



C-C Bond Formation *via* Cationic Alkyne Activation

Yiyun Chen

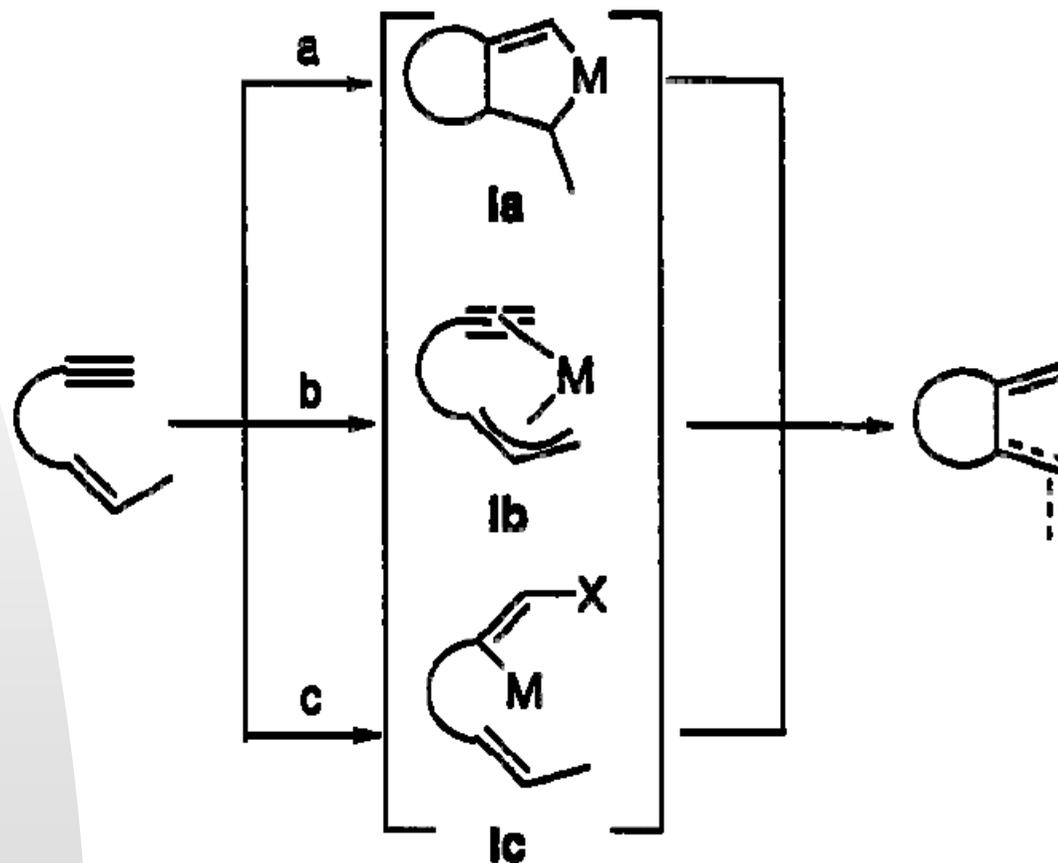
Organic Super Group Meeting,

Department of Chemistry, Princeton University

