

Literature Report

“ Buchner Ring Expansion ” — Not That Kind —

Reporter: Si-Jun Xie
Supervisor: Zhang-Jie Shi

Fudan University
2019-10-18

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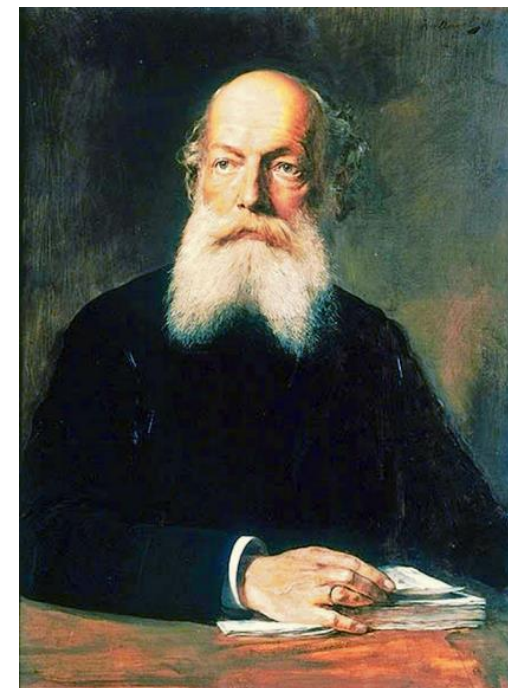
Background

It Began with a Daydream: The 150th Anniversary of the Kekulé Benzene Structure

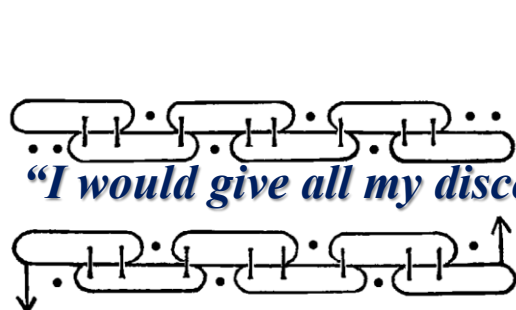
Rocke, A. J. *Angew. Chem. Int. Ed.* **2015**, 54, 46-50.

“ I was sitting there, working on my textbook, but it was not going well; my mind was on other things. I turned my chair toward the fireplace and sank into half-sleep. Again the atoms fluttered before my eyes. This time smaller groups remained modestly in the background. My mind’s eye, sharpened by repeated visions of a similar kind, now distinguished larger forms in a variety of shapes. Long lines, often combined more densely; everything in motion, twisting and turning like snakes. But look, what was that? One of the snakes had seized its own tail, and the figure whirled mockingly before my eyes. I awoke in a flash, and this time, too, I spent the rest of the night working out the consequences of the hypothesis. ”

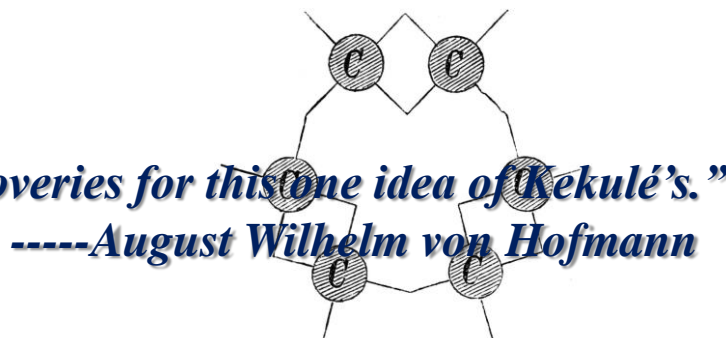
Kekulé A., *Ber. Dtsch. Chem. Ges.* **1890**, 23, 1305 – 1306.



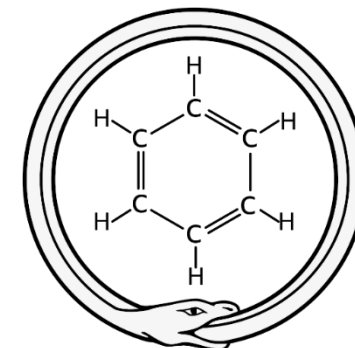
August Kekulé (1829–1896)



“sausage” formulas
1865



“ball-and-stick” formulas
1866



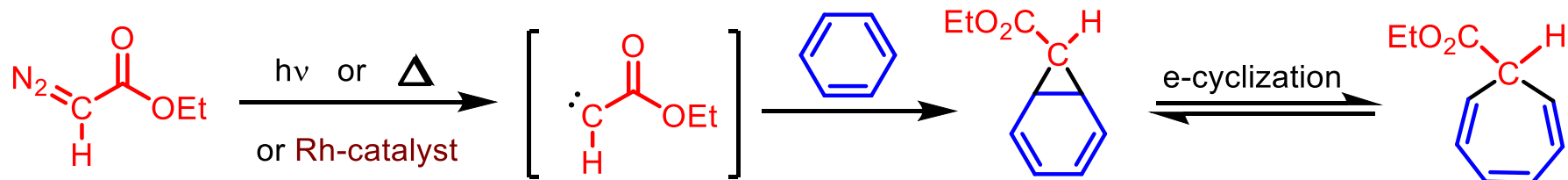
“oscillating single and double bonds”
1872

Background



Eduard Buchner (1860–1917)
The Nobel Prize in Chemistry 1907

"for his biochemical researches and his discovery of cell-free fermentation."

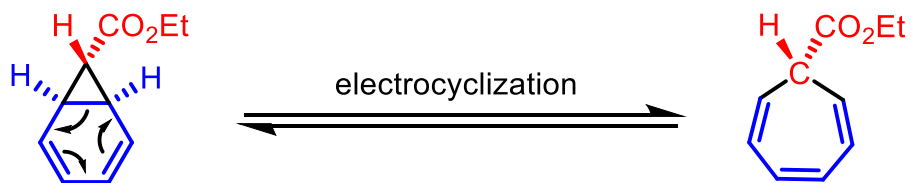
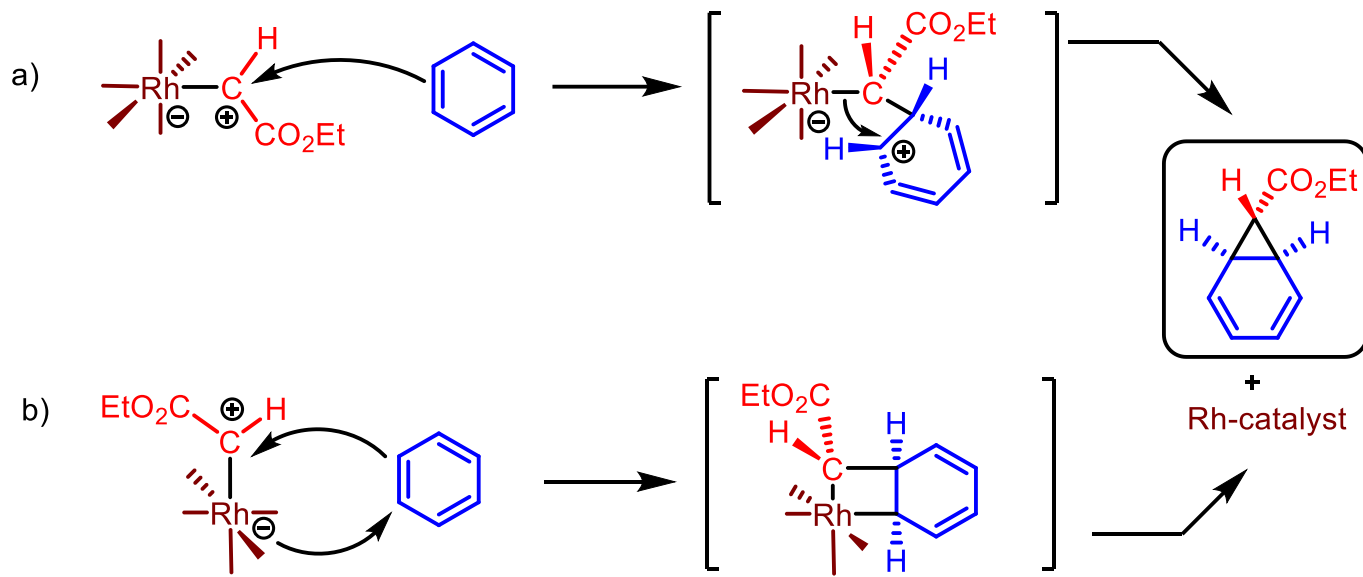
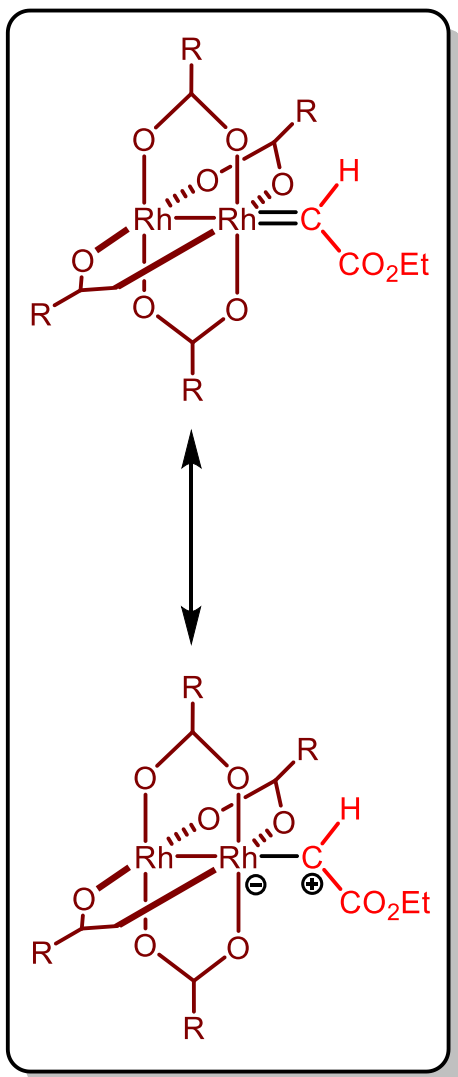


Buchner, E. and co-authors. *Berichte der deutschen chemischen Gesellschaft* **1885**, 18, 2371-2377.

Buchner, E. and co-authors. *Berichte der deutschen chemischen Gesellschaft* **1885**, 18, 2377-2379.

Background

Mechanism:



Teyssie, P. and co-authors. *Fundam. Res. Homogeneous Catal.* **1979**, 3, 421-432.
Doyle, M. P. *Chem. Rev.* **1986**, 86, 919-940.
Ramachandran, K. and co-authors. *Helv. Chim. Acta.* **1987**, 70, 1429-1438.

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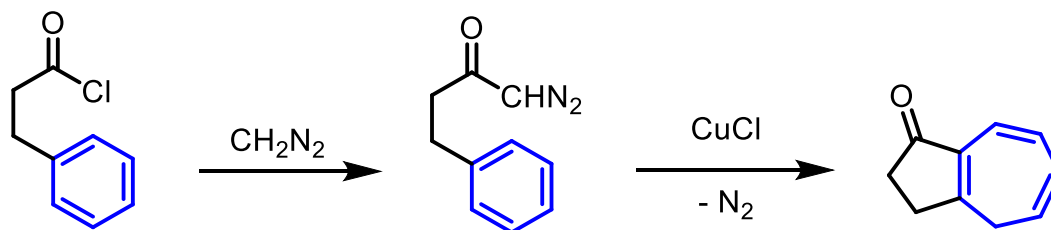
III. New Kinds of Buchner Ring Expansion Reactions

P/Si Insertion into Aromatic Rings

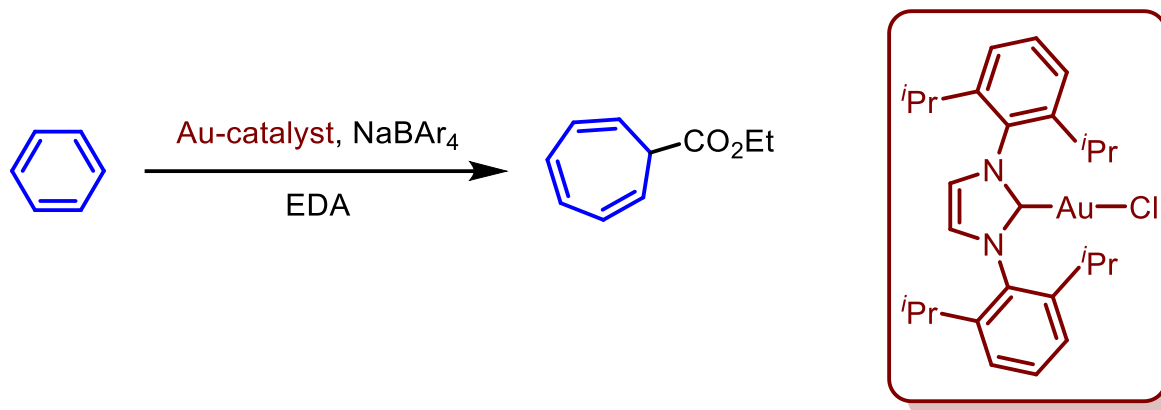
Metal Insertion into Aromatic Rings

IV. Summary

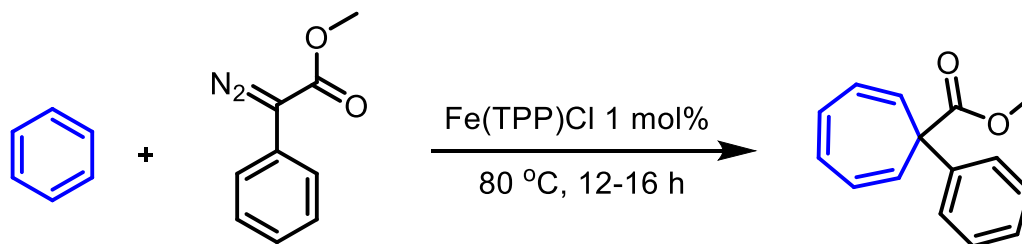
Brief Introduction of Buchner Ring Expansion



Scott, L. T. and co-authors. *J. Am. Chem. Soc.* **1980**, *102*, 6311-6314.

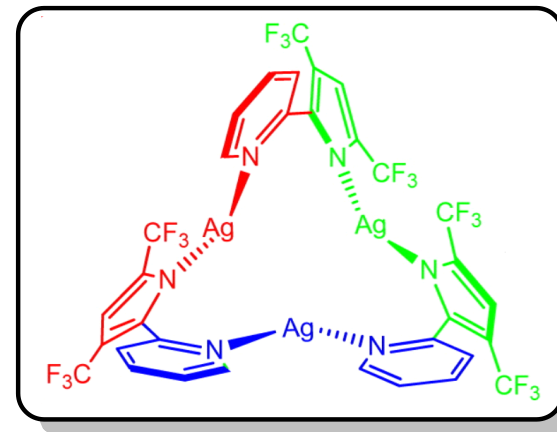
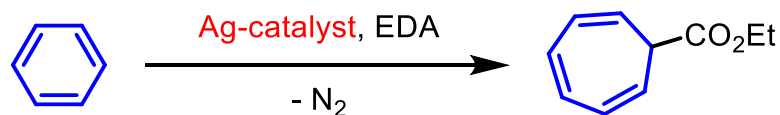


Pérez, J. P. and co-authors. *Angew. Chem. Int. Ed.* **2005**, *44*, 5284-5288.



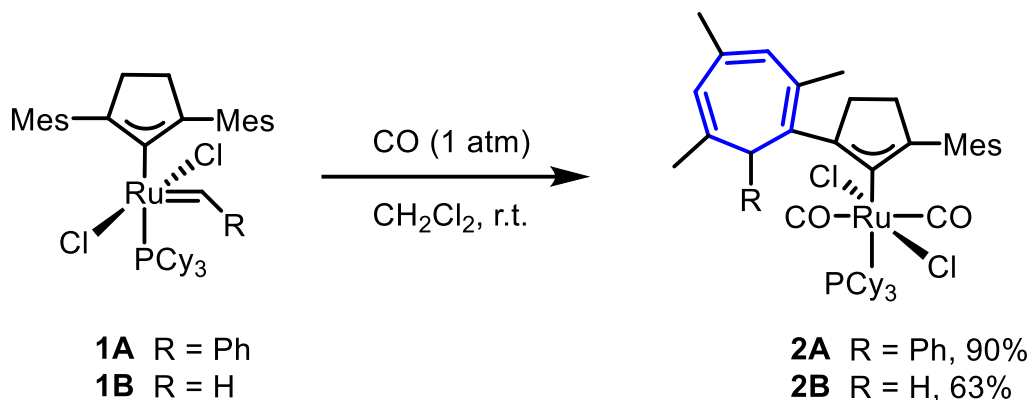
Mbuvu, H. M. and co-authors. *J. Porphyrins Phthalocyanines* **2009**, *13*, 136-152.

