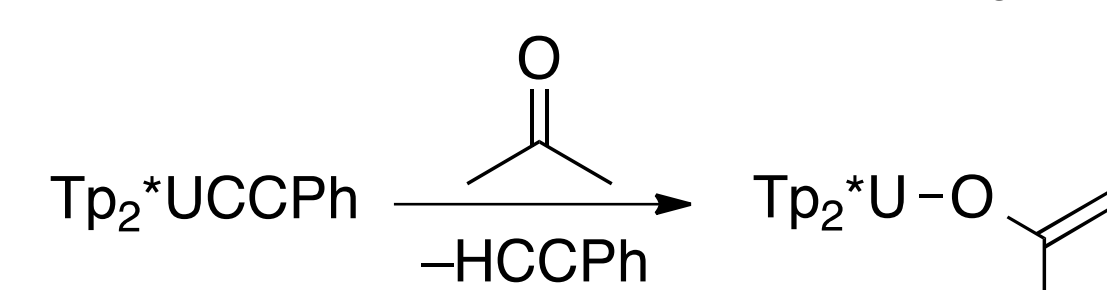
## Background

f-block metal alkyl complexes and their reactions with ketones

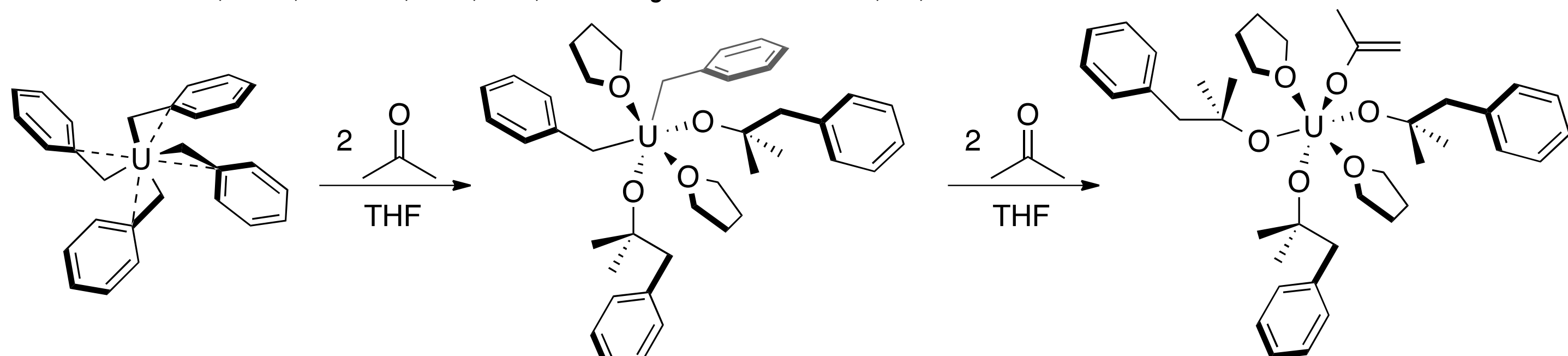
What controls selectivity?: Enolation vs. Carbonyl addition



Heeres, H. J.; Maters, M.; Teuben, J. H.; Helgesson, G.; Jagner, S.: *Organometallics* **1992**, 11, 350-356.



Matson, E. M.; Fanwick, P. E.; Bart, S. C.: *Organometallics* **2011**, 30, 5753-5762.