Wednesday, April 20th, 2005



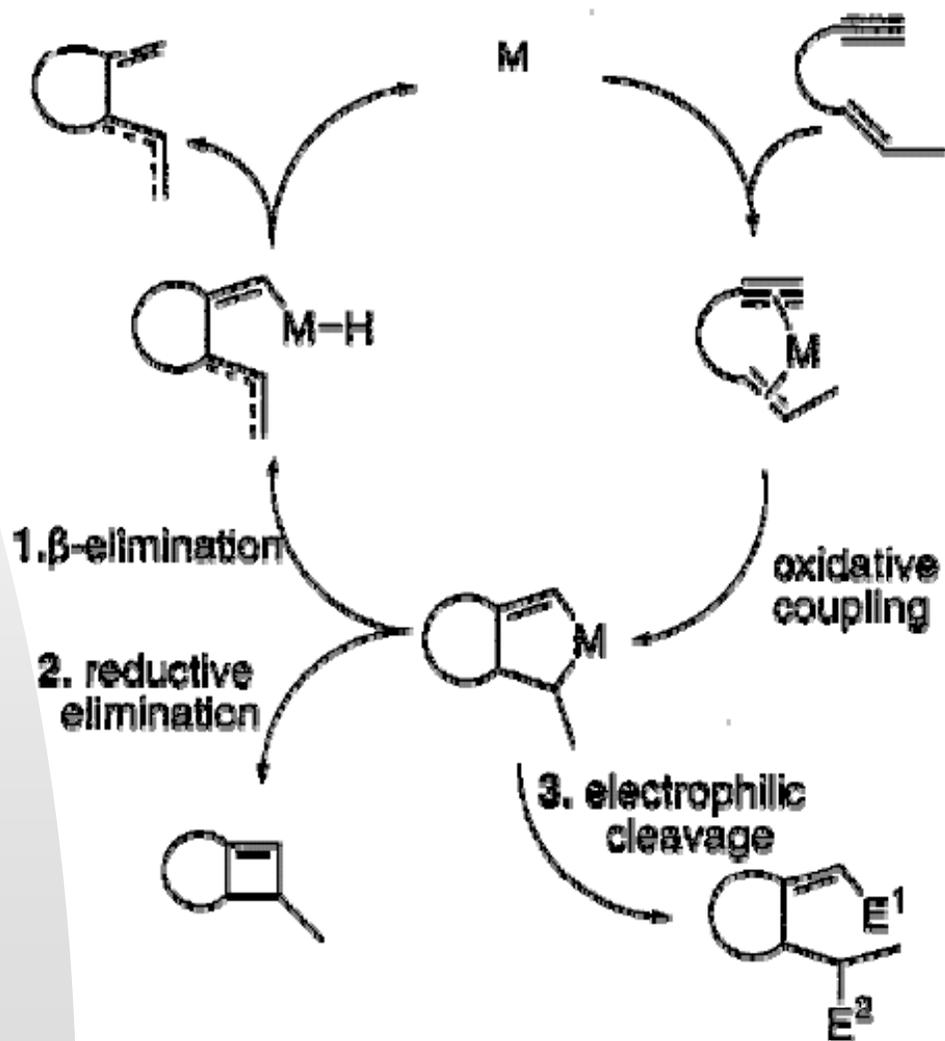
Reactivity of 1,n-Enyne



Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* 2002, 102, 813-834.