Brief Introduction of Buchner Ring Expansion



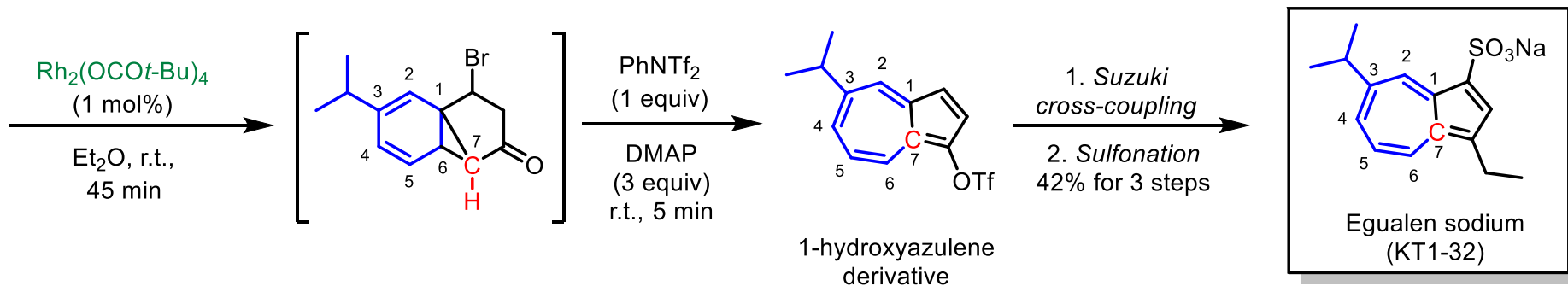
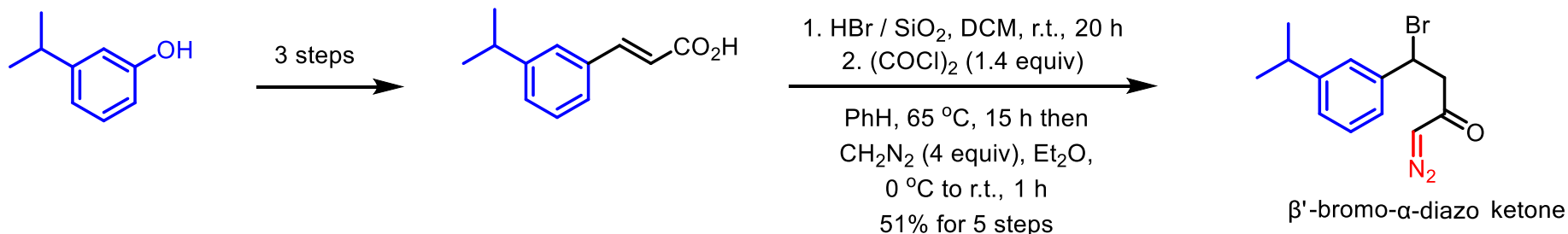
Lovely, C. J. and co-authors. *Tetrahedron Lett.* **2005**, *46*, 2453-2455.

Mindiola, J. D. and co-authors. *Organometallics* **2013**, *32*, 3185-3191.

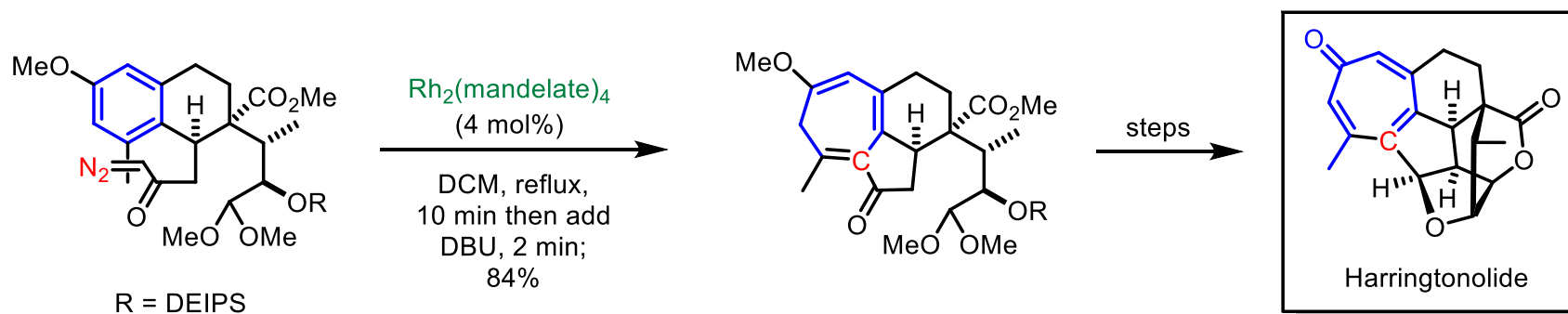


Diver, S. T. and co-authors. *J. Am. Chem. Soc.* **2005**, *127*, 15702-15703.

Brief Introduction of Buchner Ring Expansion

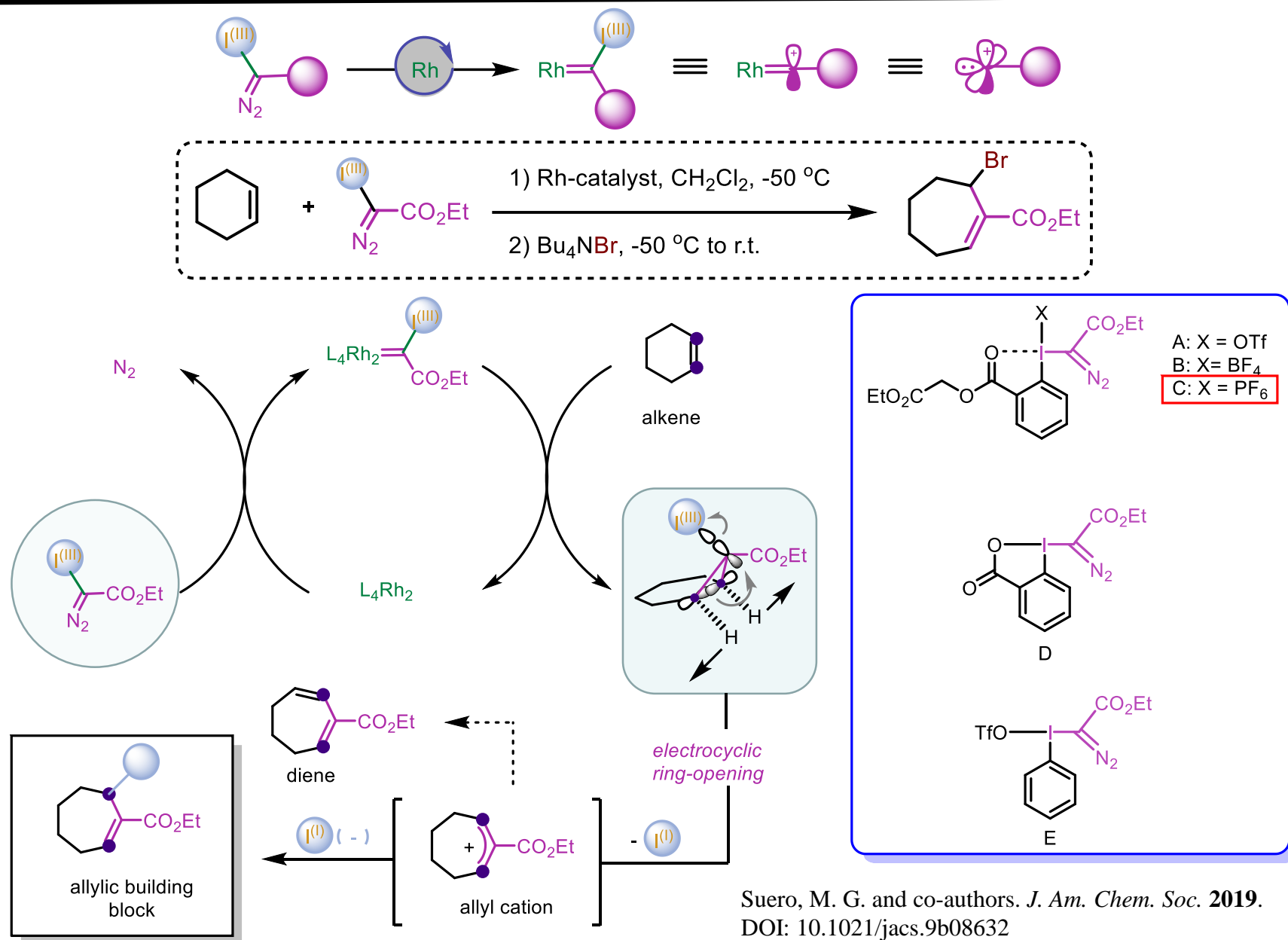


Danheiser, R. L. and co-authors. *Org. Lett.* **2001**, 3, 1081-1084.

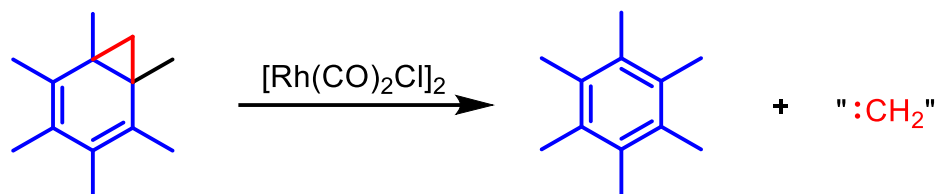


Mander, L. N. and co-authors. *J. Am. Chem. Soc.* **1998**, 120, 1914-1915.

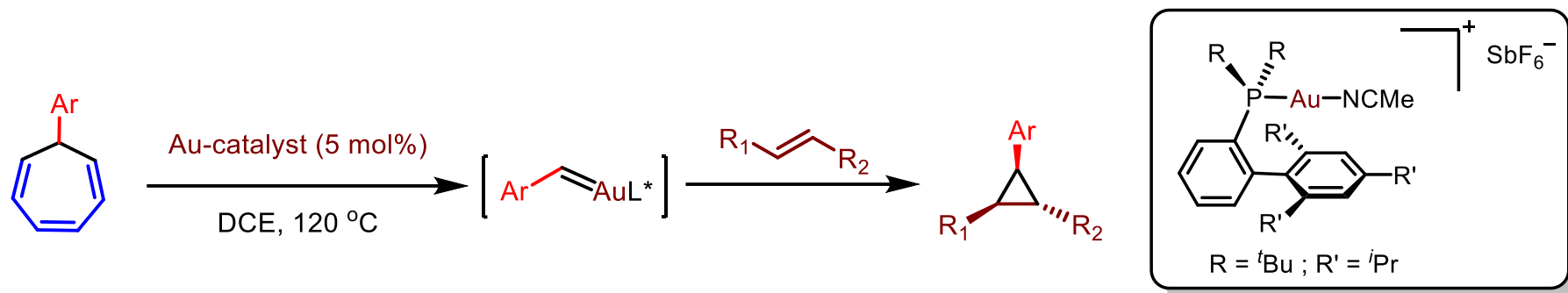
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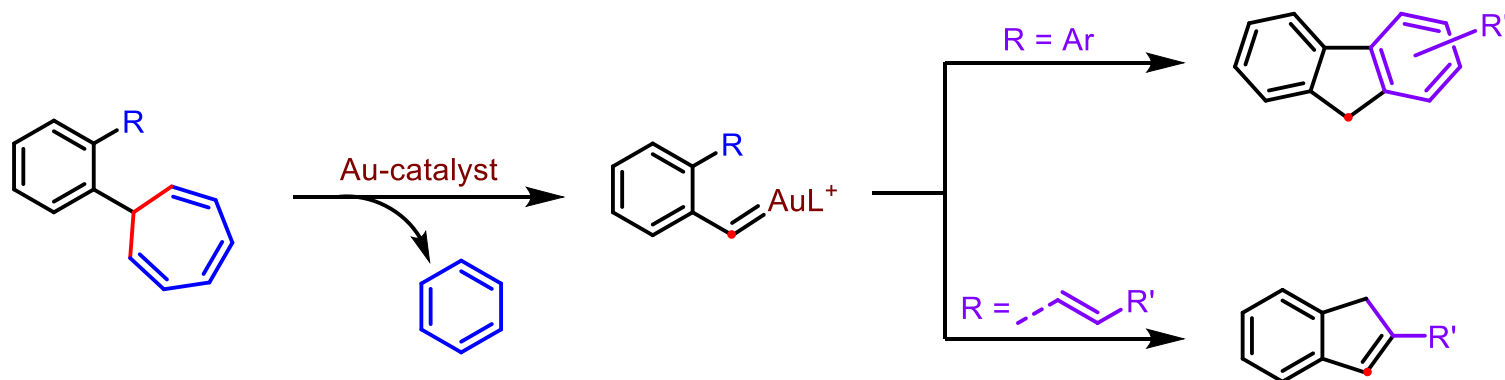
Brief Introduction of Buchner Ring Expansion



Roobeek, C. F. and co-authors. *Recl. Trav. Chim. Pays-Bas.* **1973**, 92, 1223–1231.



Echavarren, A. M. and co-authors. *J. Am. Chem. Soc.* **2011**, 133, 11952–11955.



Echavarren, A. M. and co-authors. *J. Am. Chem. Soc.* **2014**, 136, 801–809.

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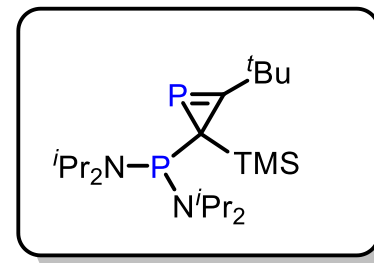
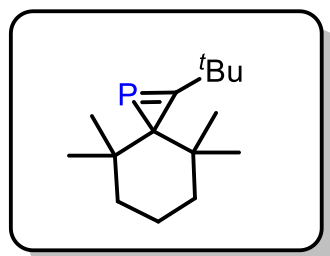
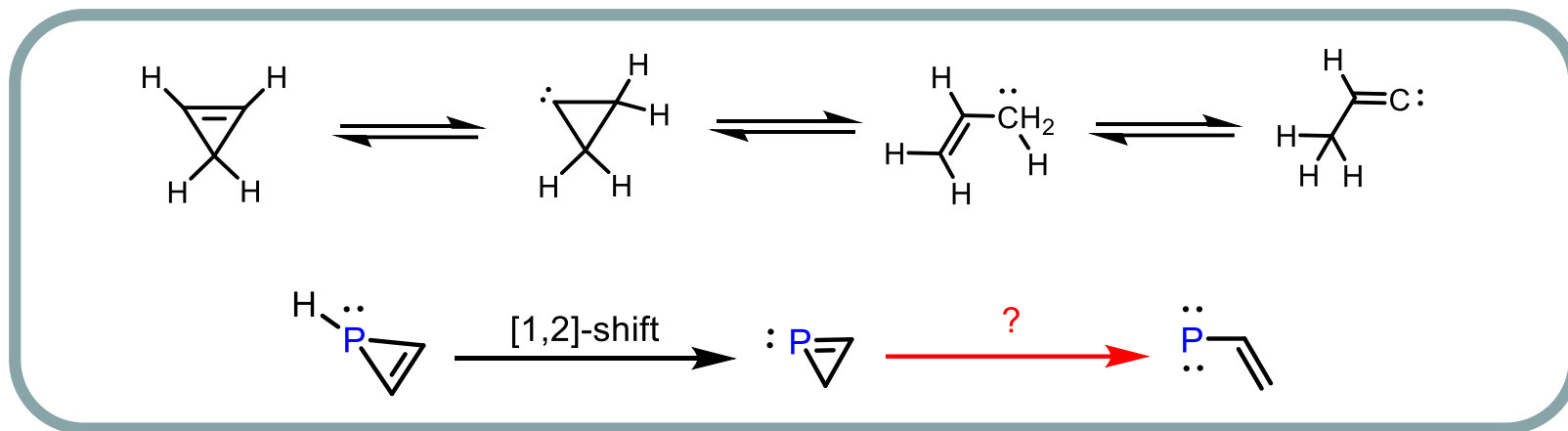
P/Si Insertion into Aromatic Rings

Metal Insertion into Aromatic Rings

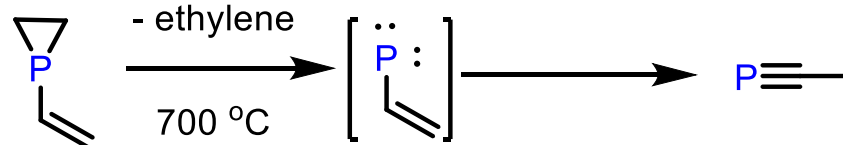
IV. Summary

New Kinds of Buchner Ring Expansion Reactions

----- P Insertion into Aromatic Rings



Regitz, M. and co-authors. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 1257–1259. Bertrand, G. and co-authors. *Chem. - Eur. J.* **1999**, 5, 274–279.