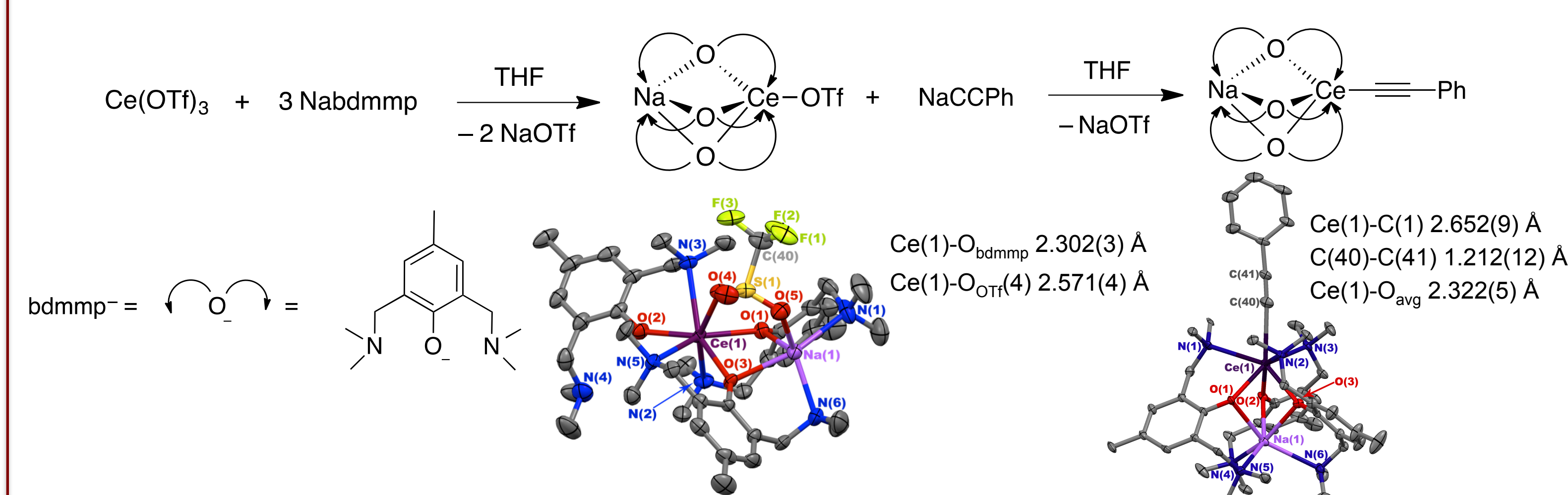


Kraft, S. J. F., P. E.; Bart, S. C.: *Organometallics* **2013**, 32, 3279-3285.

