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

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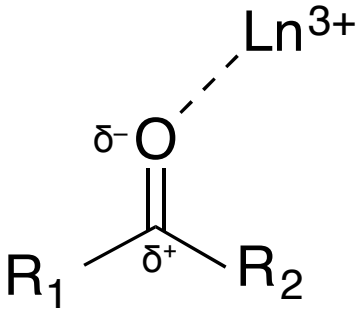
Carbonyl Addition Reaction by Lanthanide Metal Ions

Strong Lewis acidity



‘Milder’ nucleophilic alkyl group

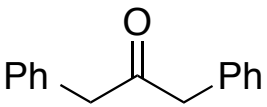
$$RLi \text{ or } RMgBr + CeX_3 \longrightarrow "RCeX_2"$$

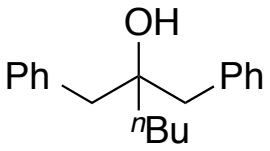
X = Cl, I

Imamoto, T.; Kusumoto, T.; Yokoyama, M., *J. Chem. Soc., Chem. Commun.,* **1982**, 1042-1044
Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y., *J. Am. Chem. Soc.,* **1989**, 111, 4392-4398

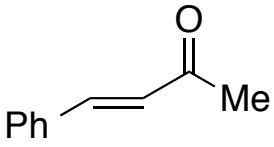
Ln Ions in Carbonyl Addition Reactions

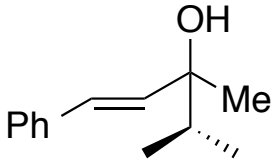
pK_a^{DMSO} 18.8

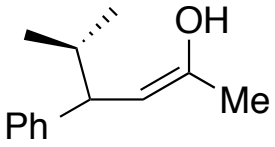




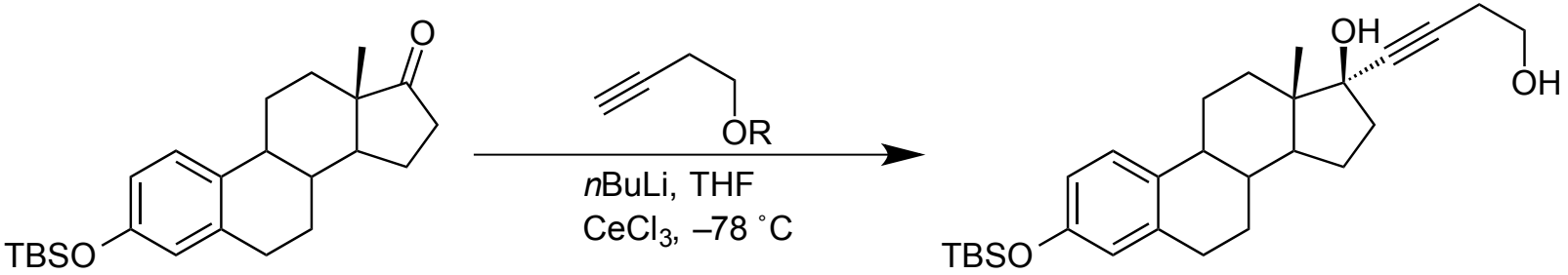
^{n}BuMgBr	20 %
^{n}BuLi/$CeCl_3$	96 %







	1,2-adduct	1,4-adduct
^{i}PrMgCl	12 %	53 %
^{i}PrMgCl/$CeCl_3$	91 %	5 %



Imamoto, T.; Kusumoto, T.; Yokoyama, M., *J. Chem. Soc., Chem. Commun.*, **1982**, 1042-1044
Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y., *J. Am. Chem. Soc.*, **1989**, 111, 4392-4398
Sadler, S.; Persons, K. S.; Jones, G. B.; Rahul R., *Bioorg. Med. Chem. Lett.*, **2011**, 21, 4638-4641

Motivation for Studies of Insertion of Ketones into Ce–C Bond

Dr. Gary Molander

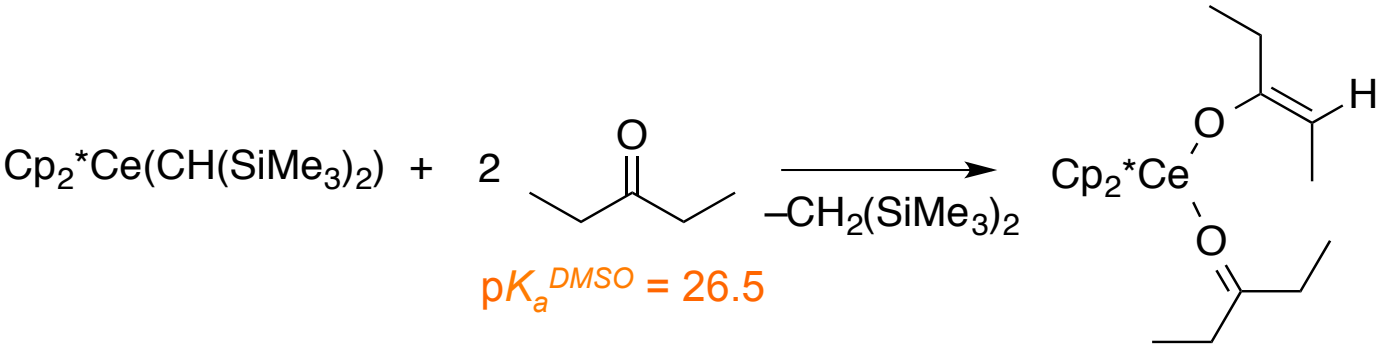
"Little is known of the structure of these organoceriums, or the exact nature of the reactive species."

Dr. Giuseppe Bartoli

"It must be noted that, despite extensive efforts, the solution structure of the reagent formed from $CeCl_3$ and Grignard reagents is still obscure."

Molander, G. A.: *Chem. Rev.* **1992**, *92*, 29-68.
Bartoli, G.; Marcantoni, E.; Marcolini, M.; Sambri, L.: *Chem. Rev.* **2010**, *110*, 6104-6143.

Ln & An Hydrocarbyl Complexes with Ketones

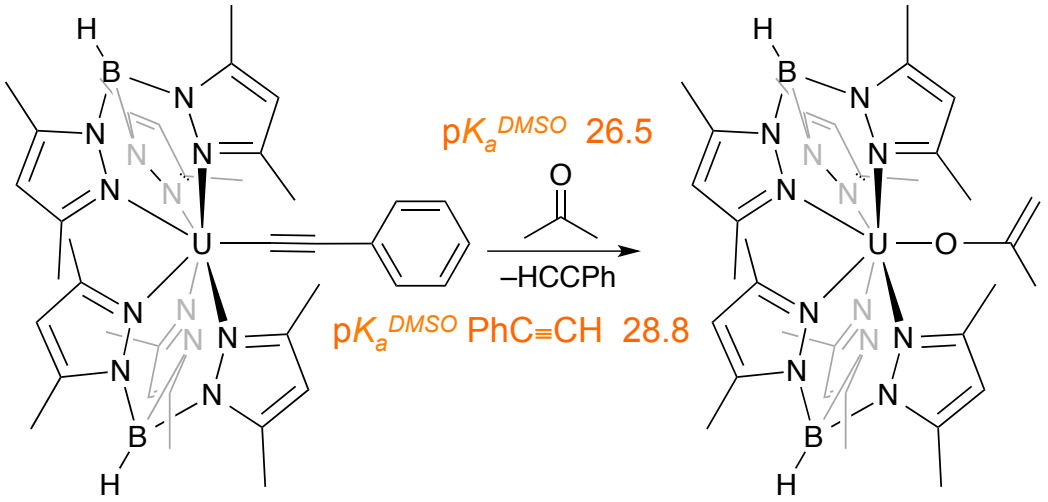


Enolization

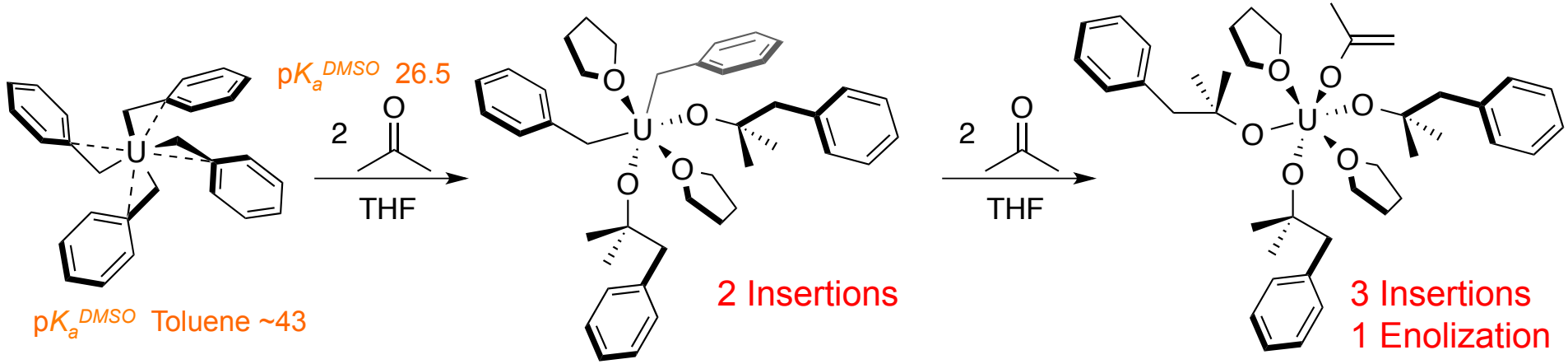
Can we make a cerium hydrocarbyl complex that shows carbonyl addition reactions?