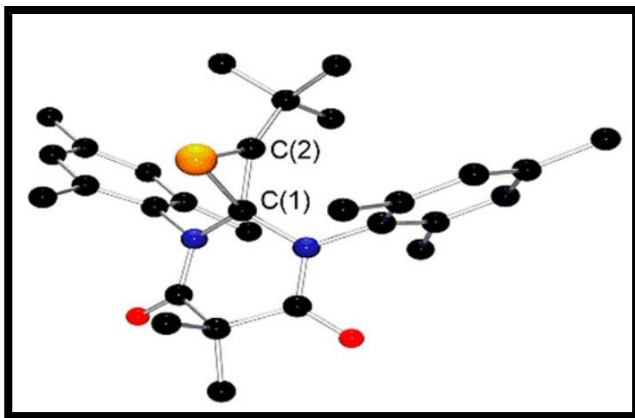
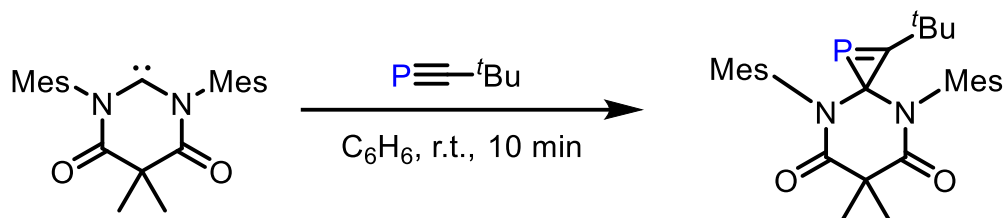
Mathey, F. J. and co-authors. *J. Chem. Soc., Chem. Commun.* **1992**, 1799–1800.

Mathey, F. J. and co-authors. *Organometallics* **1994**, 13, 640–646.

Mathey, F. J. and co-authors. *Organometallics* **1996**, 15, 4904–4915.

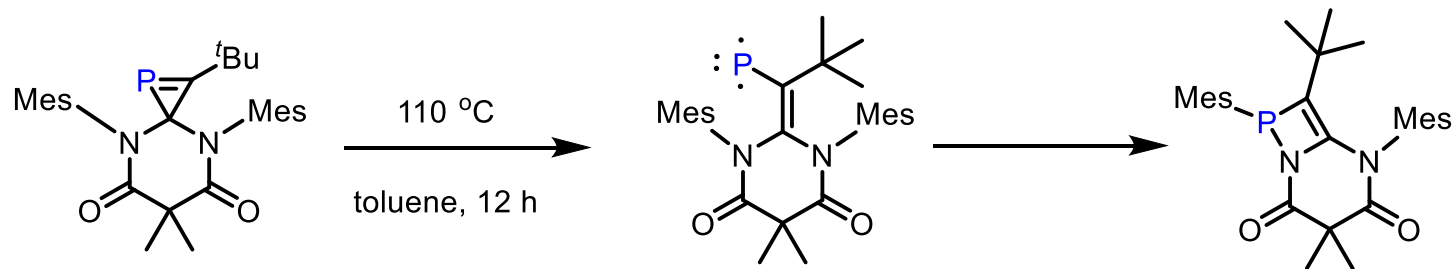
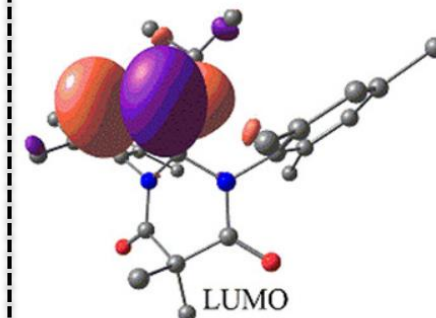
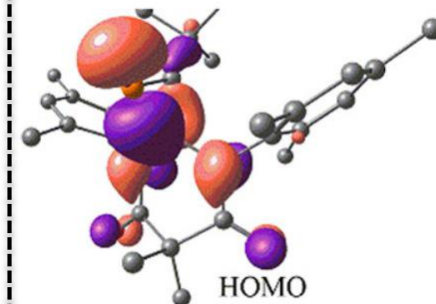
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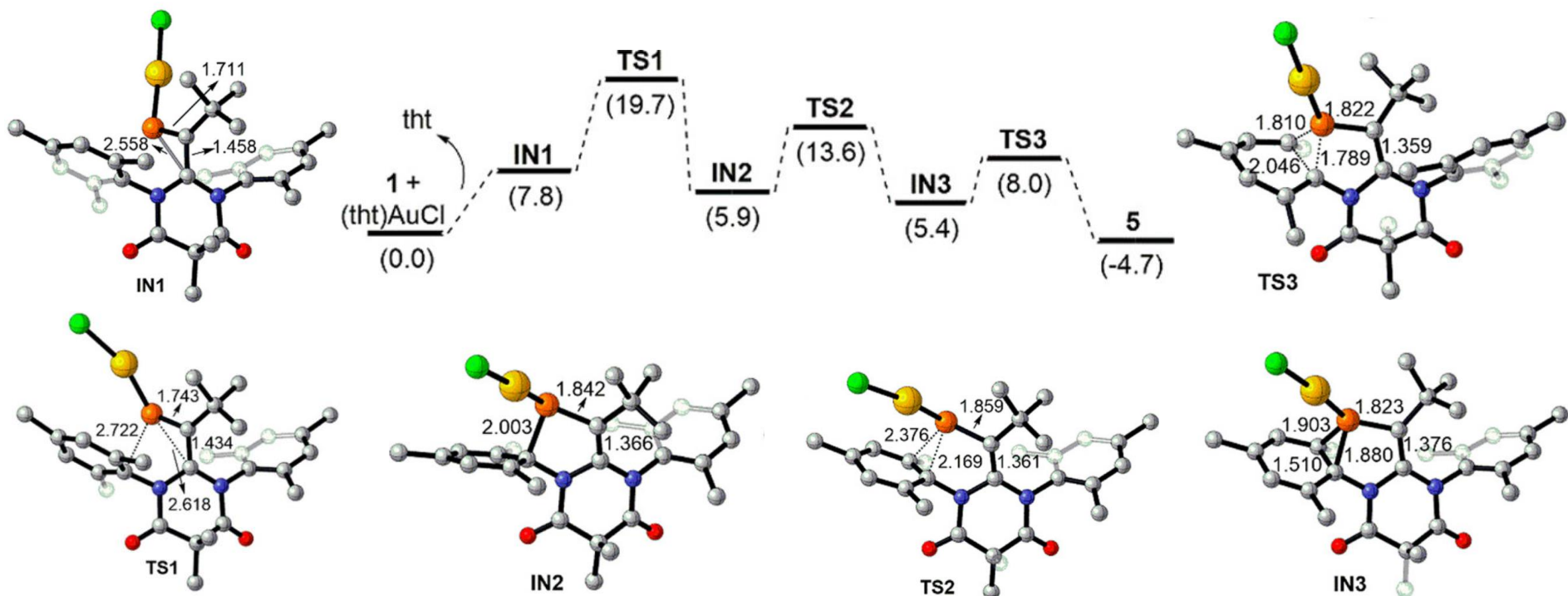
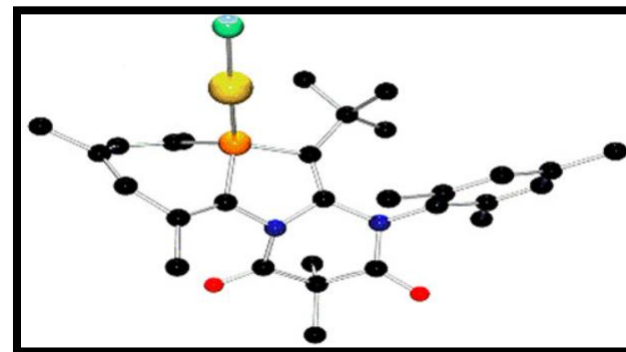
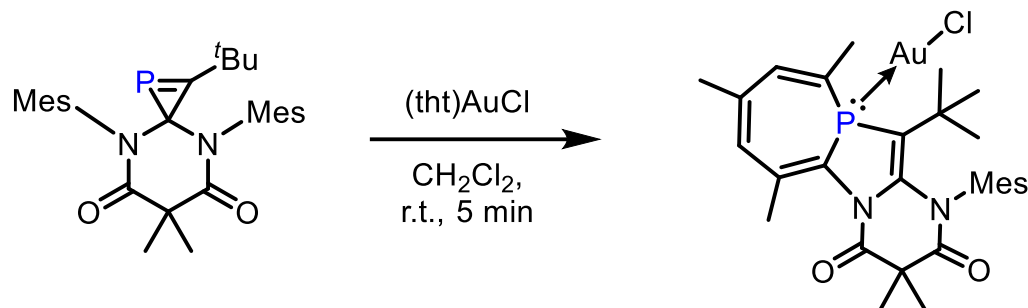
NBO analysis
(M06-2X/TZVP//M06-2X/Def2-SVP).
C(1) (0.18 au) P (0.61 au) C(2) (-0.38 au).

Wiberg Bond Order
C(1)-C(2): 1.09
C(1)-P : 0.83
C(2)-P : 1.69



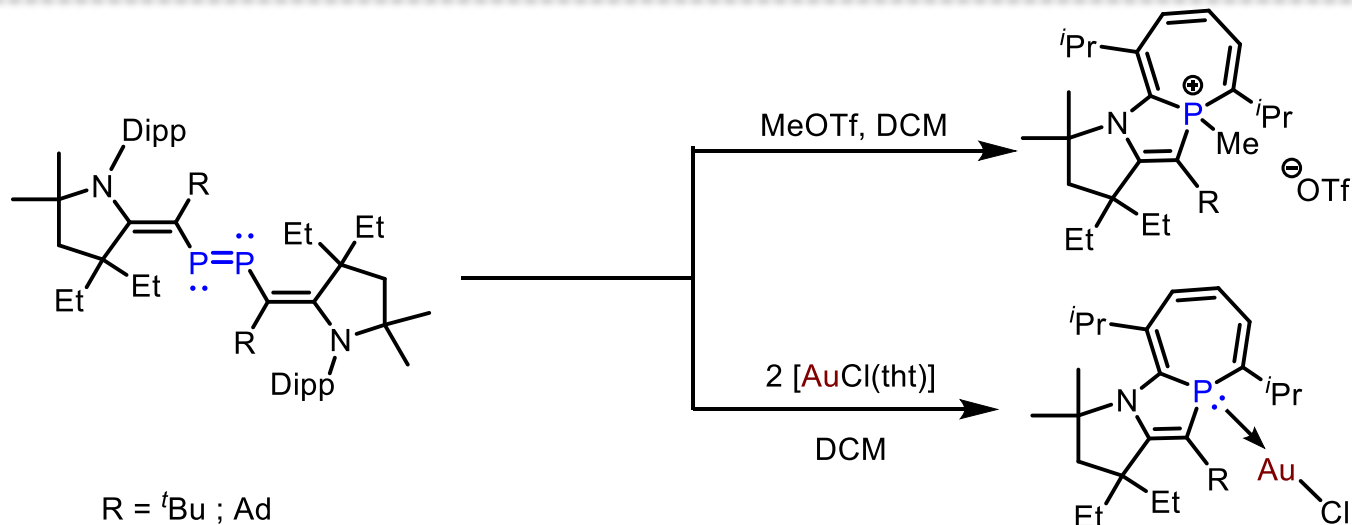
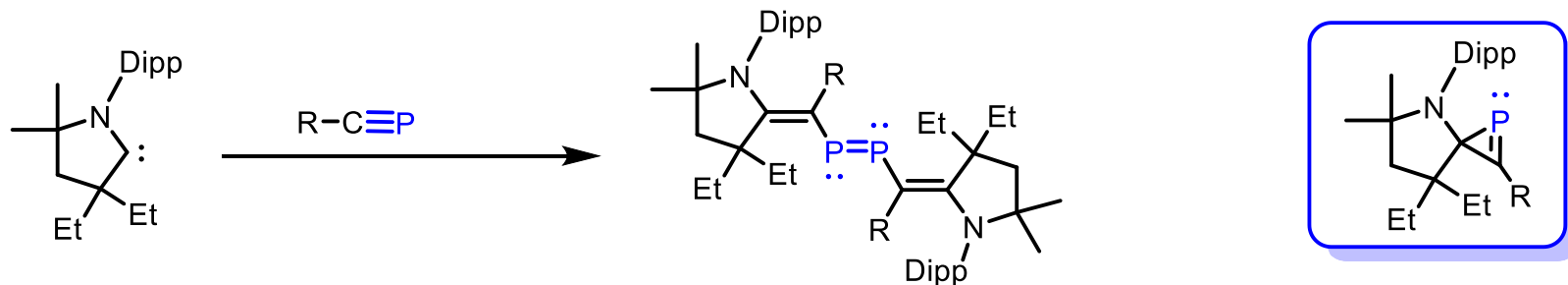
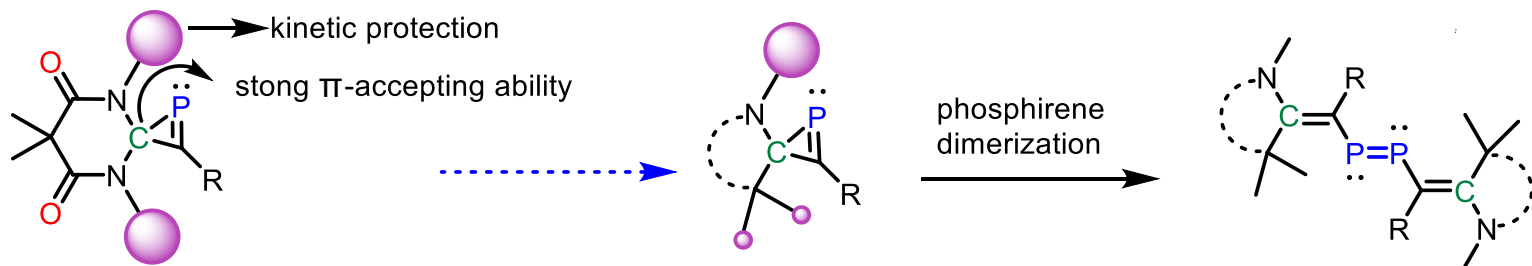
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----- P Insertion into Aromatic Rings



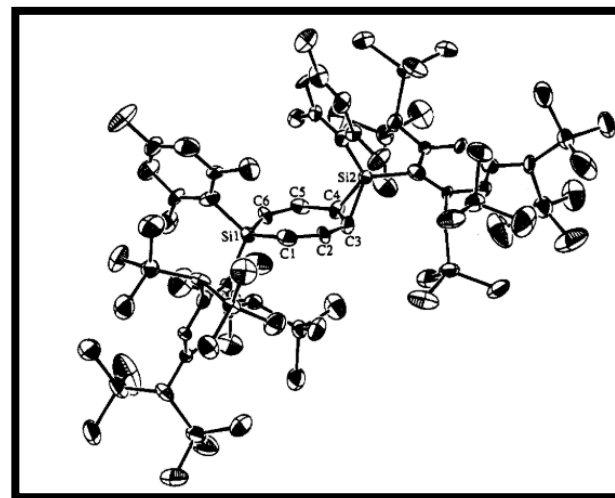
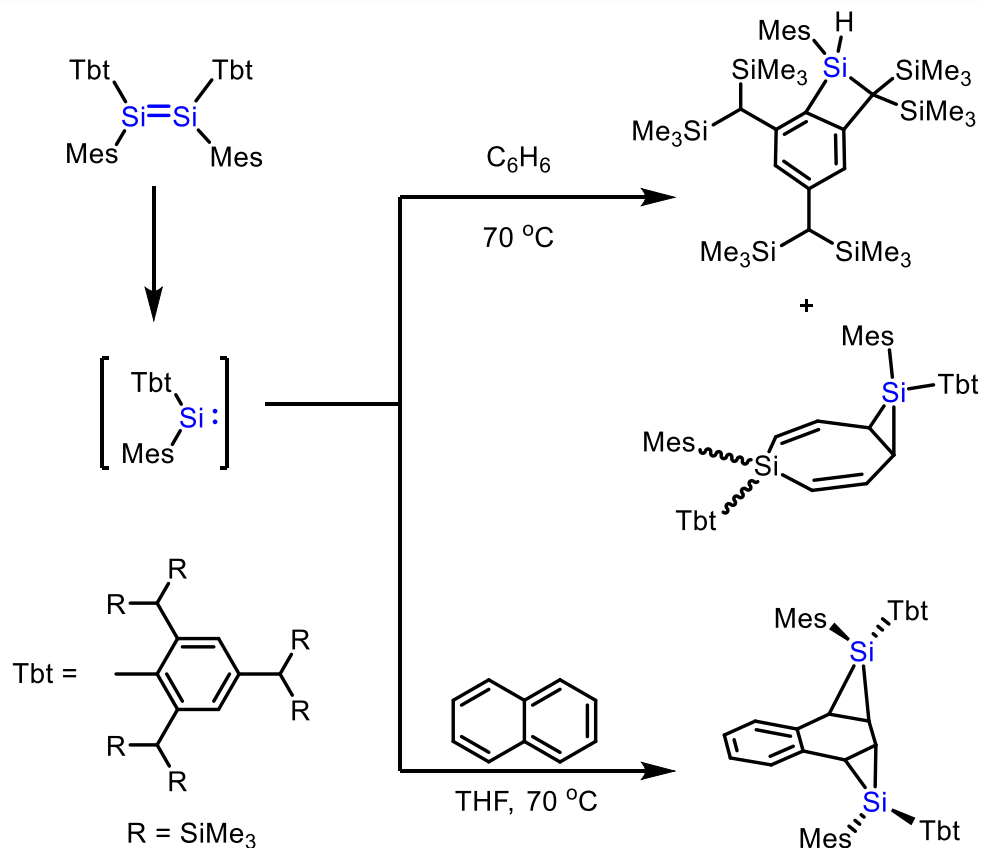
New Kinds of Buchner Ring Expansion Reactions