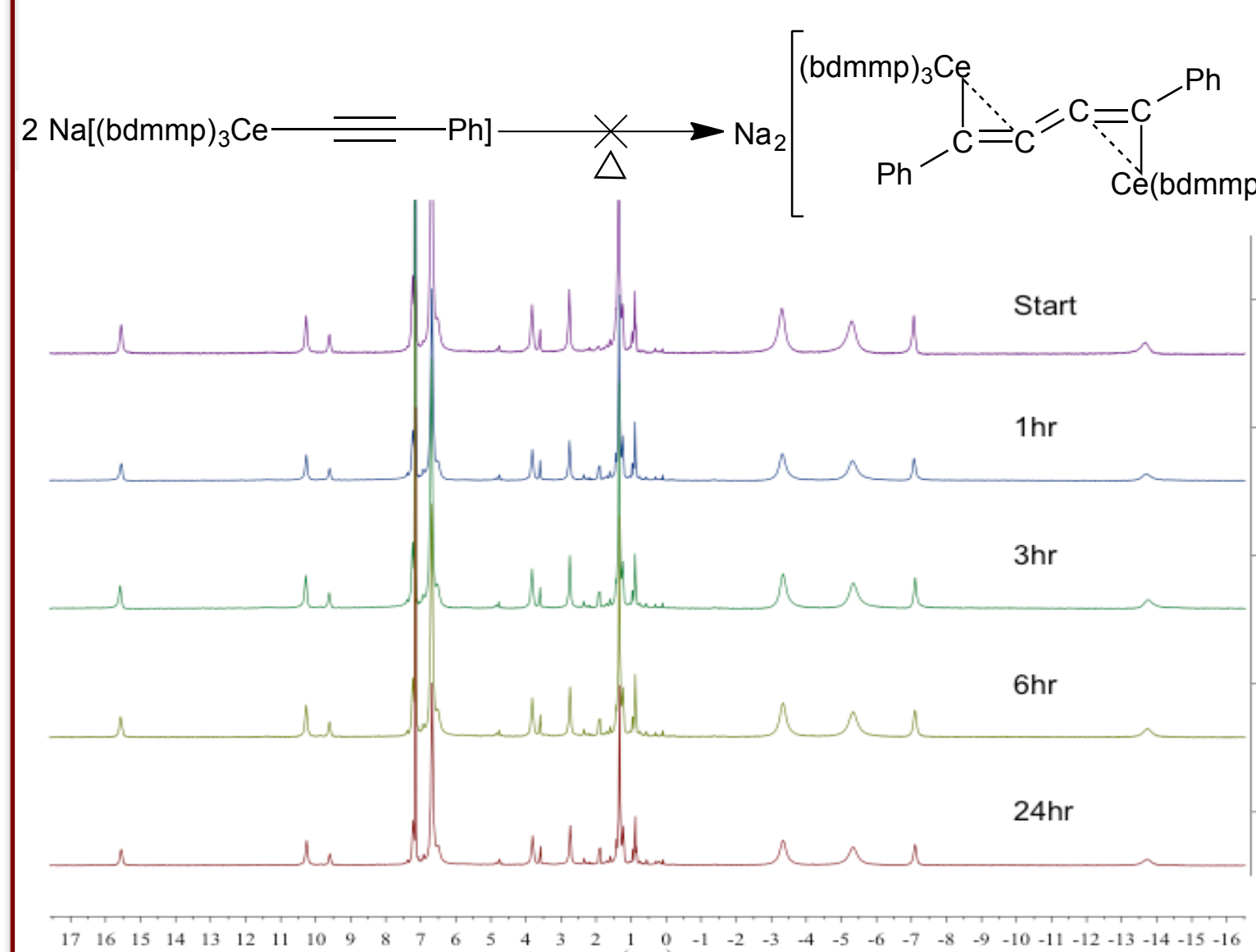
How can we study the active species of the organocerium (CeCl<sub>3</sub>/RLi) reagent?

Can we make a model system capable of carbonyl addition reaction and see what factors drive the carbonyl addition vs. enolation pathway?