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

Ln & An Hydrocarbyl Complexes with Ketones

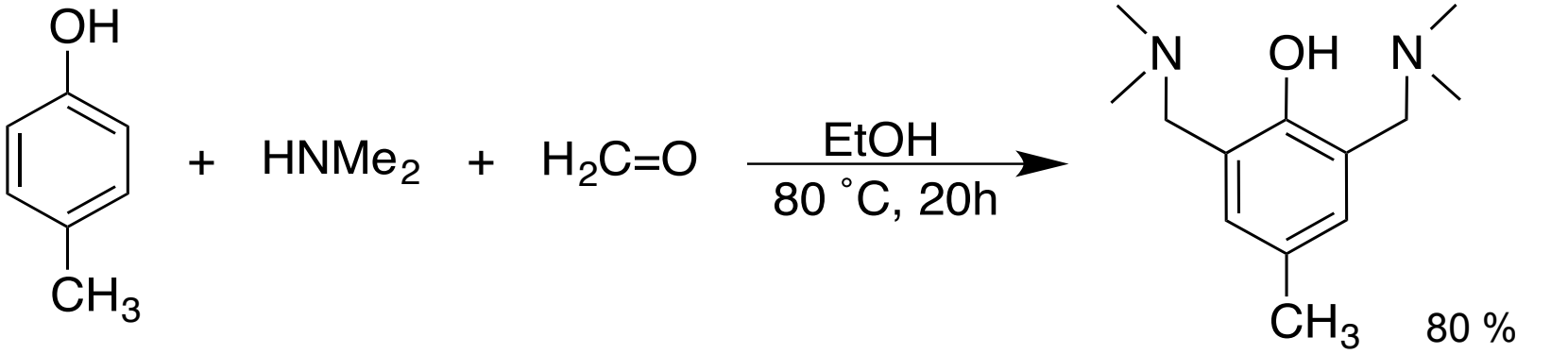


Enolization

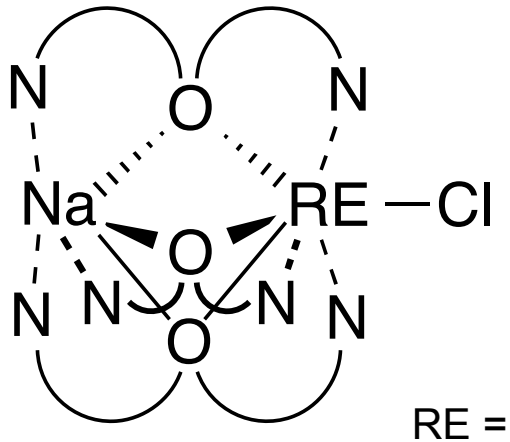


Matson, E. M.; Fanwick, P. E.; Bart, S. C.: *Organometallics* **2011**, *30*, 5753-5762.
Kraft, S. J. F., P. E.; Bart, S. C.: *Organometallics* **2013**, *32*, 3279-3285.

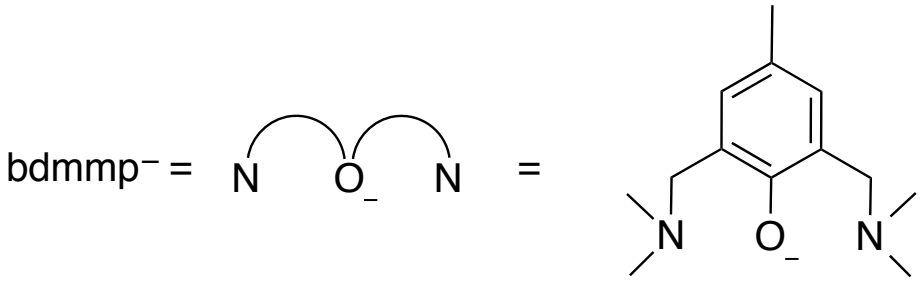
Choice of the Ligand and Hypothesis



Bis(dimethylamino)-4-methylphenol
(bdmmpH)

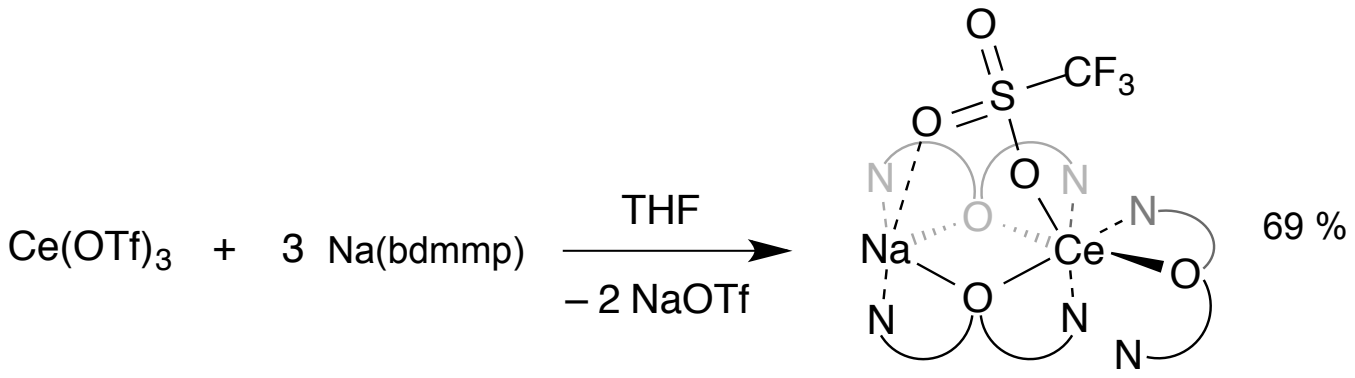


RE = Y, Lu

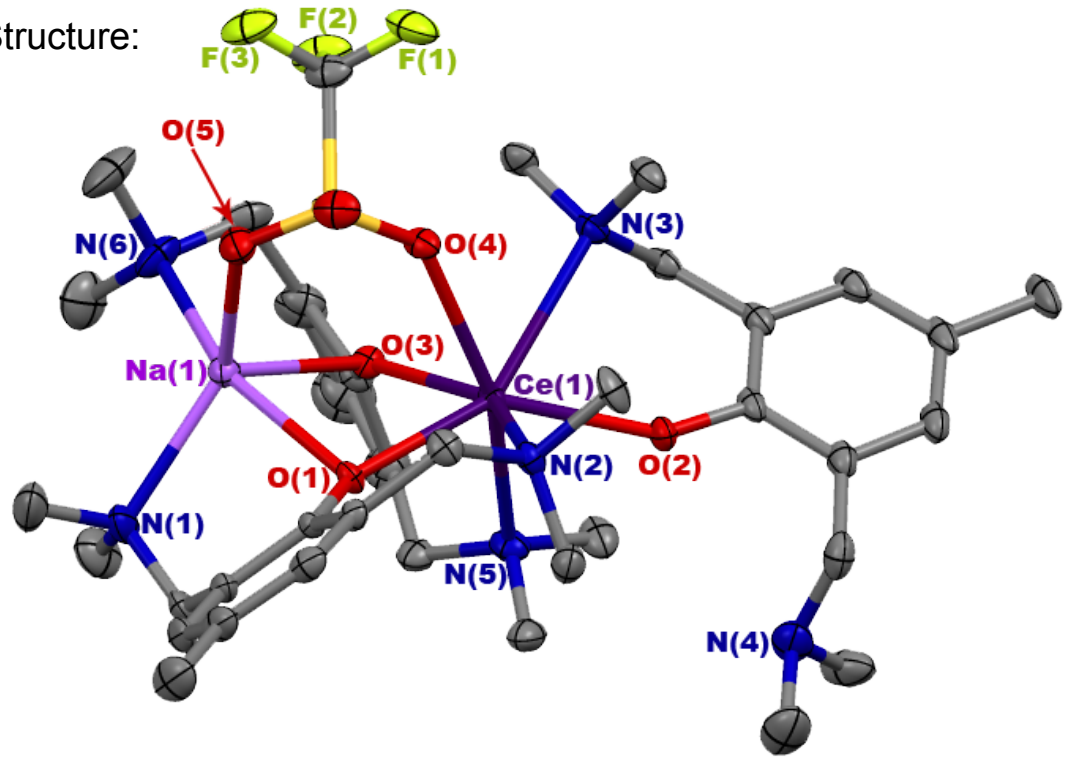


Brycki, B. M., H.; Brzezinski, B. *J. Mol. Struct.* **1991**, *246*, 61-71
Hogerheide, M. P.; Jastrzebski, J. T. B. H.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1994,** *33*, 4431-4432.
Hogerheide, M. P.; Ringelberg, S. N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1996,** *35*, 1185-1194.