----- P Insertion into Aromatic Rings

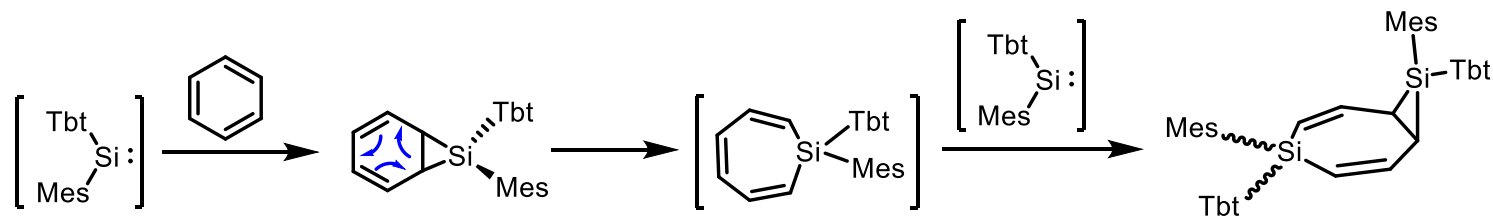


New Kinds of Buchner Ring Expansion Reactions

----- Si Insertion into Aromatic Rings

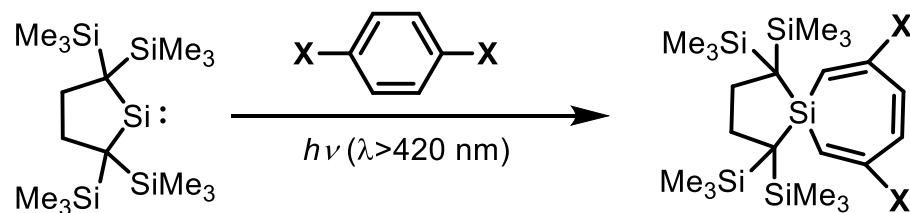
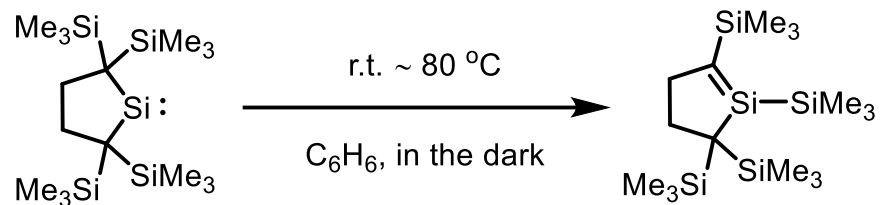


Okazaki, R. and co-authors. *J. Am. Chem. Soc.* **1994**, *116*, 11572-11573.

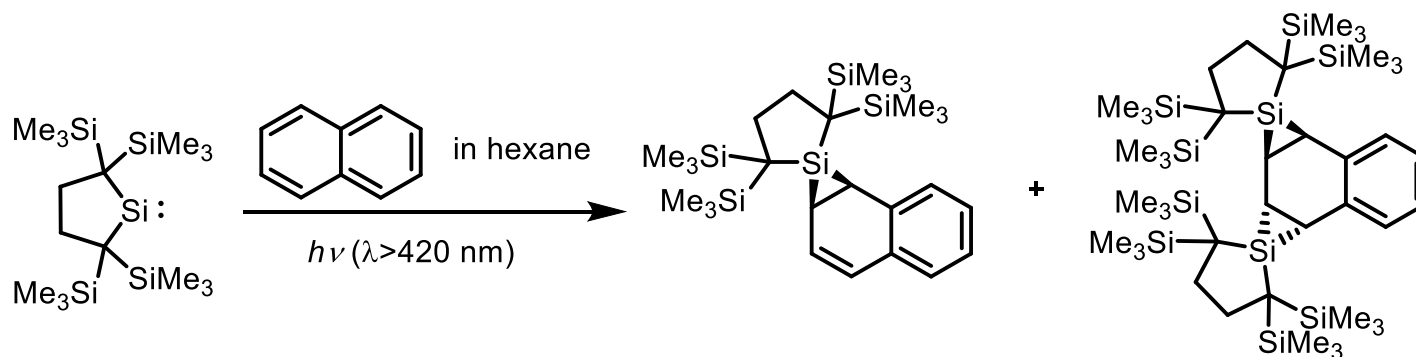


New Kinds of Buchner Ring Expansion Reactions

----- Si Insertion into Aromatic Rings



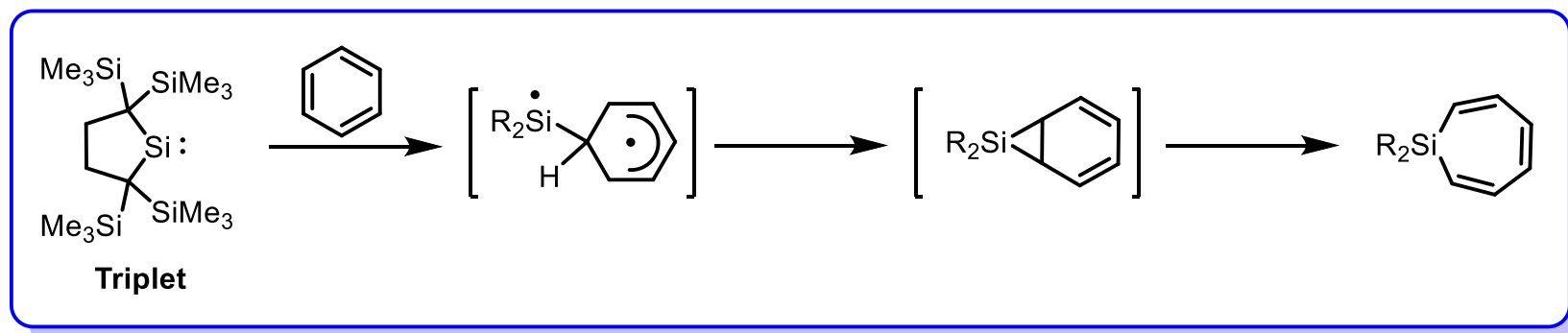
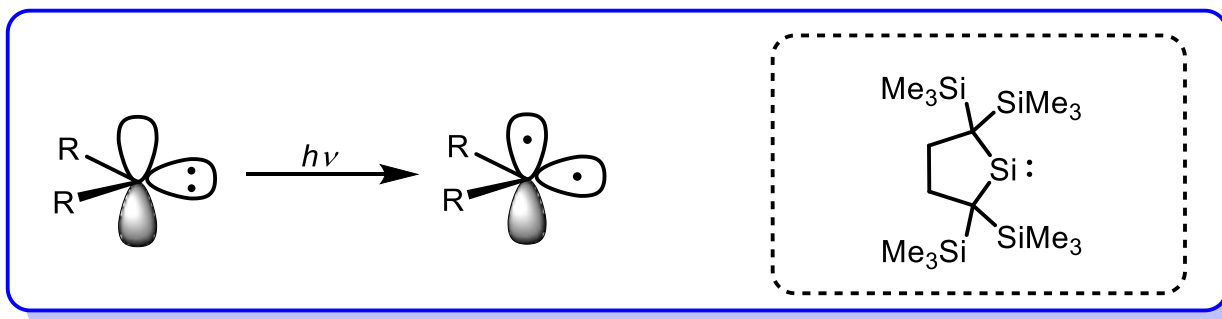
X = H, CH₃, OCH₃, F, CF₃



Kabuto, C. and co-authors. *J. Am. Chem. Soc.* **2002**, *124*, 3830-3831.

New Kinds of Buchner Ring Expansion Reactions

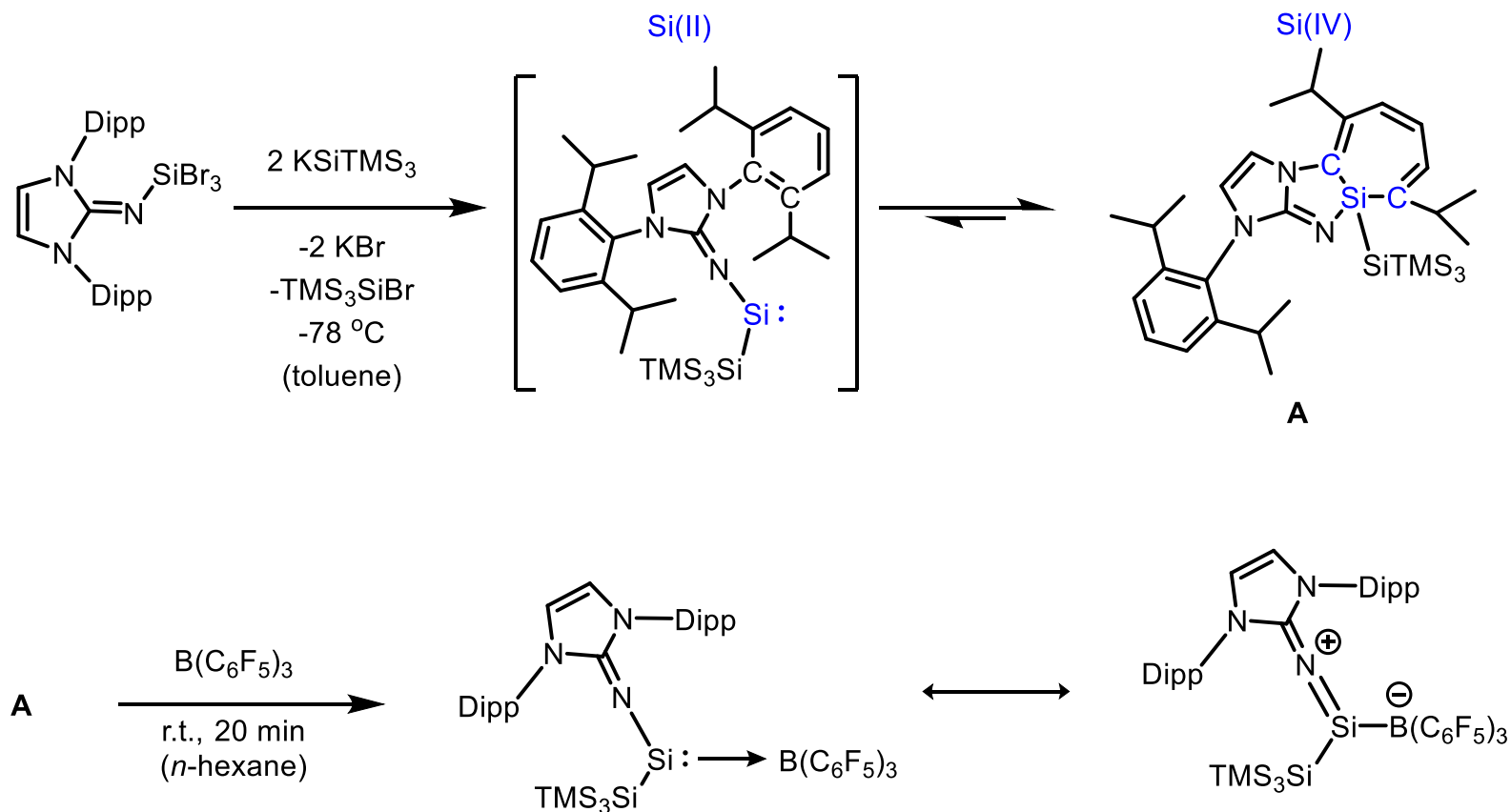
----- Si Insertion into Aromatic Rings



Kabuto, C. and co-authors. *J. Am. Chem. Soc.* **2002**, *124*, 3830-3831.

New Kinds of Buchner Ring Expansion Reactions

----- Si Insertion into Aromatic Rings



Rieger, B. and co-authors. *J. Am. Chem. Soc.* **2017**, *139*, 8134-8137.

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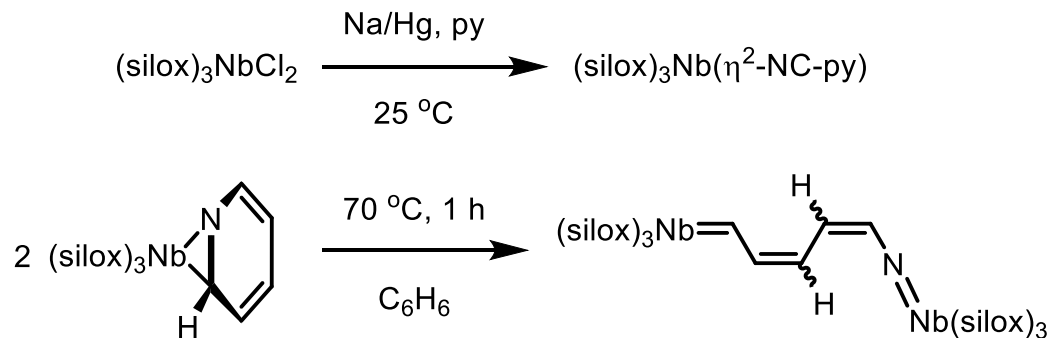
P/Si Insertion into Aromatic Rings

Metal Insertion into Aromatic Rings

IV. Summary

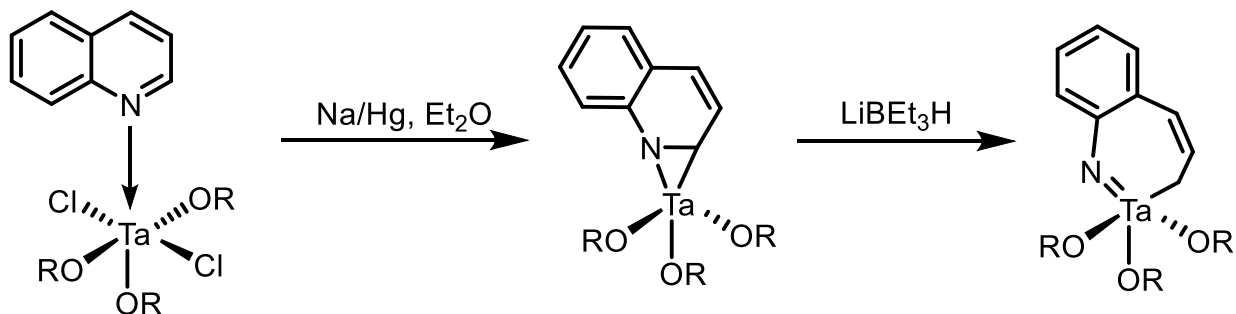
New Kinds of Buchner Ring Expansion Reactions

----- Nb/Ta Insertion into N-heterocyclic Aromatic Rings



Lobkovsky, E. B. and co-authors. *J. Am. Chem. Soc.* **1997**, *119*, 247-248.

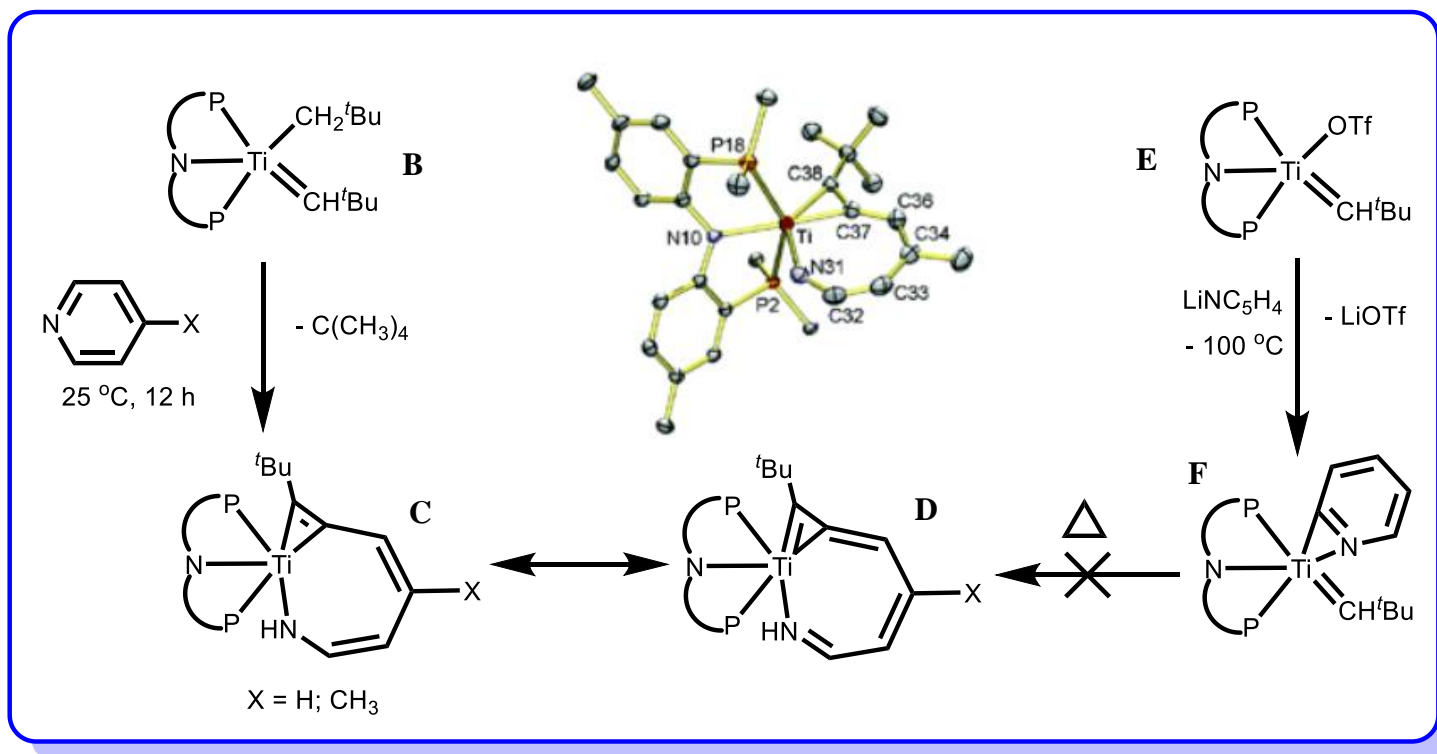
Wolczanski, P. T. *Chem. Commun.* **2009**, 740-757.