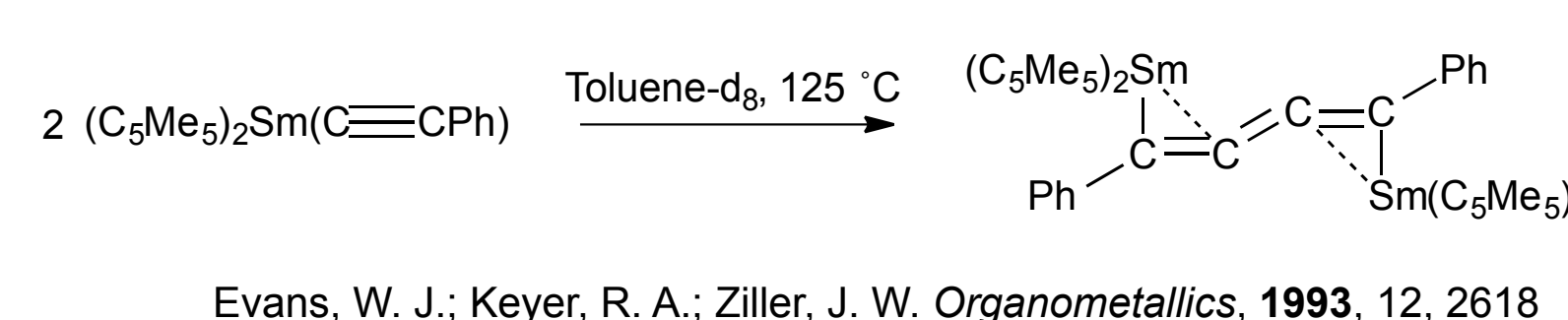
## Results



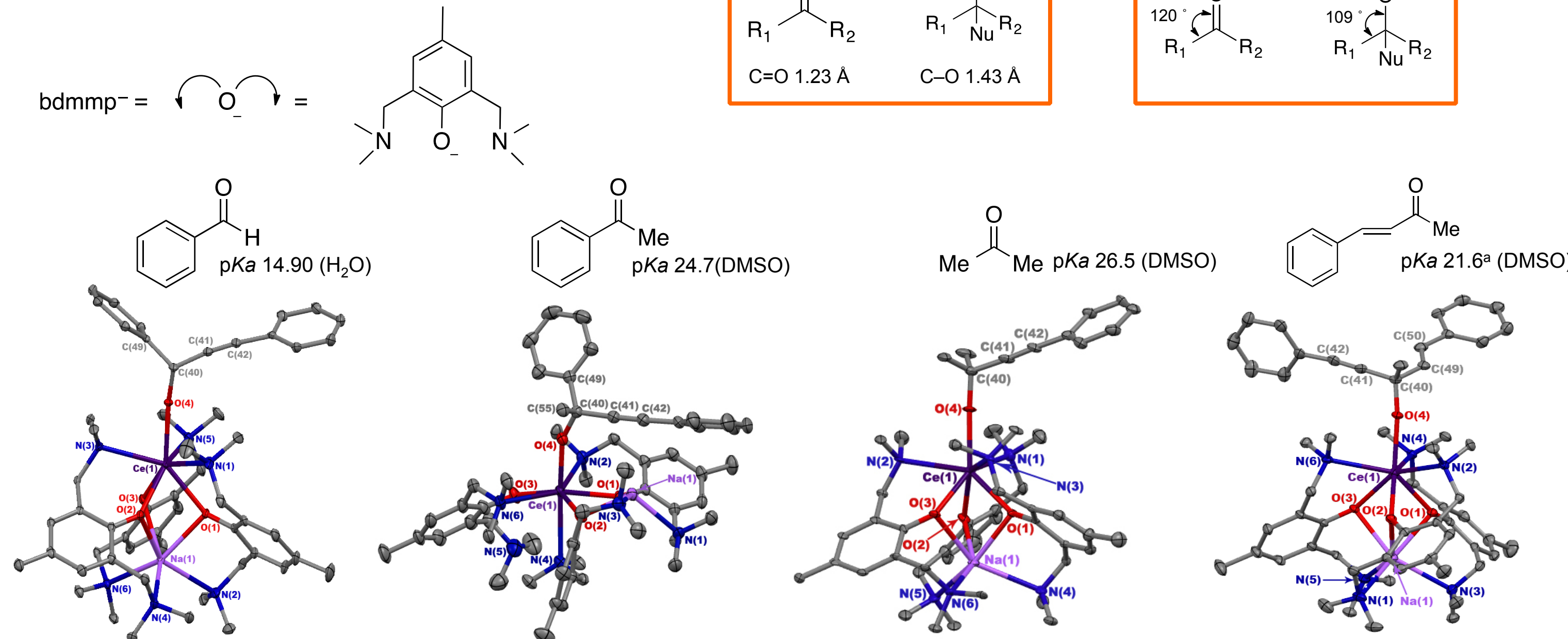
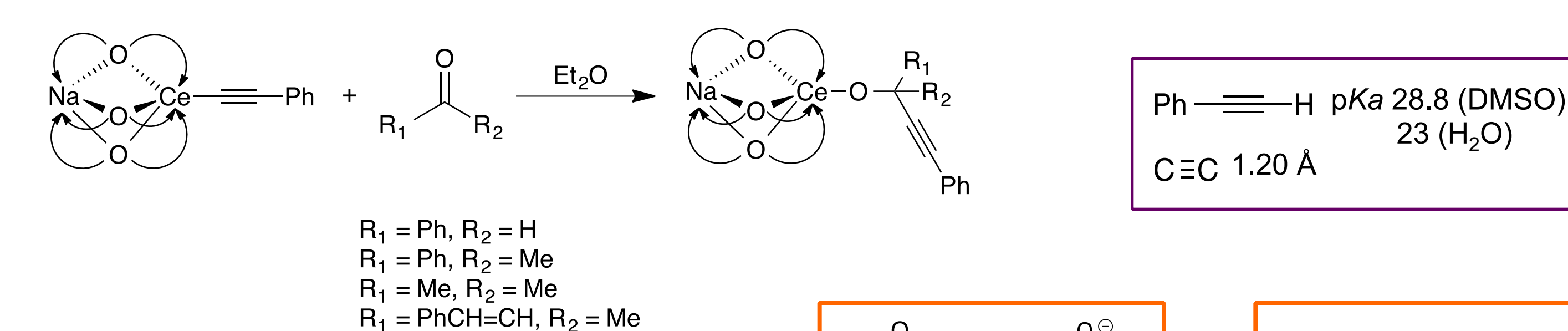
Heat stability test of Na[Ce(CCPH)(bdmmp)<sub>3</sub>]  
Na[Ce(CCPH)(bdmmp)<sub>3</sub>] in benzene-d<sub>6</sub> J-young tube at 125 °C