Synthesis of Na[Ce(OTf)(bdmmp)$_3$]



X-ray Structure:

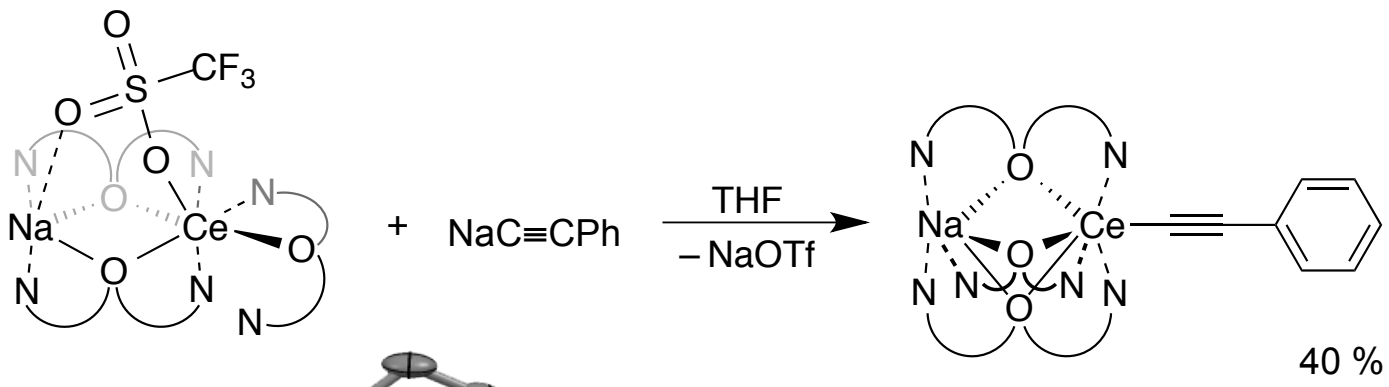


Ce(1)–O(1) 2.310(3) Å
Ce(1)–O(2) 2.280(3) Å
Ce(1)–O(3) 2.316(3) Å
Ce(1)–O(4) 2.571(3) Å

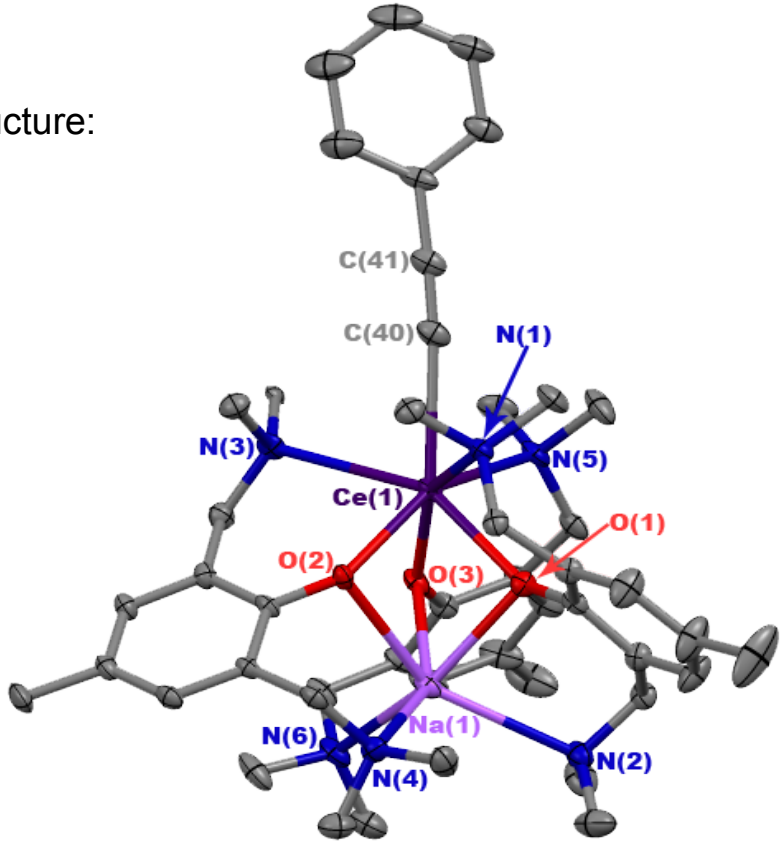
^{19}F NMR –84.4 ppm

Kim, J. E.; Weinberger, D. S.; Carroll, P. J; Schelter, E. J., *Organometallics*, **2014**, 33, 5948–5951

Synthesis of Na[Ce(C≡CPh)(bdmmp)$_3$]



X-ray Structure:

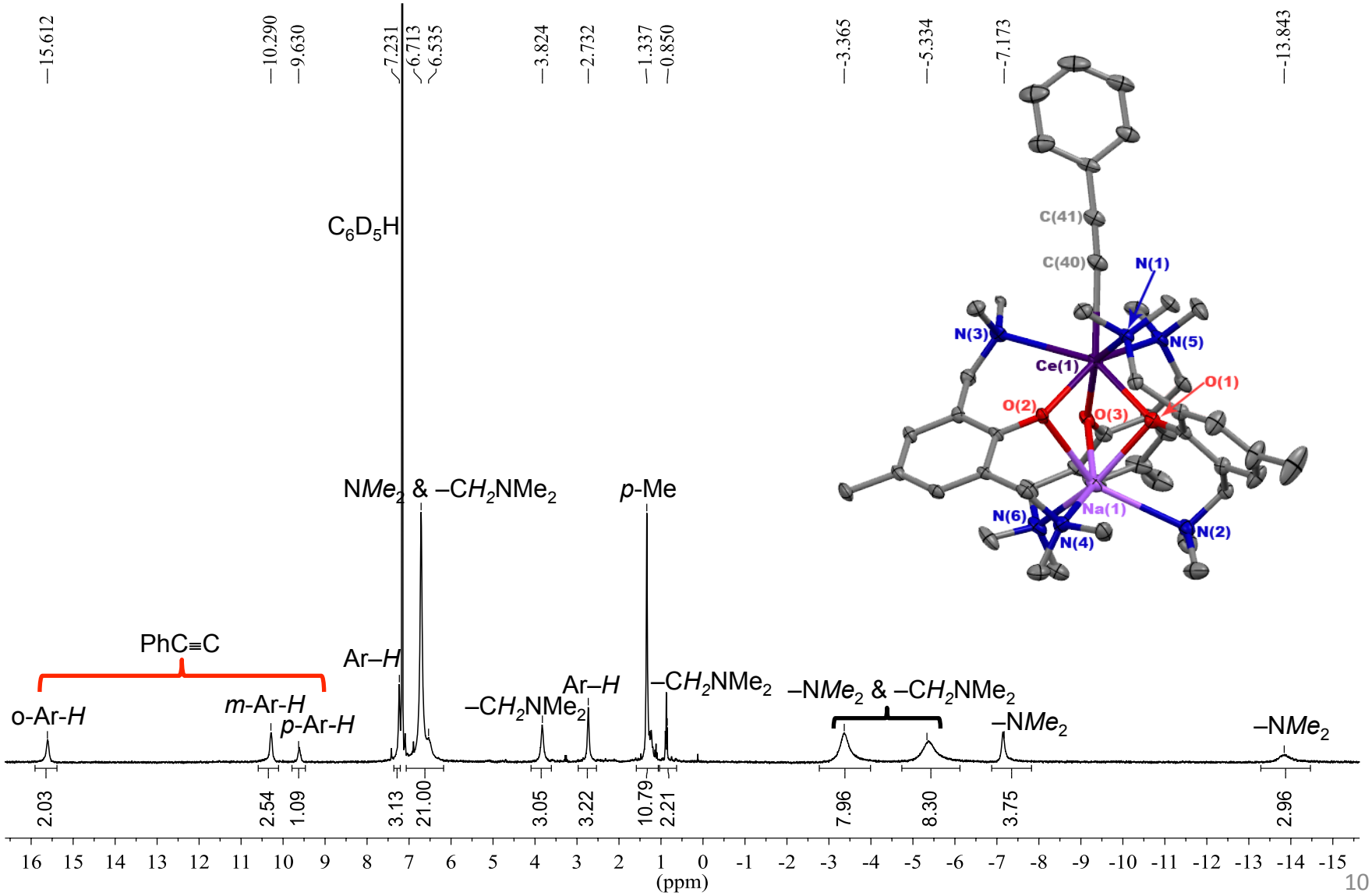


Ce(1)–O(1) 2.329(5) Å
Ce(1)–O(2) 2.304(5) Å
Ce(1)–O(3) 2.332(5) Å

Ce(1)–C(40) 2.652(9) Å
C(40)–C(41) 1.212(12) Å
Ce(1)–C(40)–C(41) 174.4(8)˚

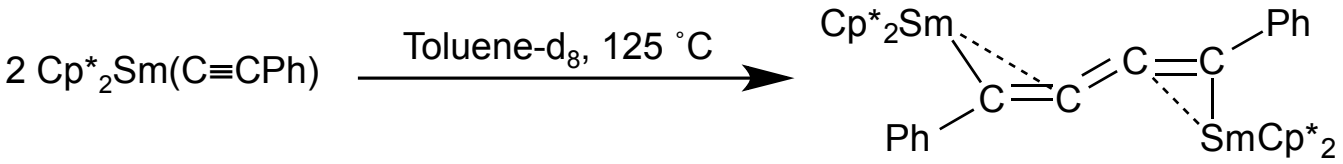
Kim, J. E.; Weinberger, D. S.; Carroll, P. J; Schelter, E. J., *Organometallics*, **2014**, 33, 5948–5951

^{1}H NMR of Na[Ce(C≡CPh)(bdmmp)$_3$] in benzene-d_6

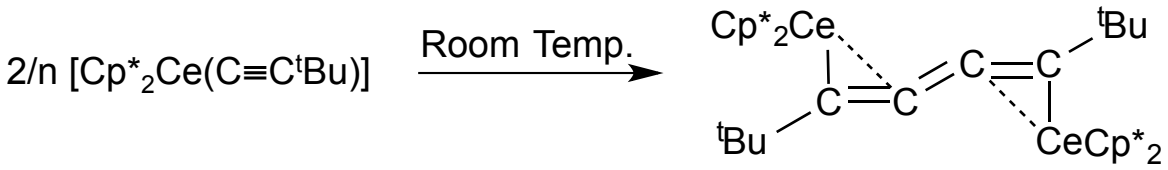


Kim, J. E.; Weinberger, D. S.; Carroll, P. J; Schelter, E. J., *Organometallics*, **2014**, 33, 5948–5951

Heat Stability of Lanthanide Alkynide Complexes

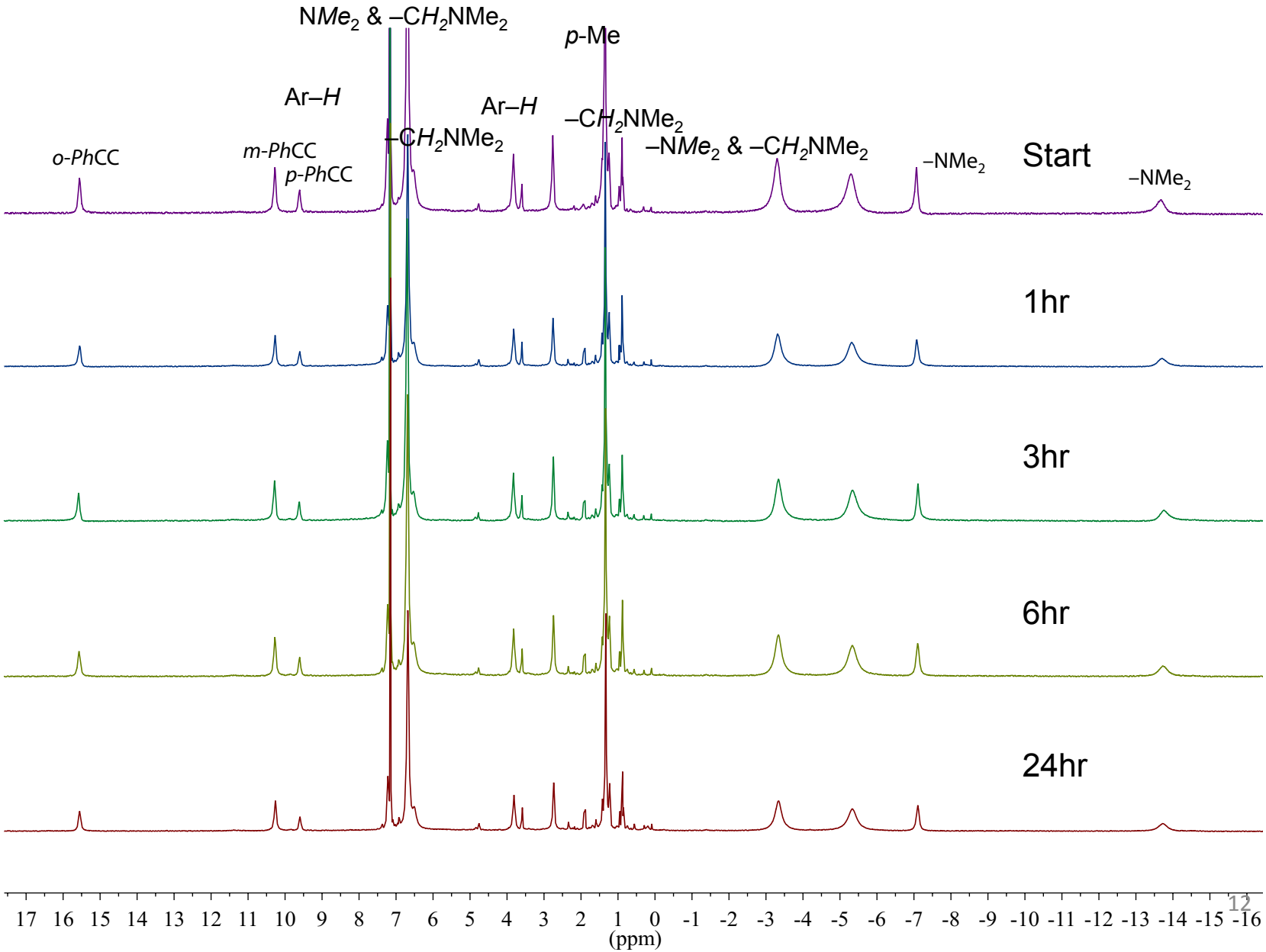


Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics*, **1993**, 12, 2618

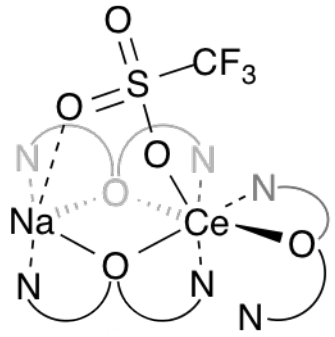


Heeres, H. J.; Nijhoff, J.; Teuben, J. H. *Organometallics*, **1993**, 12, 2609

Na[Ce(C≡CPh)(bdmmp)$_3$] in benzene-d$_6$, 130 ºC in J. Young tube

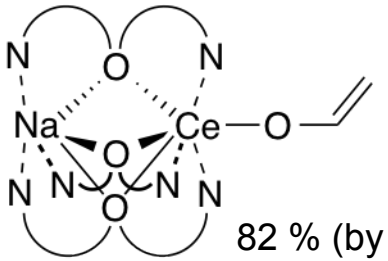


Reactions to Coordinate Other Hydrocarbyl Groups

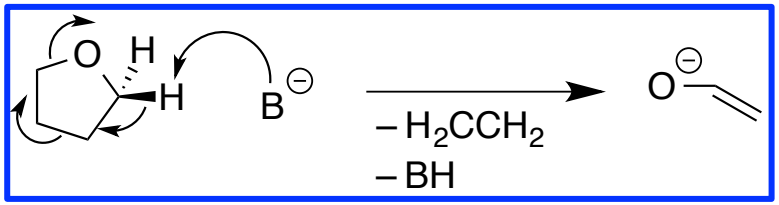


NaR (R = –$CH_2C_6H_5$, –Me, –CH_2SiMe_3, –C_6H_5)