Wigley, D. E. and co-authors. *J. Am. Chem. Soc.* **1992**, *114*, 5462-5463.

New Kinds of Buchner Ring Expansion Reactions

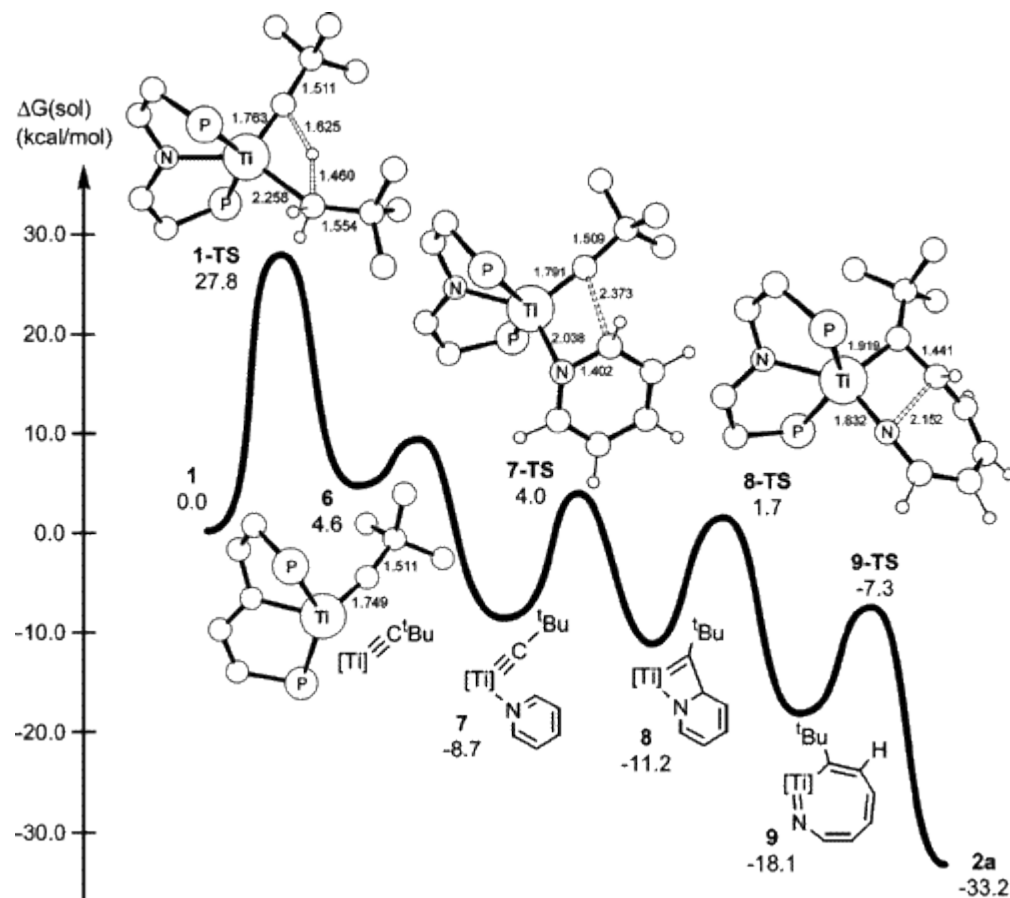
----- Ti Insertion into N-heterocyclic Aromatic Rings



Mindiola, D. J. and co-authors. *J. Am. Chem. Soc.* **2006**, *128*, 6798-6799.

New Kinds of Buchner Ring Expansion Reactions

----- Ti Insertion into N-heterocyclic Aromatic Rings

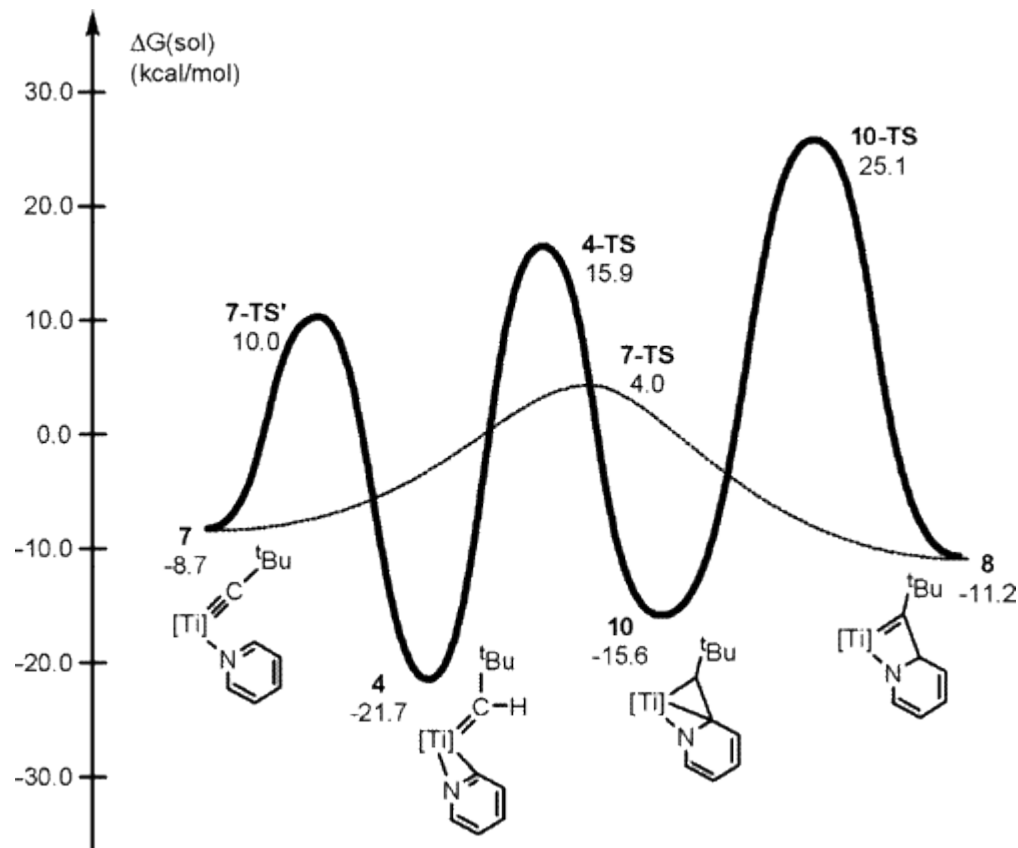


Proposed mechanism of the ROM of pyridine. Only core structures are shown for illustration. All energies are solution phase free energies, and all bond lengths are given in Å.

Examination of the volatile components in the **1** — **2a** conversion reveals CH_3^tBu to be the only product, suggesting that α -H abstraction precedes C-N bond activation.

New Kinds of Buchner Ring Expansion Reactions

----- Ti Insertion into N-heterocyclic Aromatic Rings

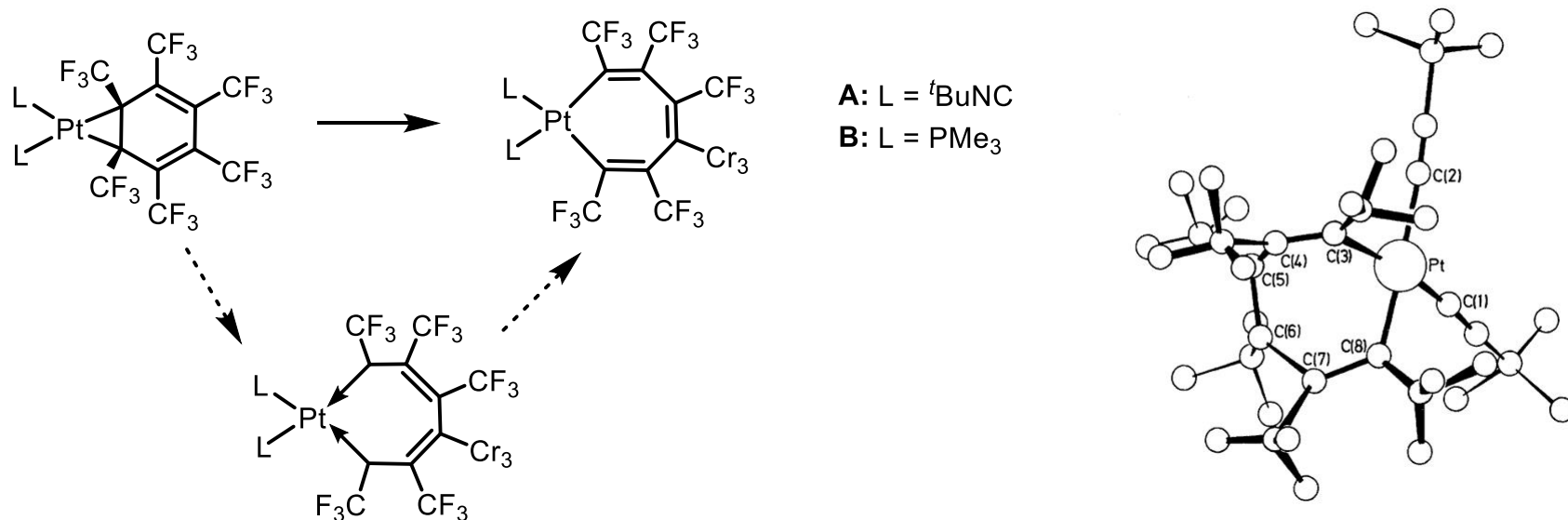


Proposed mechanism of the ROM of pyridine. All energies are solution phase free energies. The dotted line represents the conversion of **7** directly to **8**.

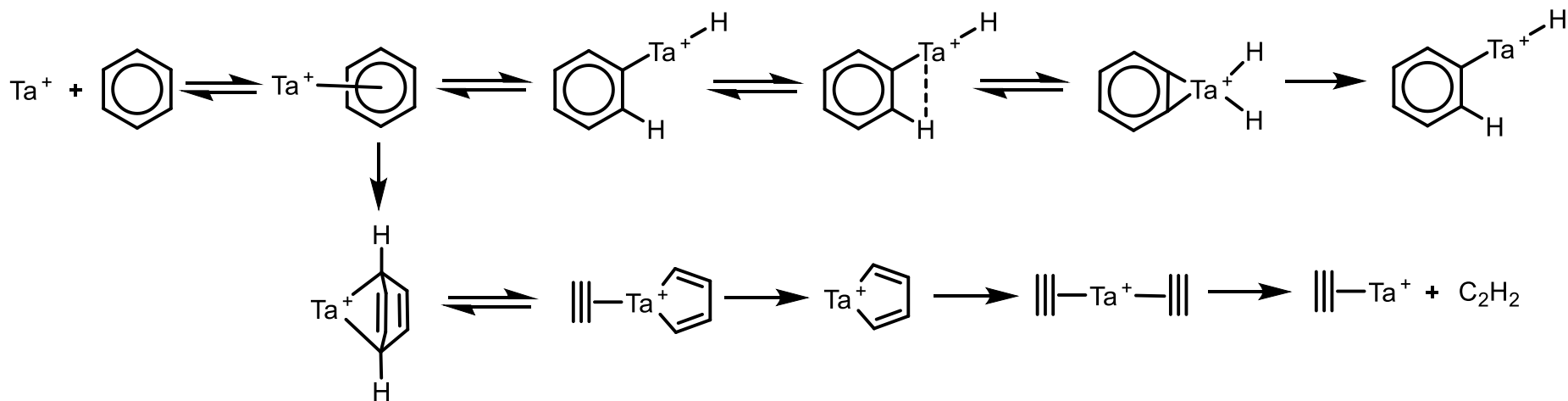
Intermediate **7**, one could envision orthometalation to afford complex **4**, which could subsequently undergo ring expansion concomitant with C-C bond formation to produce intermediate **10**.

New Kinds of Buchner Ring Expansion Reactions

----- Pt/Ta Insertion into Aromatic Rings



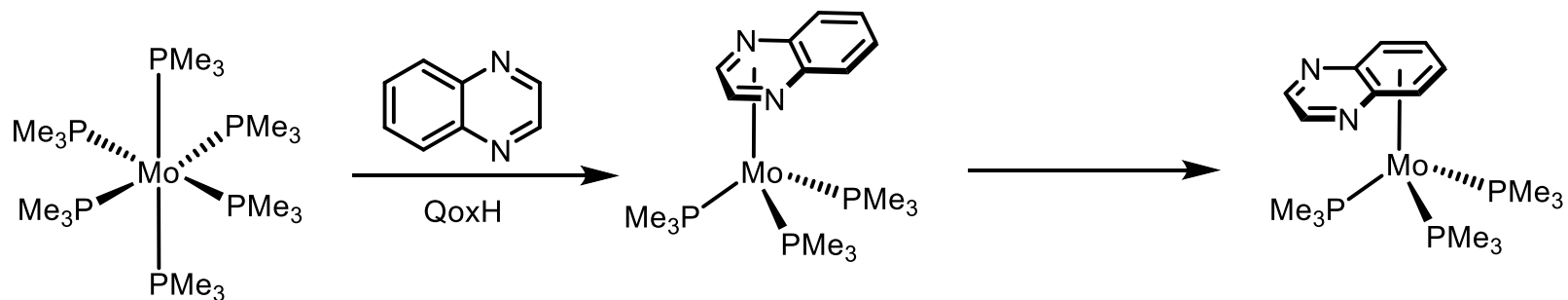
Stone, F. G. and co-authors. *J. Chem. Soc., Chem. Commun.* **1975**, 17, 723-724.



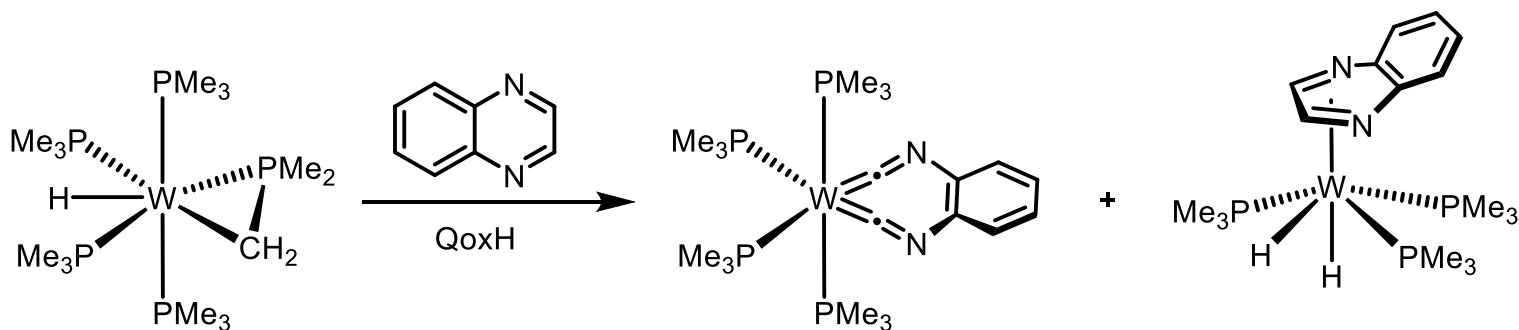
Pope, R. M. and co-authors. *Organometallics* **1992**, 11, 2001-2003.