Formation of butatrienediyl group with lanthanides



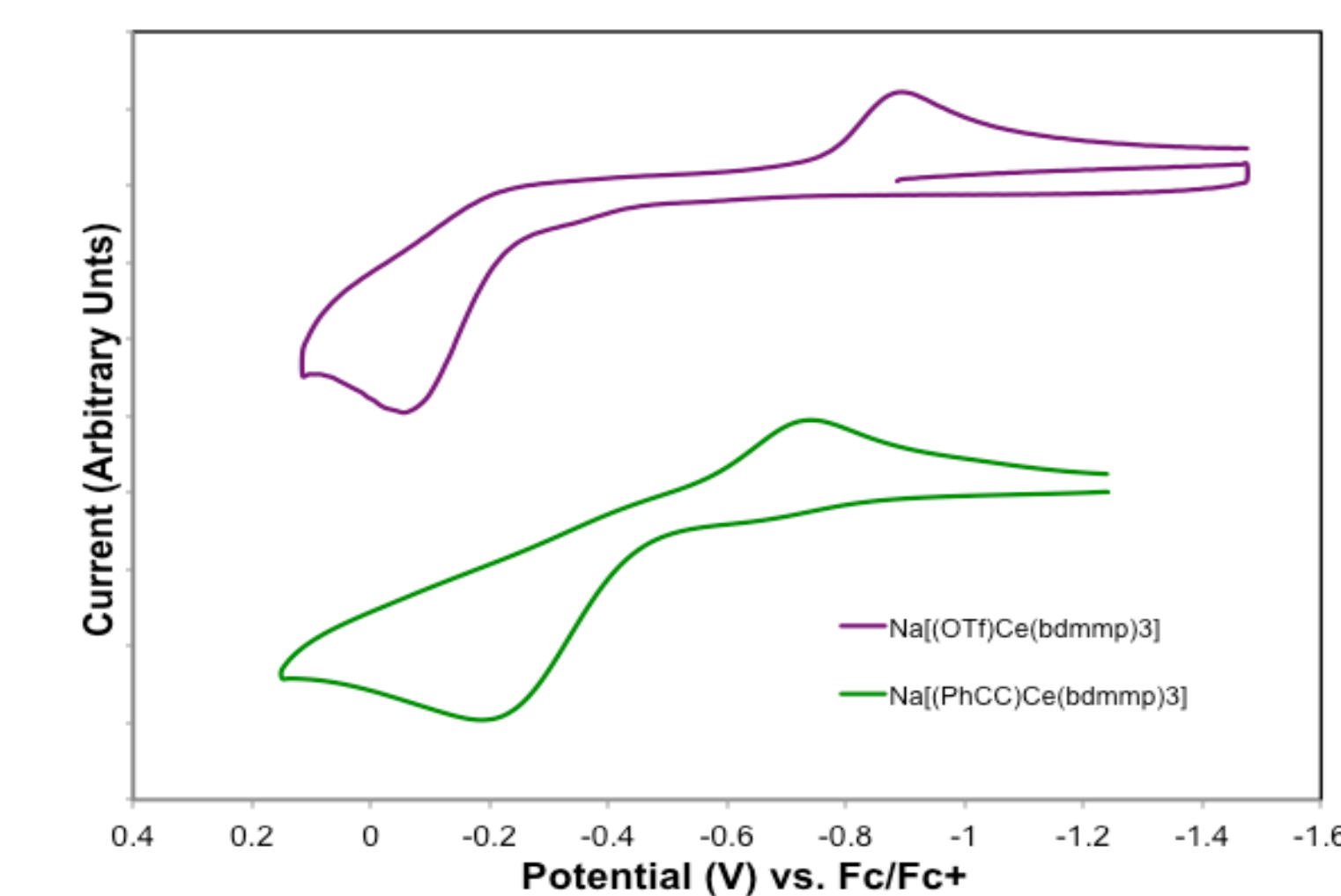
Carbonyl addition reactions of Na[Ce(CCPH)(bdmmp)<sub>3</sub>]