THF
– NaOTf
– H_2CCH_2

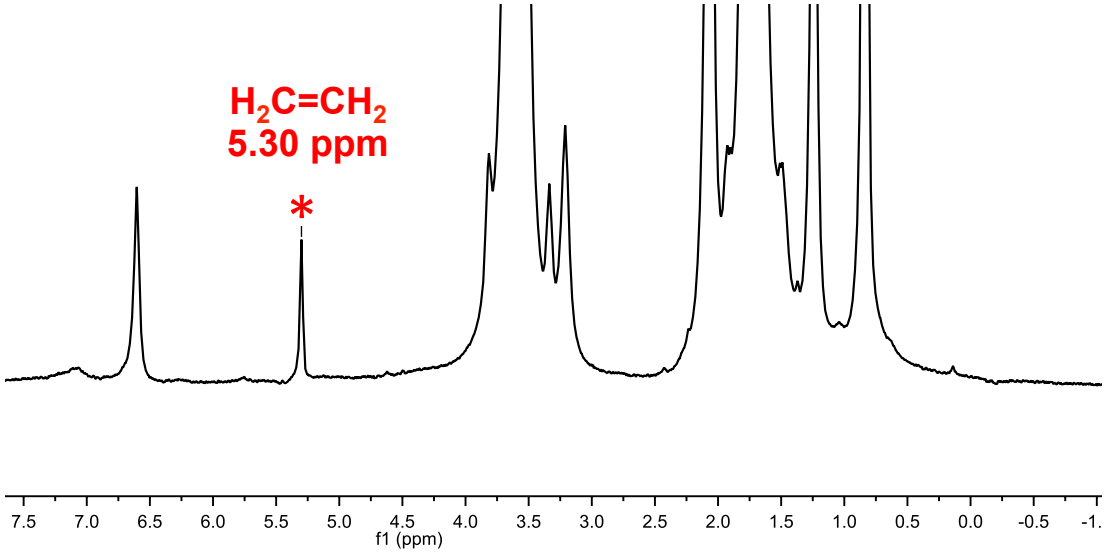


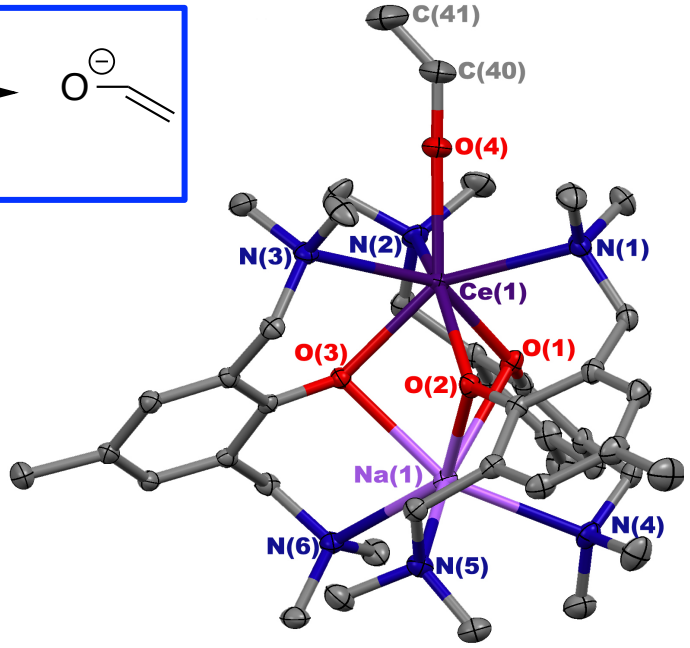
82 % (by $NaCH_2C_6H_5$)



– H_2CCH_2
– BH

in *proteo*-THF in a J. Young tube





Ce(1)–O(1) 2.3529(10) Å
Ce(1)–O(2) 2.3522(11) Å
Ce(1)–O(3) 2.3189(11) Å
Ce(1)–O(4) 2.2993(12) Å
C(40)–C(41) 1.255(4) Å

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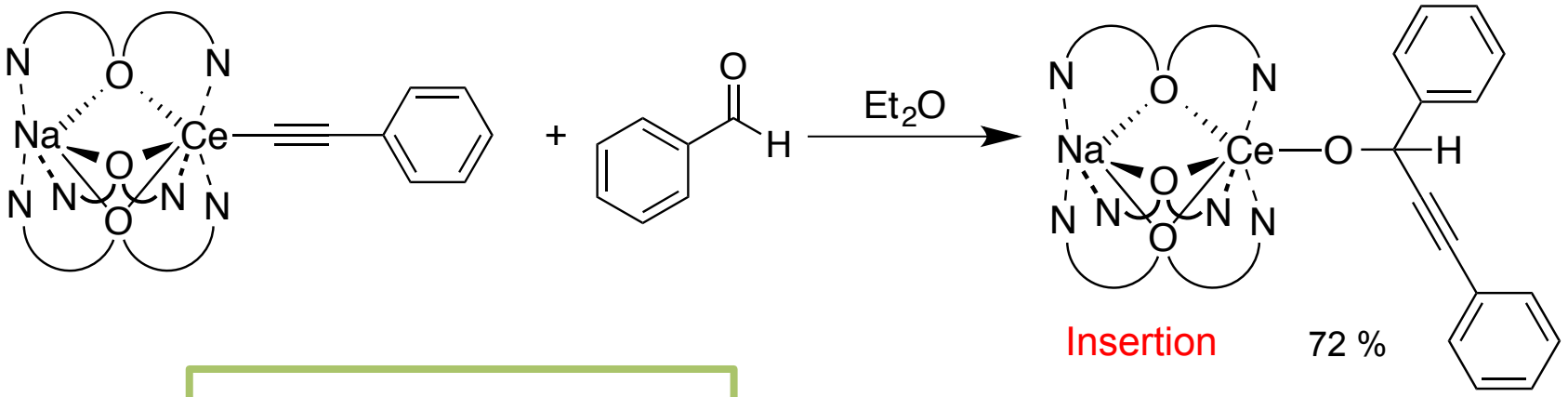
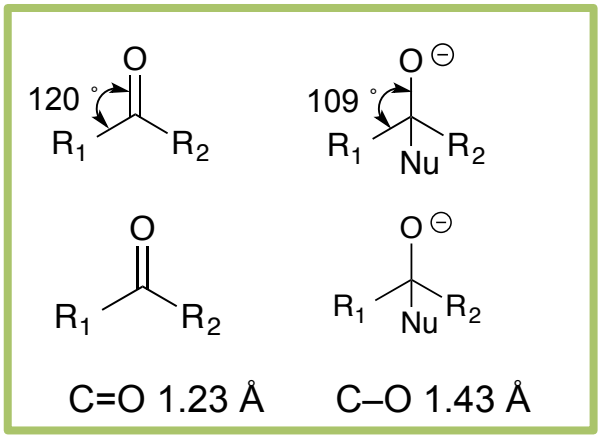
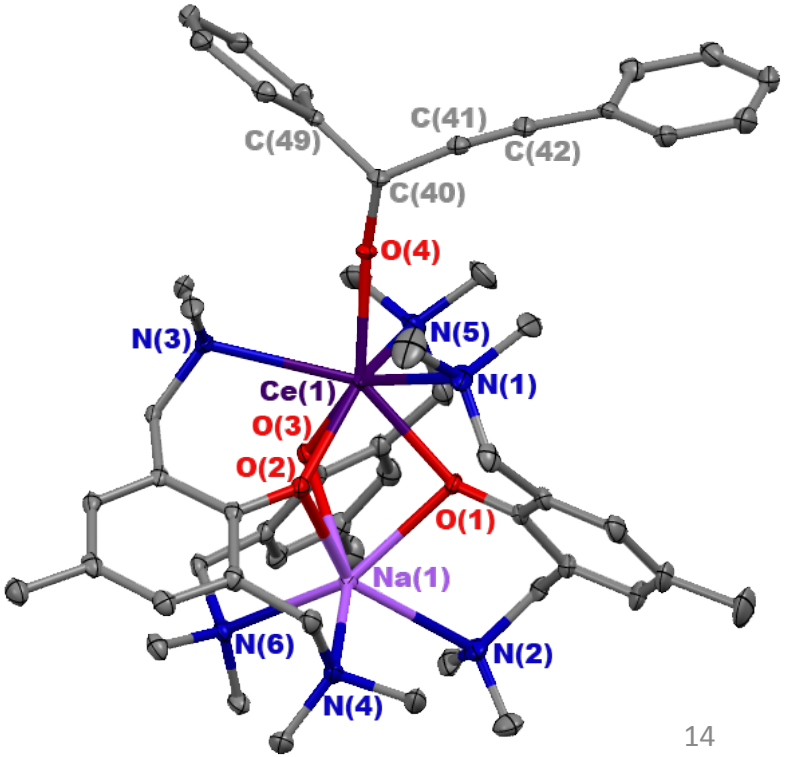
Reactivity of Ce–$C_{acetylide}$ Bond with Benzaldehyde







C(40)–O(4) (Å) 1.395(4)

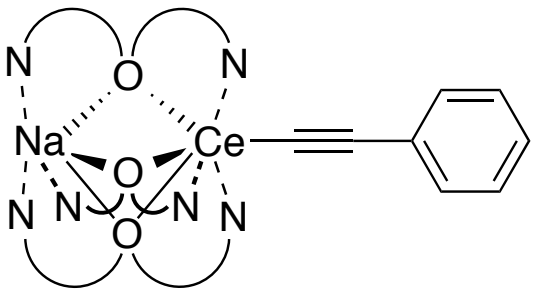
C(41)–C(42) (Å) 1.184(10)