New Kinds of Buchner Ring Expansion Reactions

----- W Insertion into Aromatic Rings



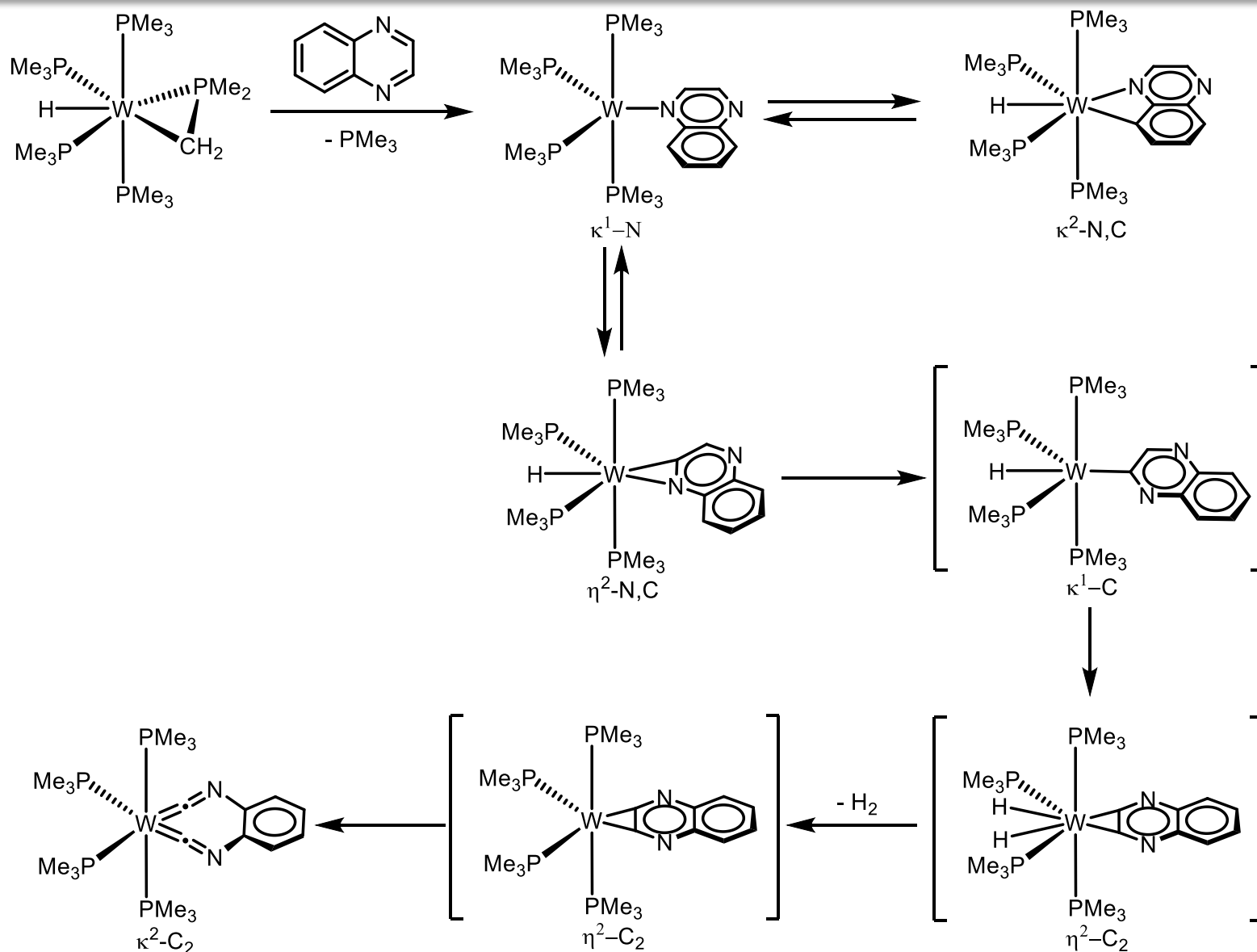
Parkin, G. and co-authors. *J. Am. Chem. Soc.* **2008**, *130*, 1564–1565.



Parkin, G. and co-authors. *Nature* **2010**, *463*, 523.

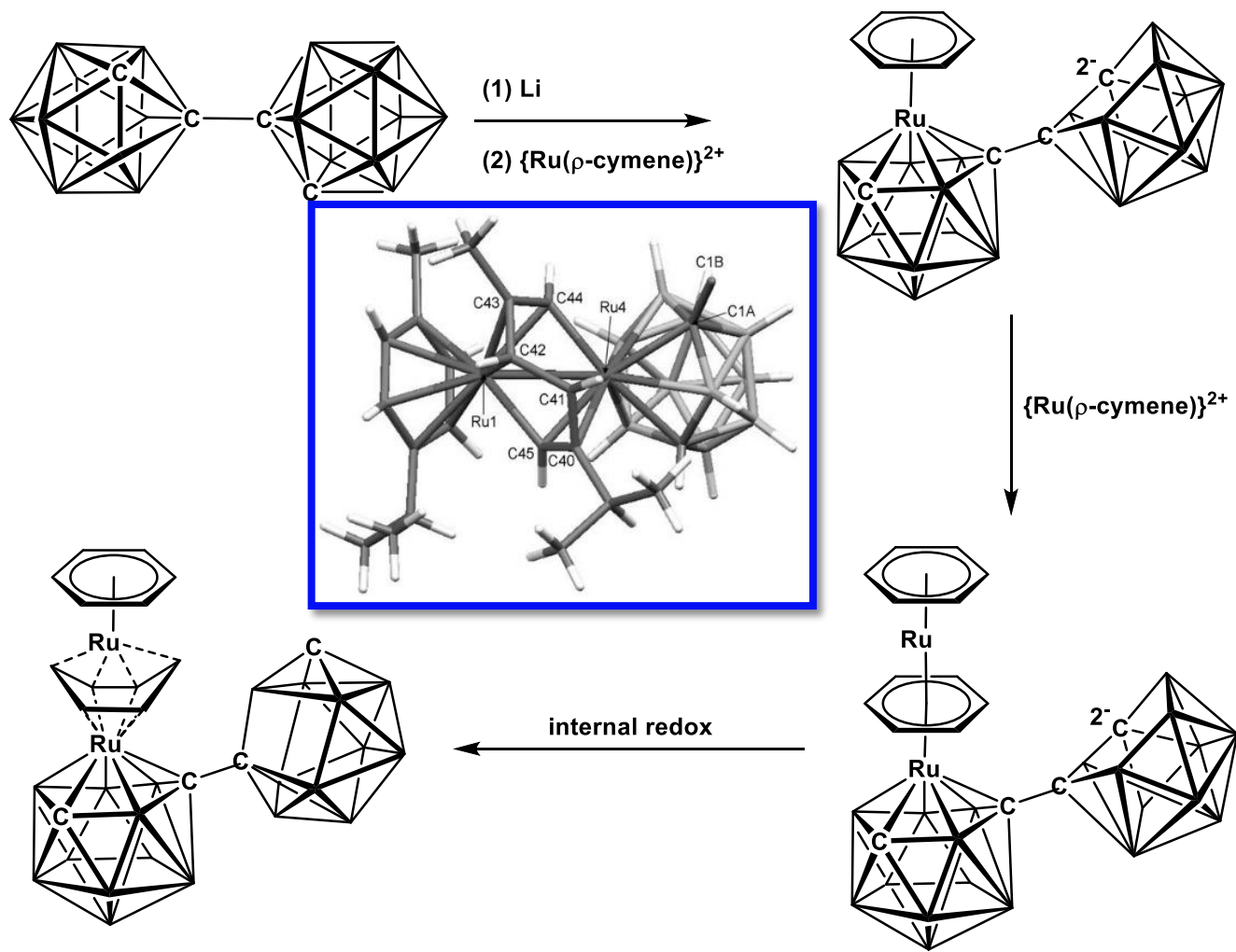
New Kinds of Buchner Ring Expansion Reactions

----- W Insertion into Aromatic Rings



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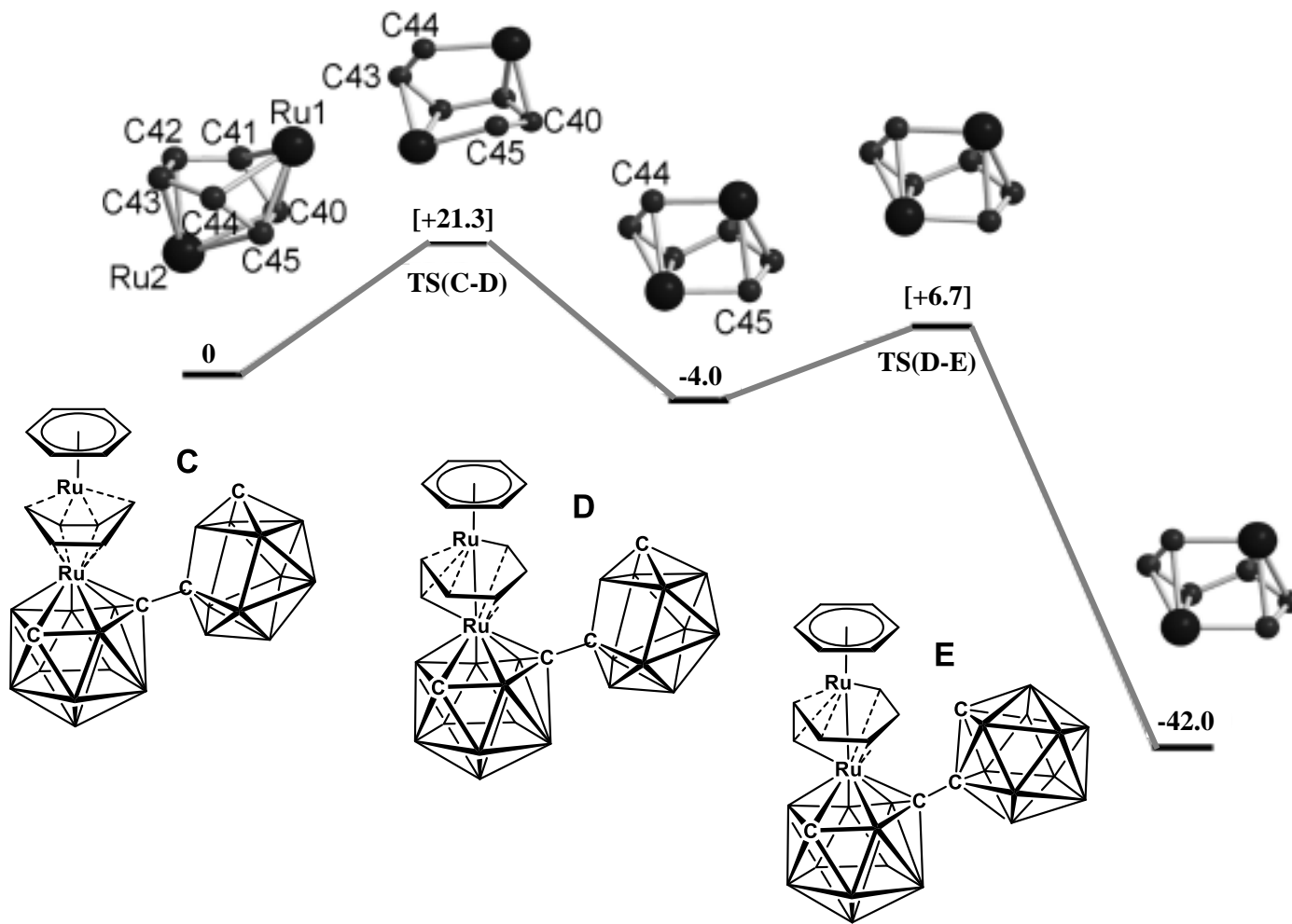
----- Ru Insertion into Aromatic Rings



Welch, A. J. and co-authors. *Angew. Chem. Int. Ed.* **2010**, *49*, 4943-4945.

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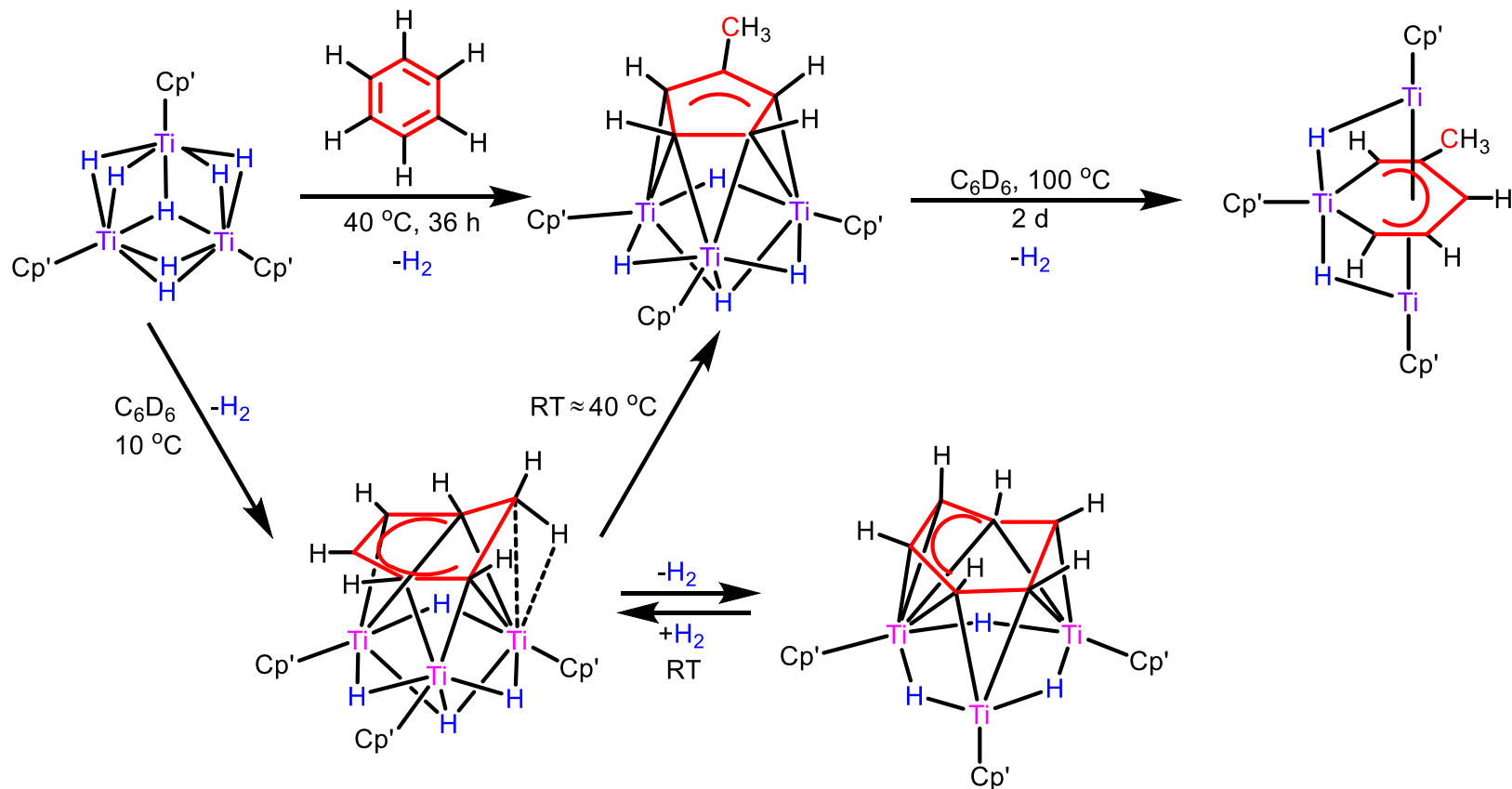
----- Ru Insertion into Aromatic Rings



Welch, A. J. and co-authors. *Angew. Chem. Int. Ed.* **2010**, *49*, 4943-4945.

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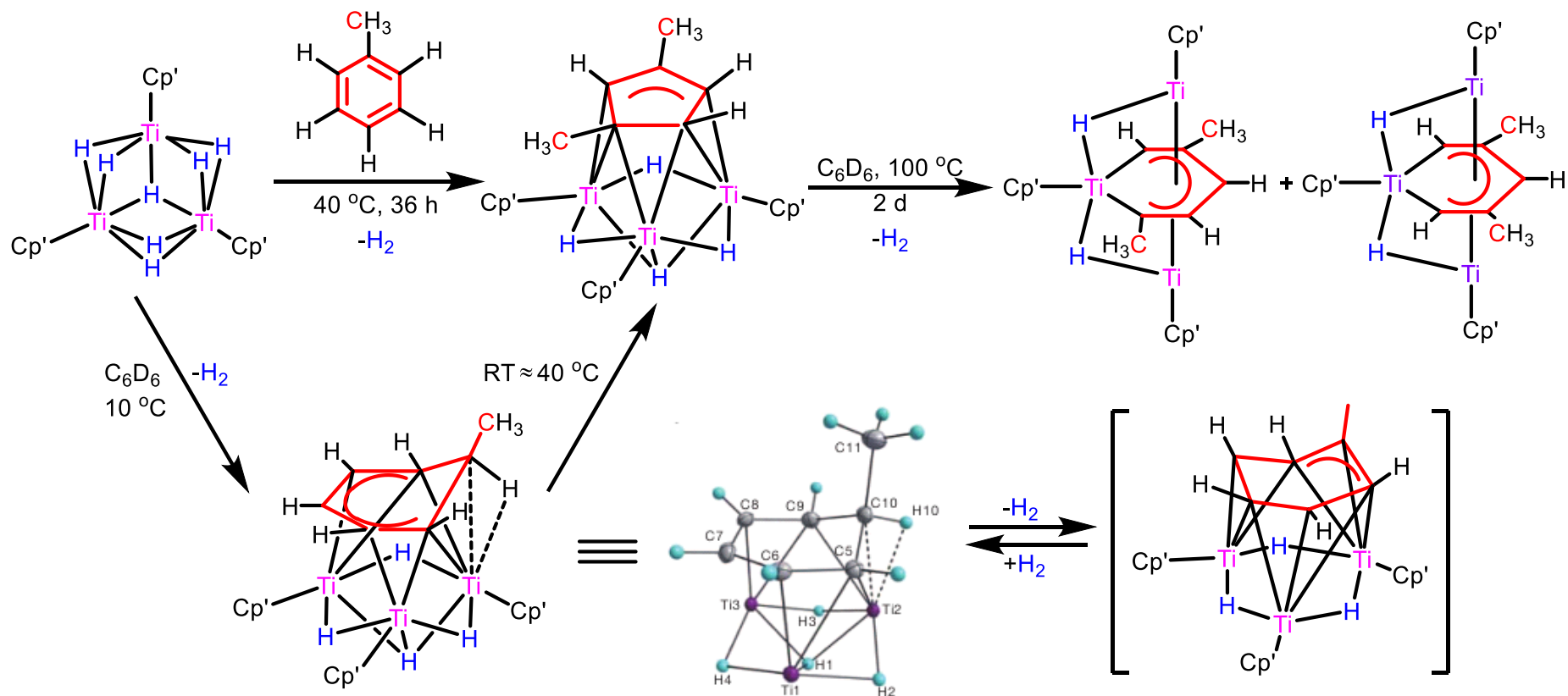
----- Ti Insertion into Aromatic Rings



Hou, Z. and co-authors. *Nature* **2014**, 512, 413.