	1	2	3	4
C(40)-O(4) (Å)	1.397(6)	1.397(4)	1.418(13)	1.422(4)
C≡C (Å)	1.194(8)	1.202(5)	1.201(17)	1.169(6)
Ce(1)-O(4) (Å)	2.266(4)	2.237(2)	2.268(7)	2.292(2)
X-C(40)-Y (°)	109.7(5)-112.5(4)	107.0(3)-112.0(3)	105.0(11)-111.8(11)	108.1(3)-111.0(3)

a. Hamdi, S. T. et al., *J. Chem. Soc., Perkin Trans. 2*, **1976**, 846-847

## Electrochemical analysis



Compound	E	E	Δ	E
Na[Ce(OTf)(bdmmp) <sub>3</sub> ]	-0.06	-0.90	0.84	-0.48
Na[Ce(CCPH)(bdmmp) <sub>3</sub> ]	-0.20	-0.74	0.54	-0.47

a. Versus Fc/Fc<sup>+</sup> in methylene chloride with 0.1 M supporting electrolyte, [Pr<sub>4</sub>N][BAr<sub>4</sub>F].

- Coordination of bdmmp<sup>-</sup> ligands impacts a mildly Lewis acidic cerium metal center.
- Phenyl acetylide stabilizes the tetravalent cerium by around 0.2 V over the triflate anion.

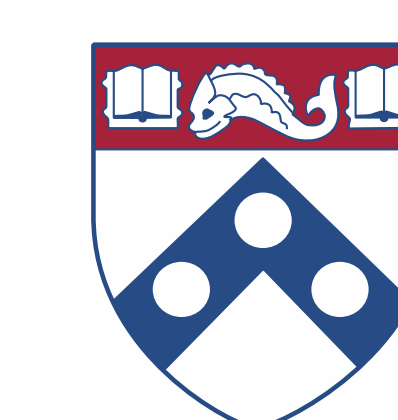
## Conclusions

- Isolation and full characterizations of the first terminal trivalent cerium acetylide complex, Na[Ce(CCPH)(bdmmp)<sub>3</sub>].
- Unusual heat stability of Ce-C<sub>acetylide</sub> bond up to 125 °C for 24hr.
- Isolated the carbonyl addition products resulting from the reaction of the terminal cerium acetylide complex as with highly enolizable ketones.
- Suggested a model system to study the mechanism of the *Imamoto's organocerium reagent* (CeCl<sub>3</sub>/RLi).
- Calculations on the transitions states to support the mechanism are underway.

## References

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## Acknowledgements



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