Ce(1)–O(4) (Å) 2.268(3)

X–C(40)–Y (˚) 111.0(3)–112.7(3)

Chemical Principles 7th edition, Zumdahl & Decoste, 2013, Brooks/Cole Cengage learning

Reactivity of Ce–$C_{acetylide}$ Bond on Enolizable Ketones



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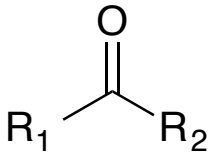
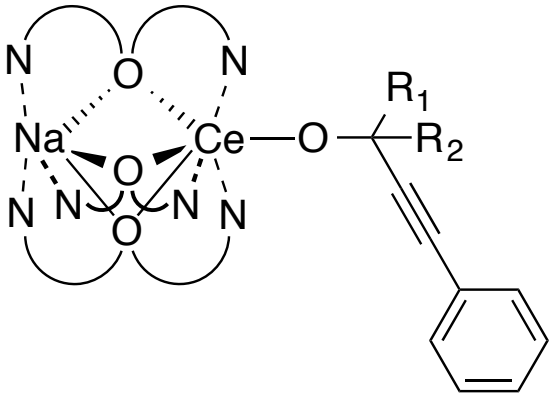
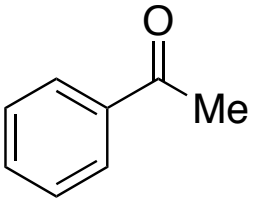


Et_2O

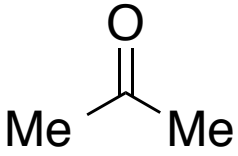


Ph—≡—H pK_a^{DMSO} 28.8

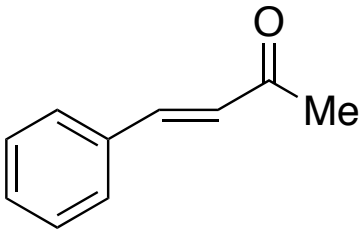
C≡C 1.20 Å



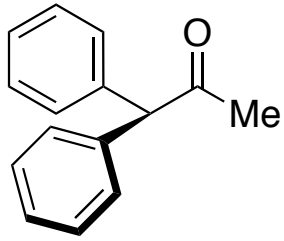
pK_a^{DMSO} = 24.7



pK_a^{DMSO} = 26.5



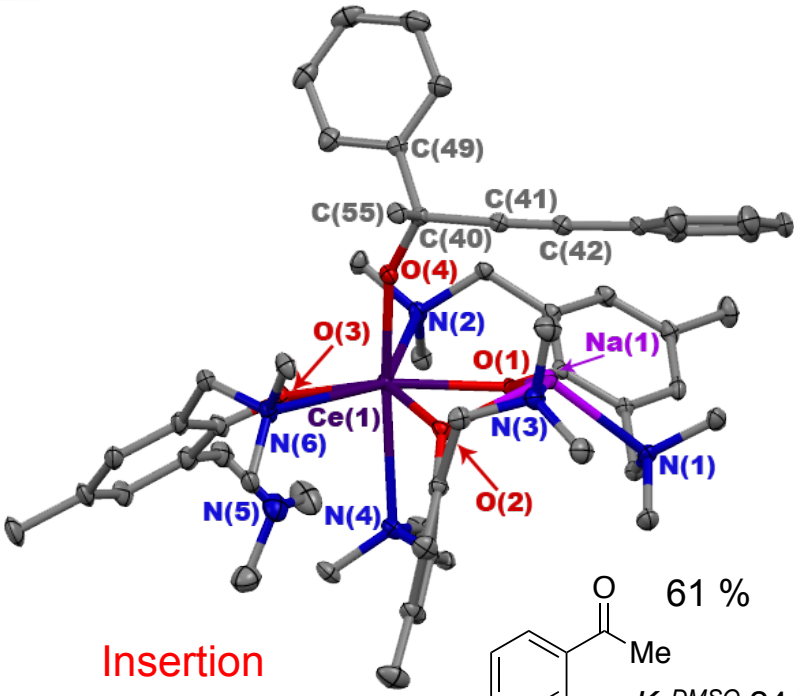
pK_a^{DMSO} = 21.5



pK_a^{DMSO} = 18.7

Chemical Principles 7th edition, Zumdahl & Decoste, 2013, Brooks/Cole Cengage learning

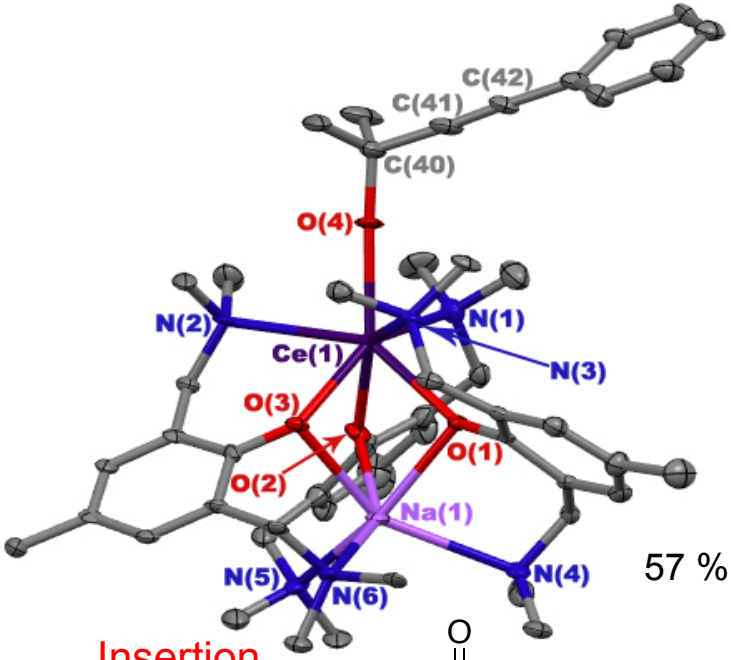
Crystal Structures



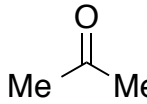
Insertion

61 %

pK_a^{DMSO} 24.7



Insertion



57 %

pK_a^{DMSO} 26.5

	Na[Ce(OC(Me)(Ph)(C≡CPh))(bdmmp)$_3$]	Na[Ce(OC(Me)(Me)(C≡CPh))(bdmmp)$_3$]
C(40)–O(4) (Å)	1.397(4)	1.418(13)
C≡C (Å)	1.202(5)	1.201(17)
Ce(1)–O(4) (Å)	2.237(2)	2.268(7)
X–C(40)–Y (˚)	107.0(3)–112.0(3)	105.0(11)–111.8(11)

http://www.chem.wisc.edu/areas/reich/pkatable/

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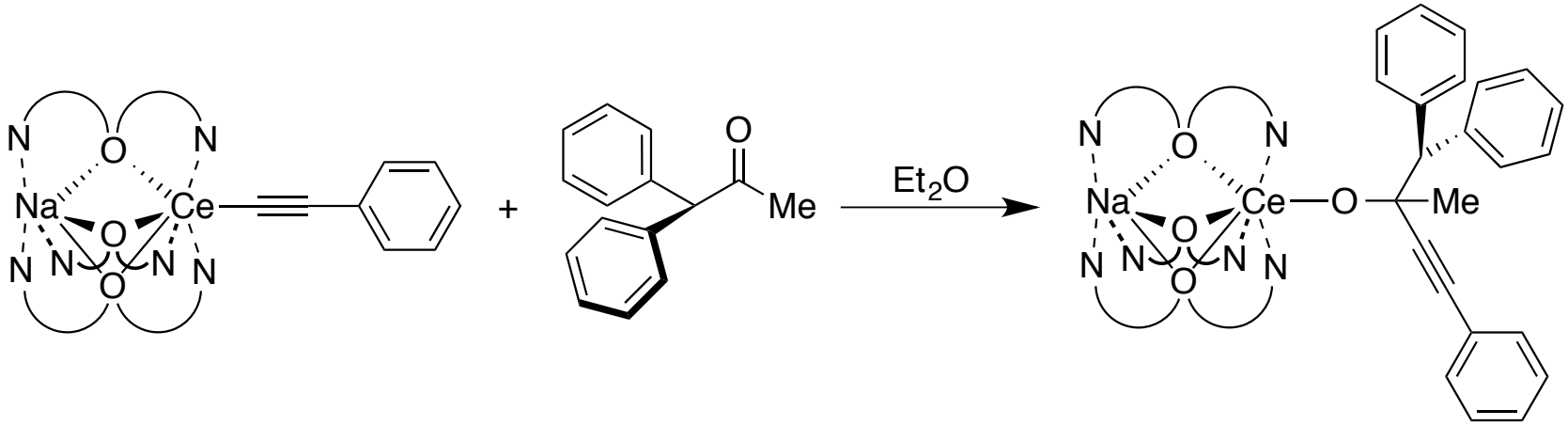
Carbonyl Addition Reaction with 1,1-diphenylacetone