New Kinds of Buchner Ring Expansion Reactions

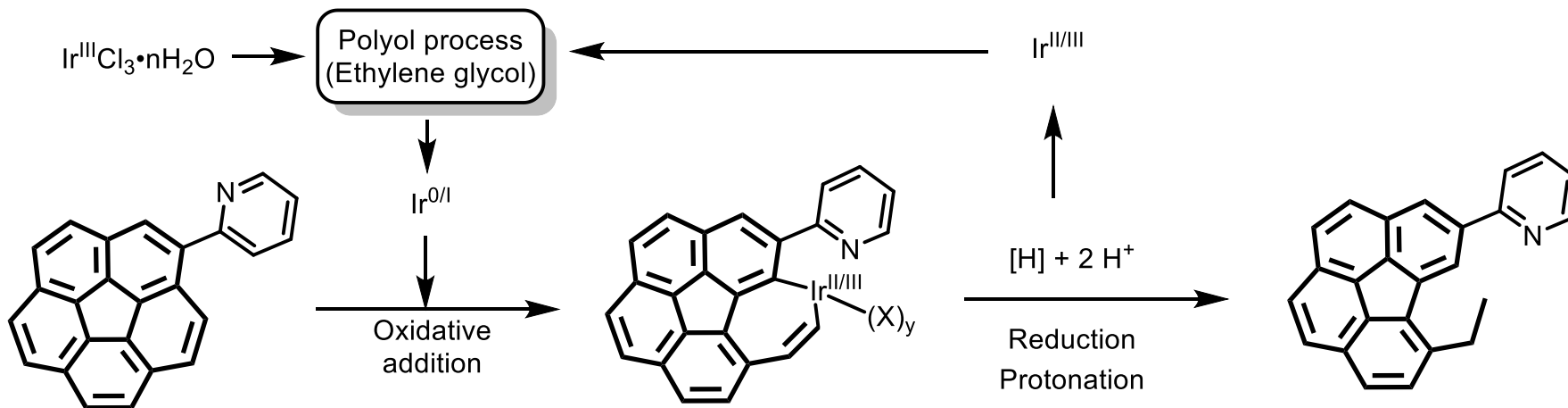
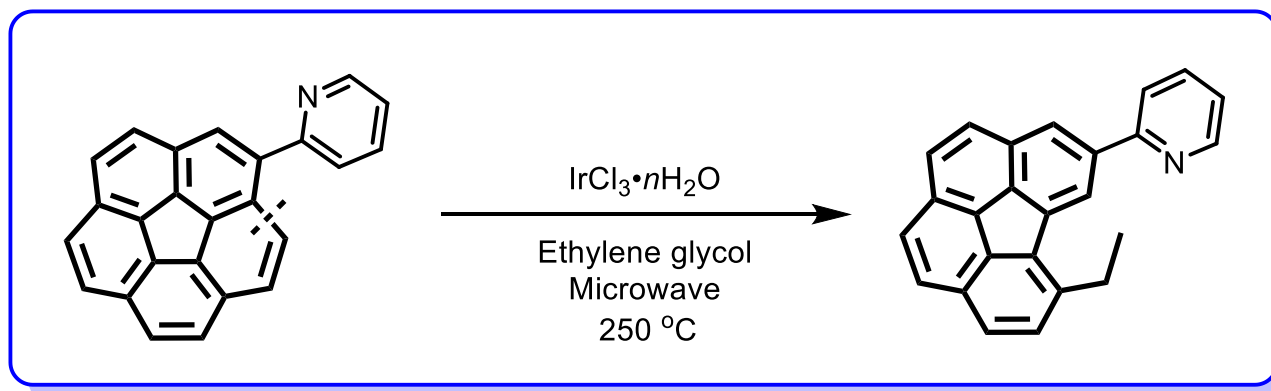
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Hou, Z. and co-authors. *Nature* **2014**, 512, 413.

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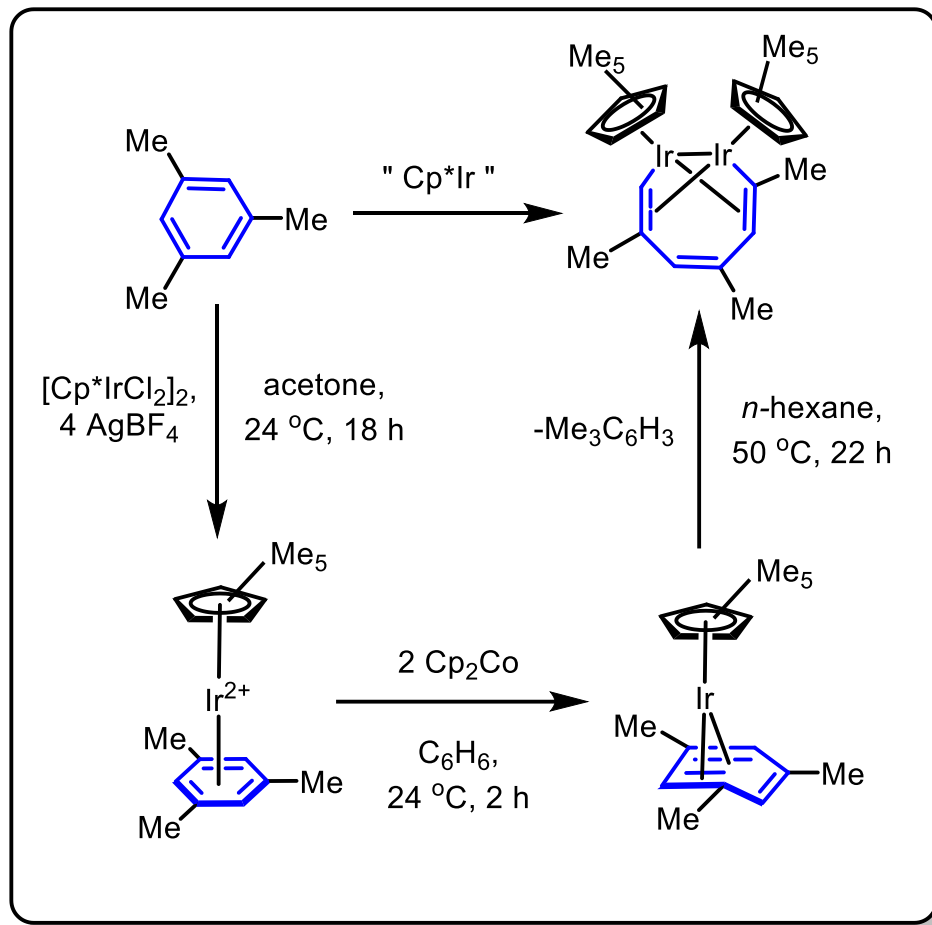
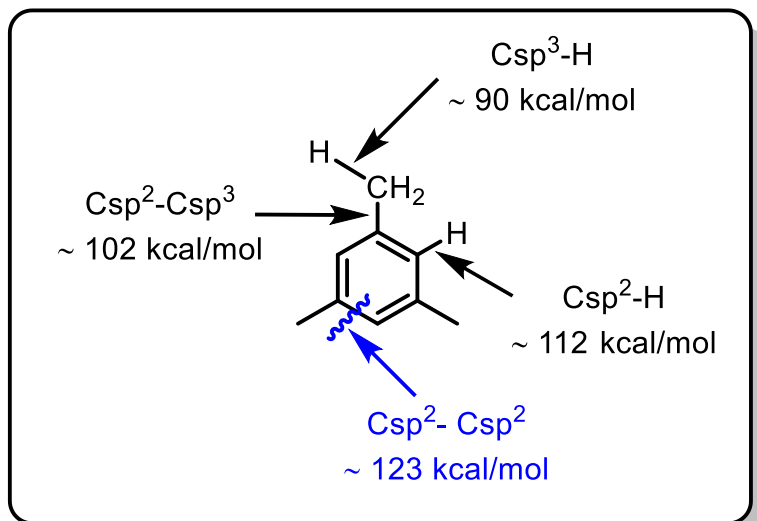
----- Ir Insertion into Aromatic Rings



Shionoya, M. and co-authors. *Angew. Chem. Int. Ed.* **2015**, *54*, 5351-5354.