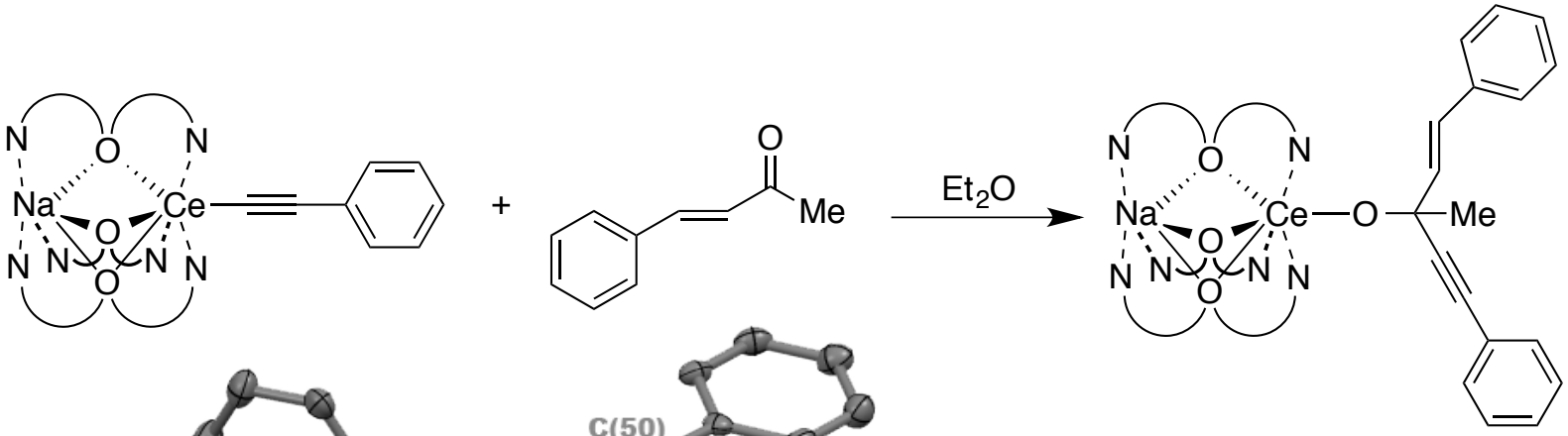


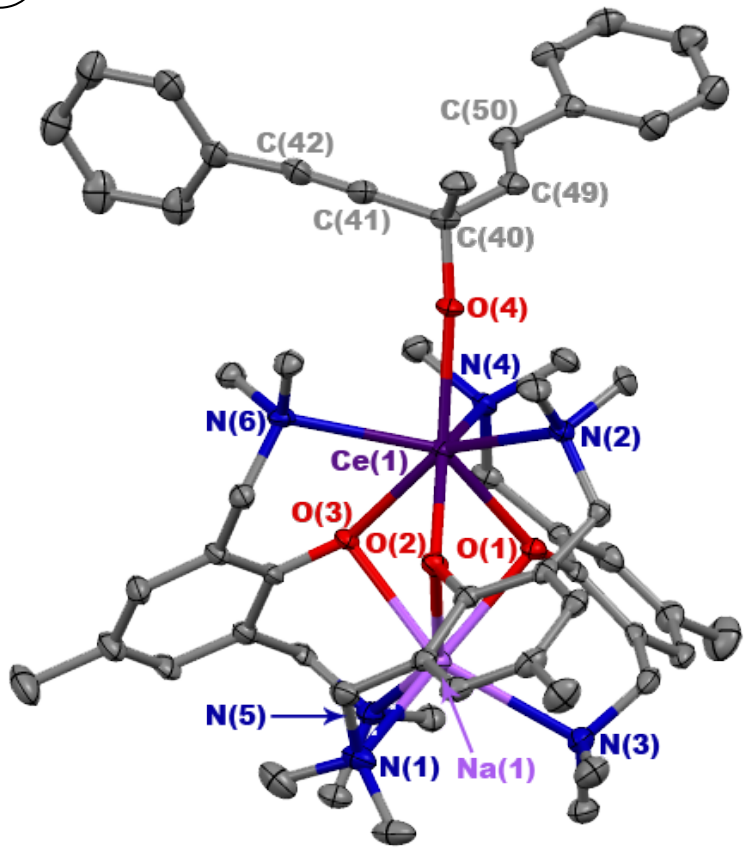
Elemental analysis

C –0.13 H –0.18 N +0.17

C –2.83 H +0.13 N +0.73

1,2-addition of Benzylidene acetone into Ce–$C_{acetylide}$ Bond

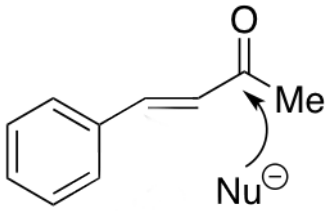




C(49)–C(50) 1.326(6) Å cf.) C=C 1.34 Å
Ce(1)–O(4) 2.292(2) Å
C(40)–O(4) 1.422(4) Å
C(41)–C(42) 1.169(6) Å

X–C(40)–Y (˚)
108.1(3)–111.0(3) °

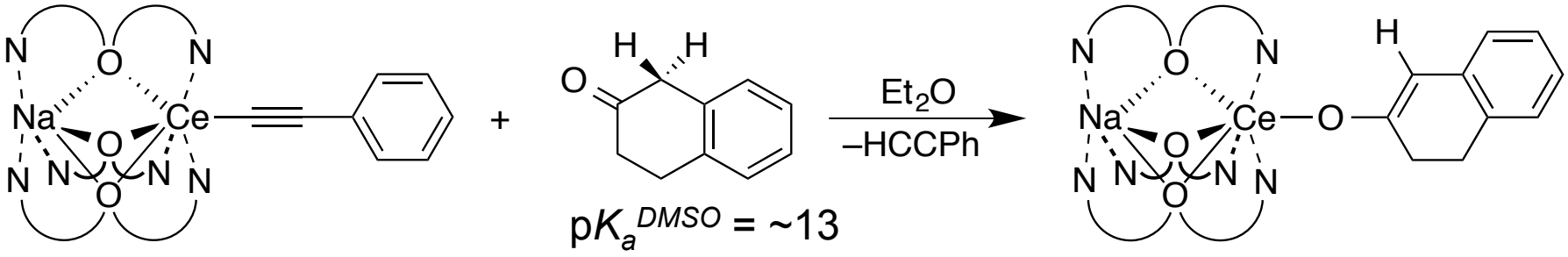
1,2-Insertion



40 %

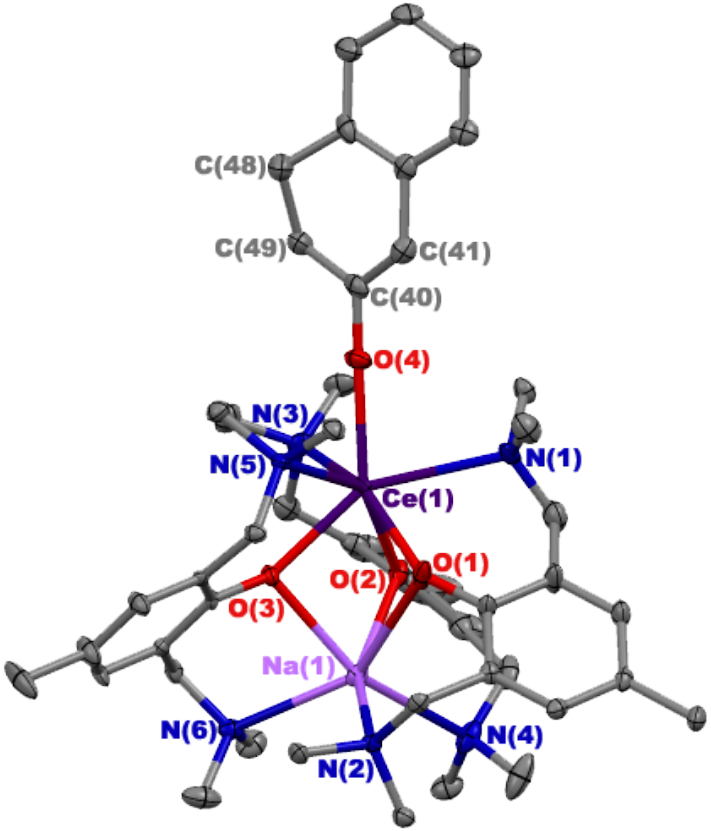
Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y.: *J. Am. Chem. Soc.* **1989**, *111*, 4392-4398.
Chemical Principles 7th edition, Zumdahl & Decoste, 2013, Brooks/Cole Cengage learning

With Highly Enolizable Ketone, β–tetralone



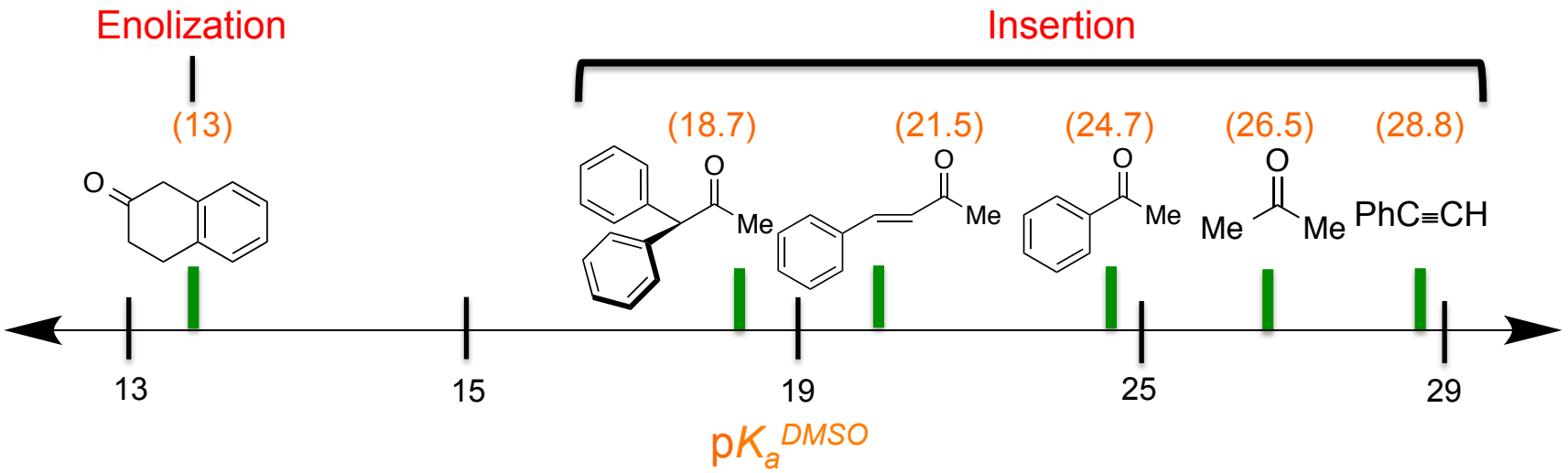
pK_a^{DMSO} = ~13

Enolization



C(40)–O(4) 1.333(5) Å,
C(40)–C(41) 1.316(6) Å,
Ce(1)–O(4) 2.318(3) Å,
X–C(40)–Y 116.5(4)–123.6(5)˚

pK_a^{DMSO} Range and the Limit

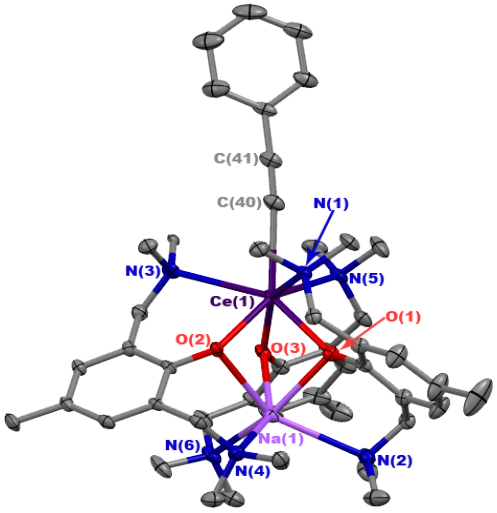


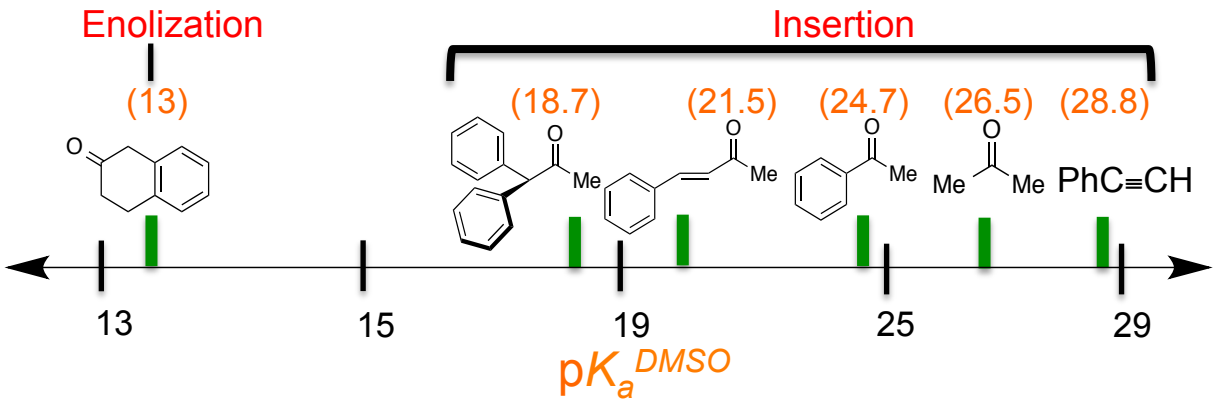
Conclusions

1. The structure of the first terminal trivalent cerium acetylide complex was determined.

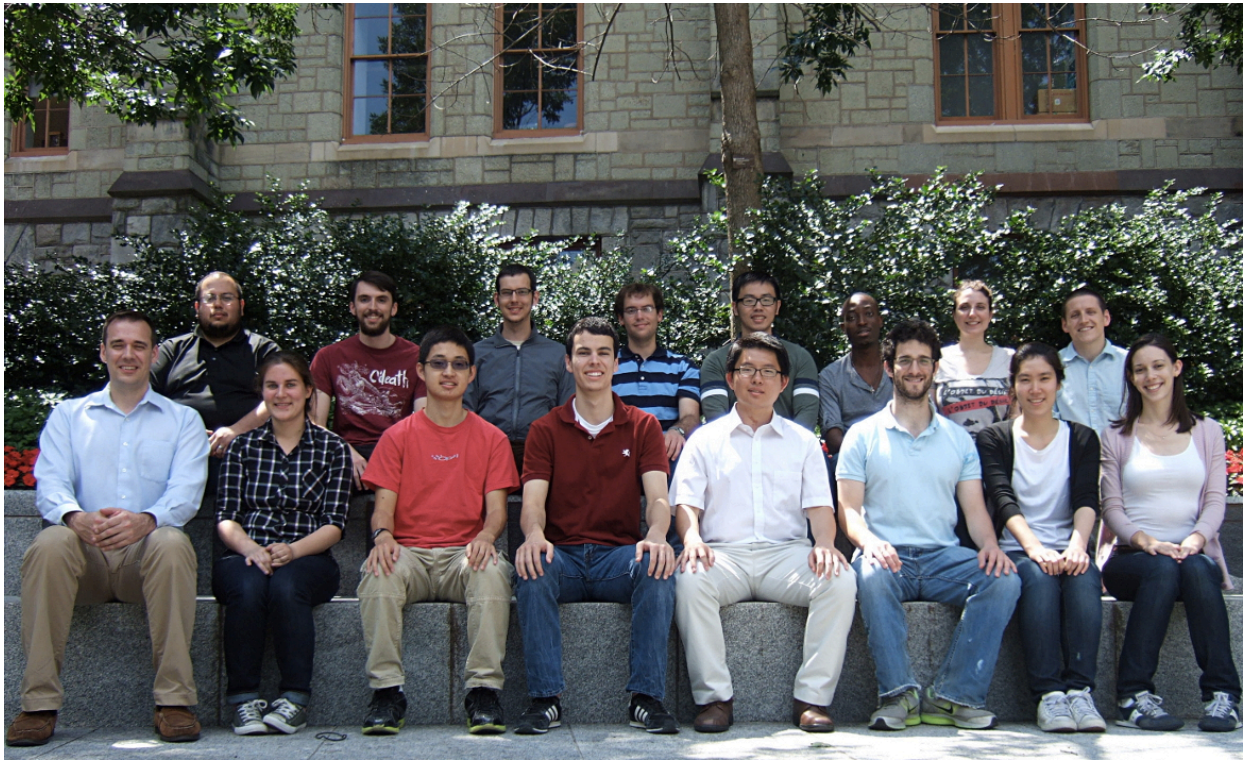
2. Utilization of high Lewis acidity of the cerium metal ion;
   a) Even though deprotonation of α-proton was thermodynamically favorable, insertion into Ce–C bond occurred.
   b) Successfully proved 1,2-adduct from benzylidene acetone

3. Lability of pendant amine groups on bdmmp⁻ afford the ketone substrates accessible to the cerium metal center, making carbonyl group more vulnerable to nucleophilic attack by the acetylide.





Acknowledgements



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