New Kinds of Buchner Ring Expansion Reactions

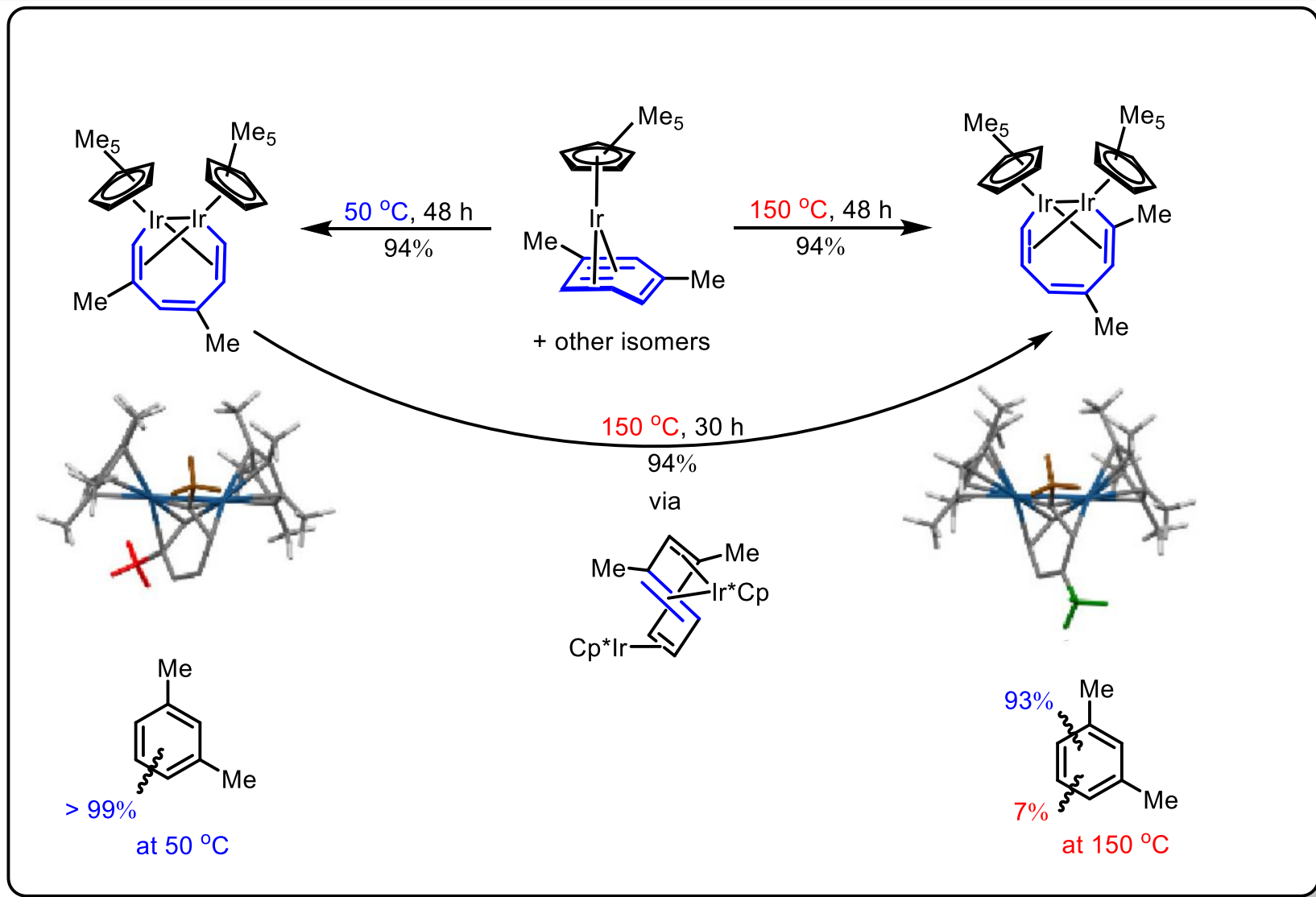
----- Ir Insertion into Aromatic Rings



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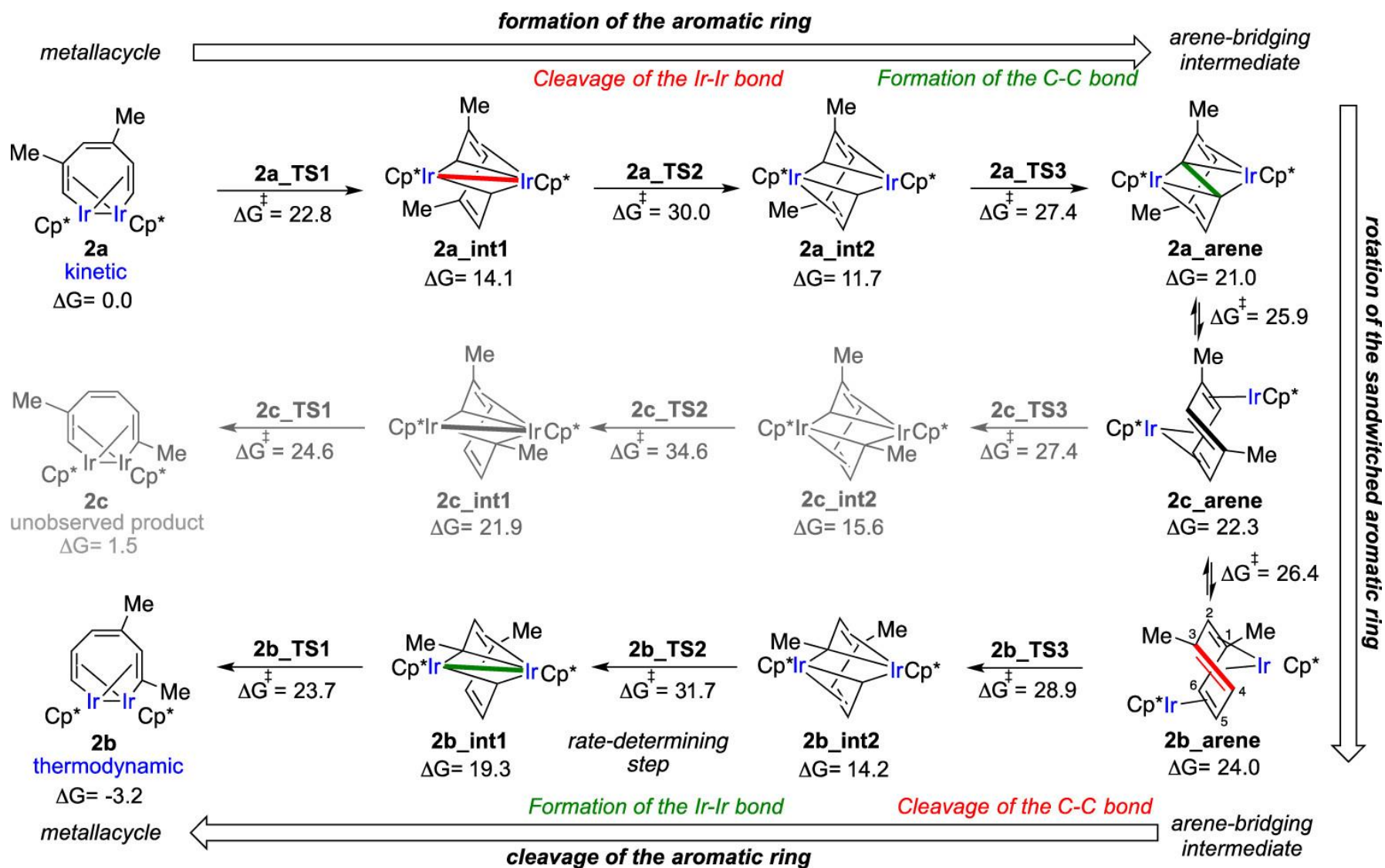
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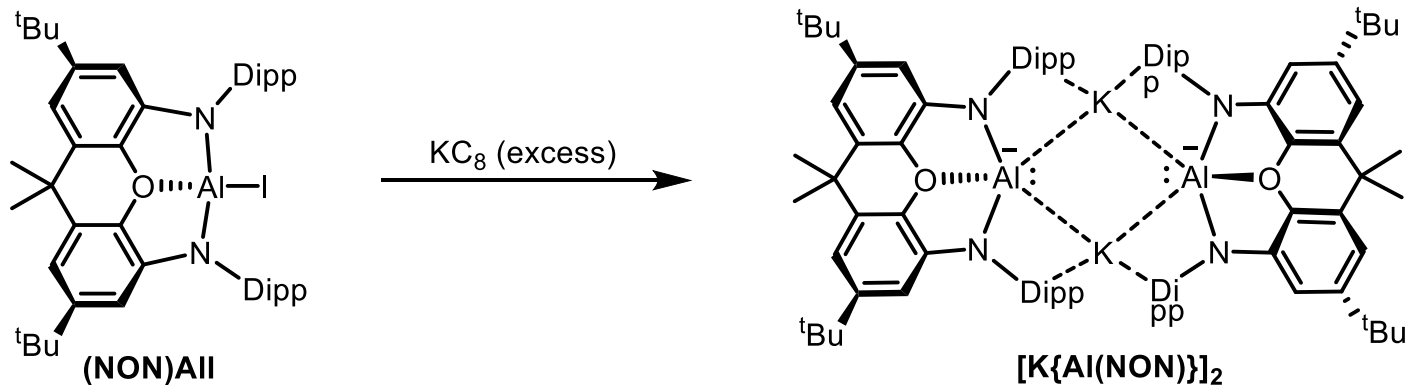
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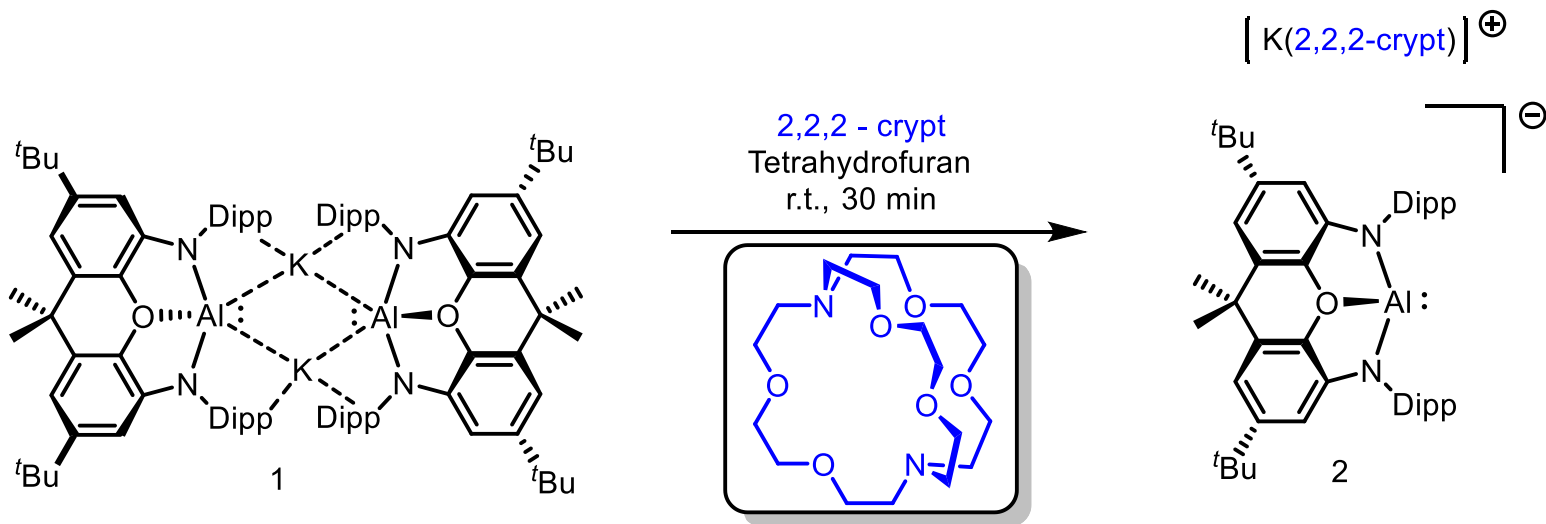


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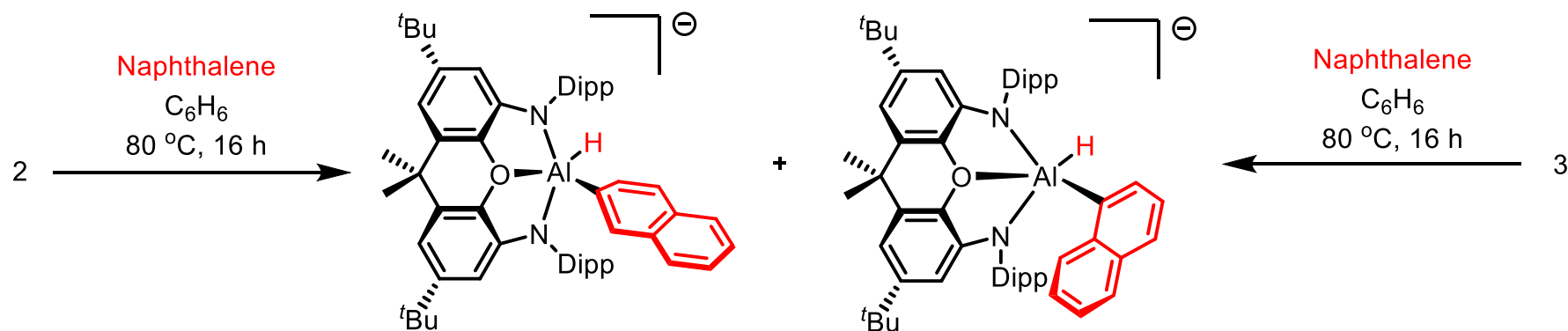
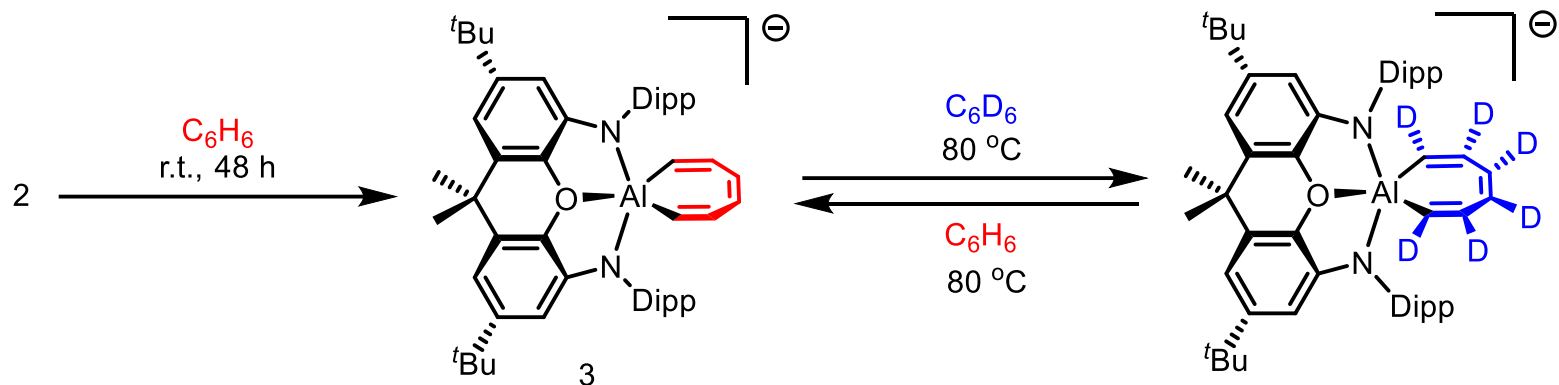
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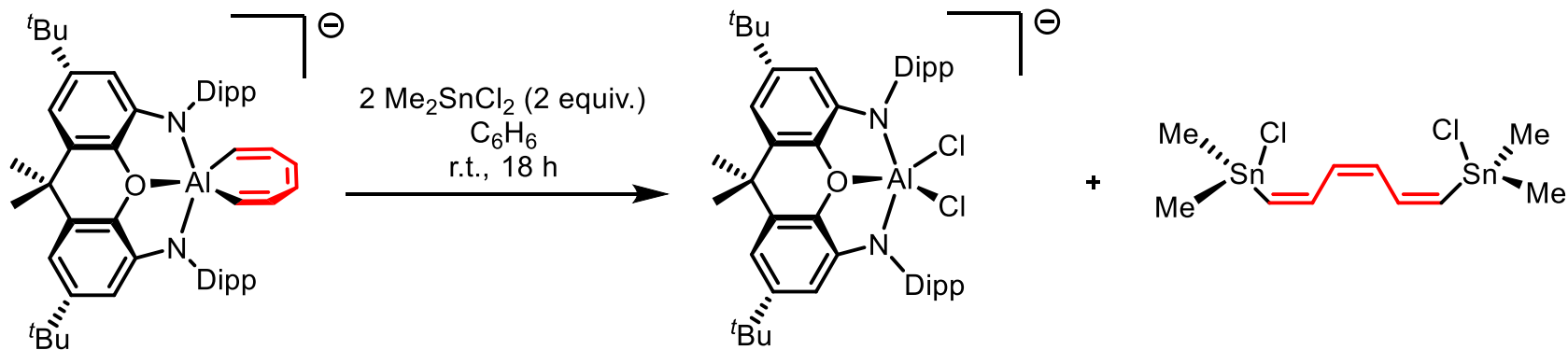
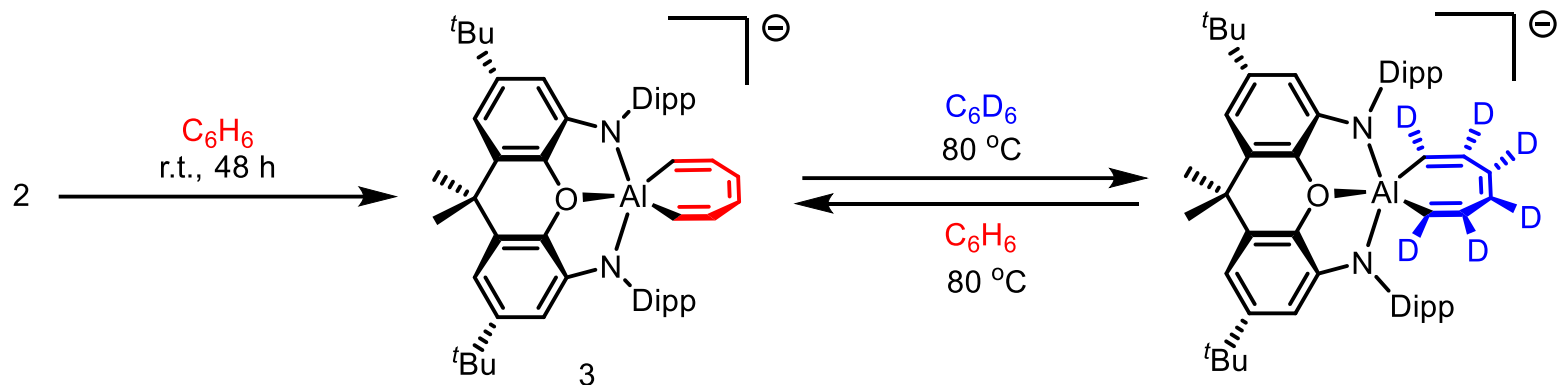
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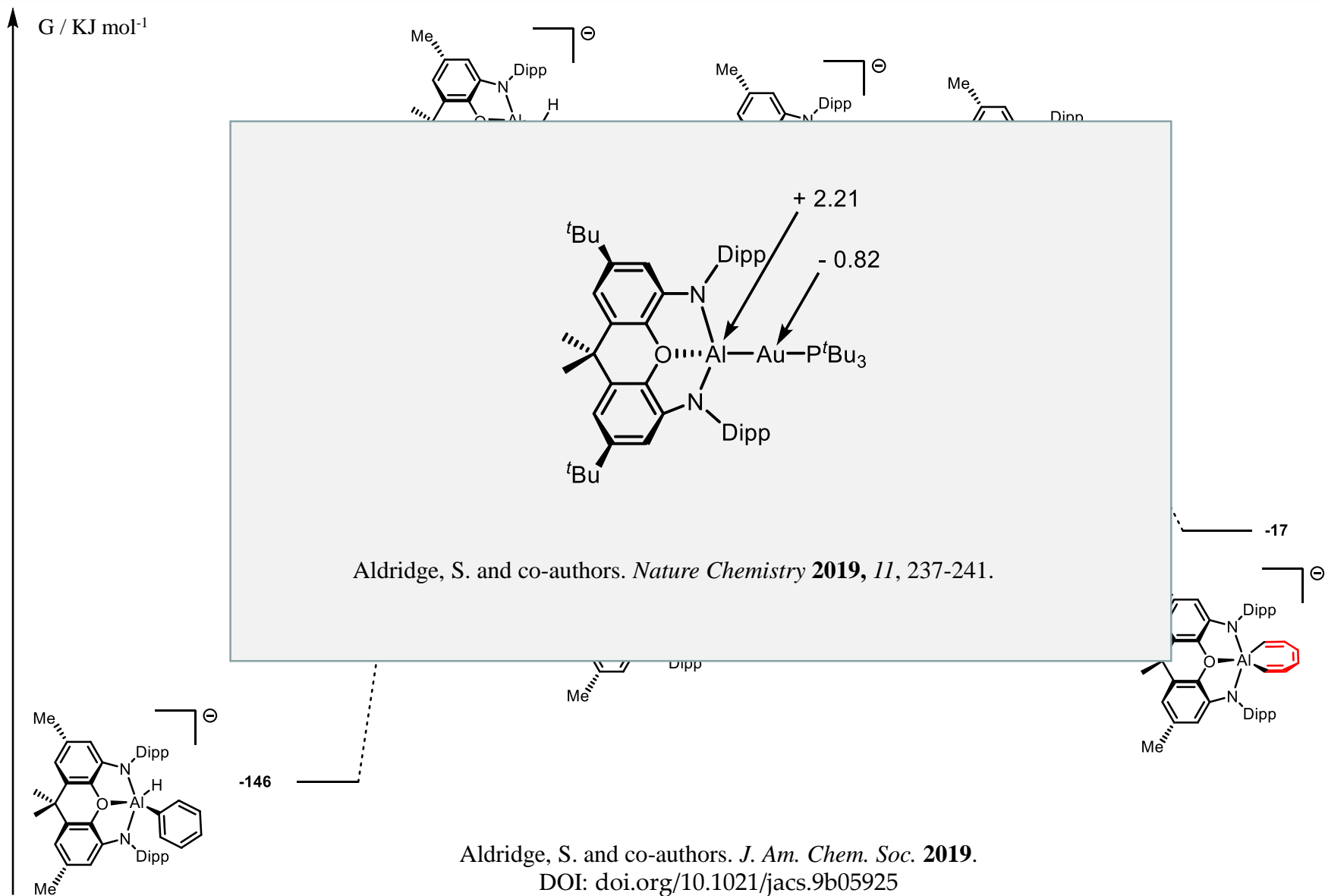
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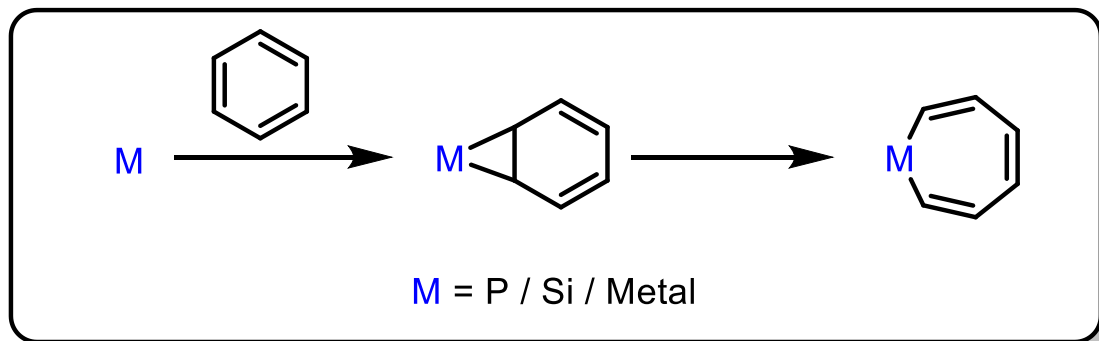
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Summary

- ◆ *Copper(I), silver(I), gold(I), rhodium(II), ruthenium and iron complexes have been reported as catalysts for the Buchner reaction.*
- ◆ *The copper and rhodium-catalyzed processes have often been used in total synthesis.*
- ◆ *Retro-Buchner Reaction can in situ generate metal carbene.*



Thanks!