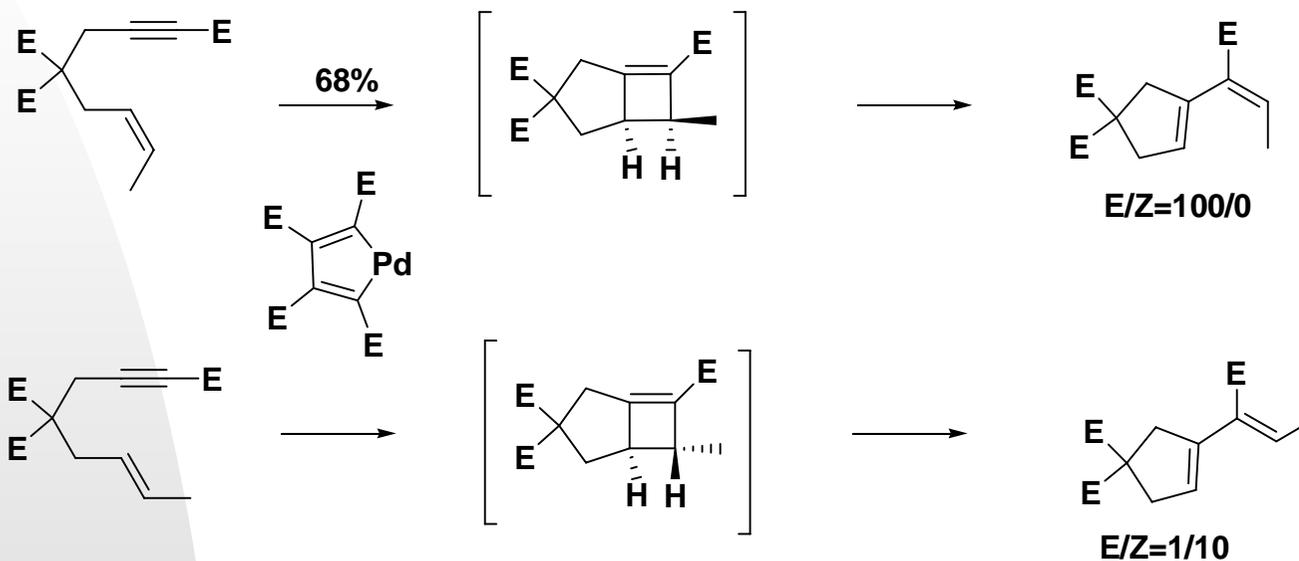


Metallacycle Pathway





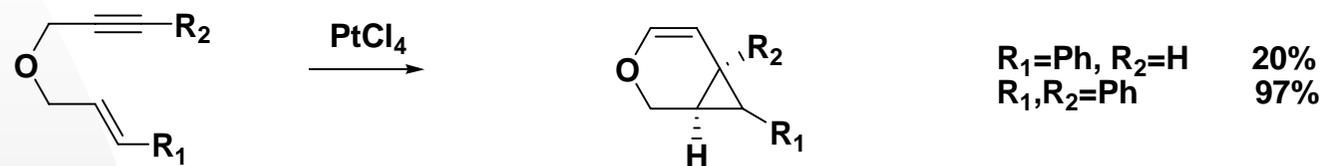
Skeletal Reorganization



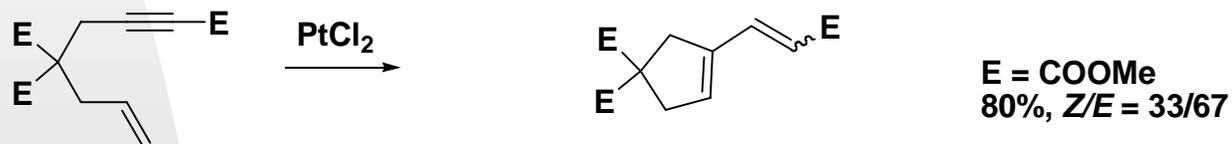
Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* 1988, 110,1636-1638.



Skeletal Reorganization



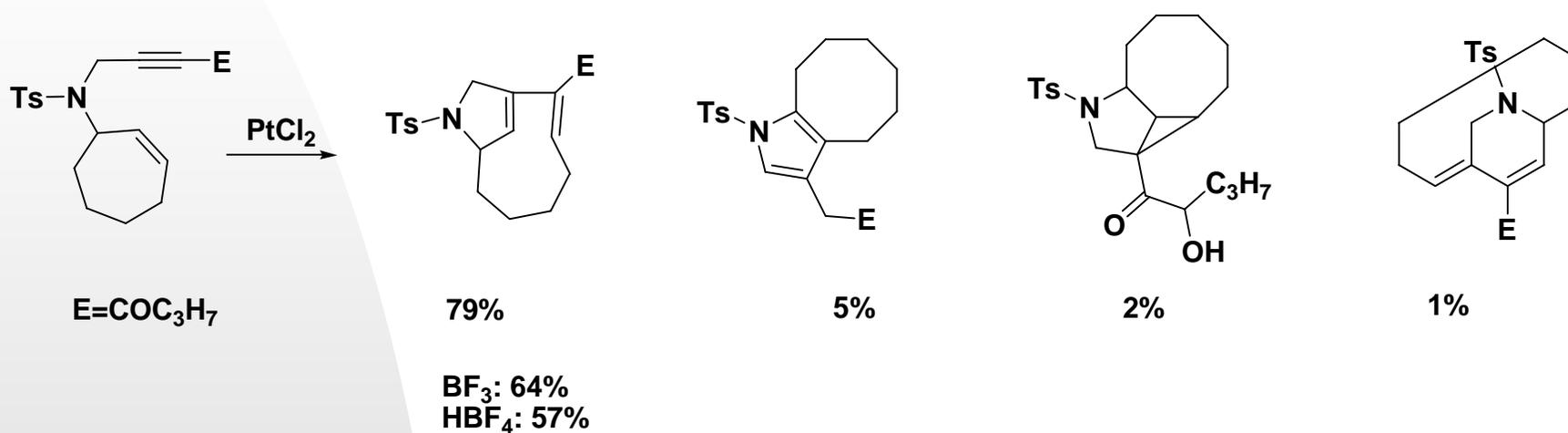
Blum, J.; Beer-Kraft, H.; Badrieh, Y. *J. Org. Chem.* 1995, 60, 5567-5569.



Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* 1996, 15, 901-903.



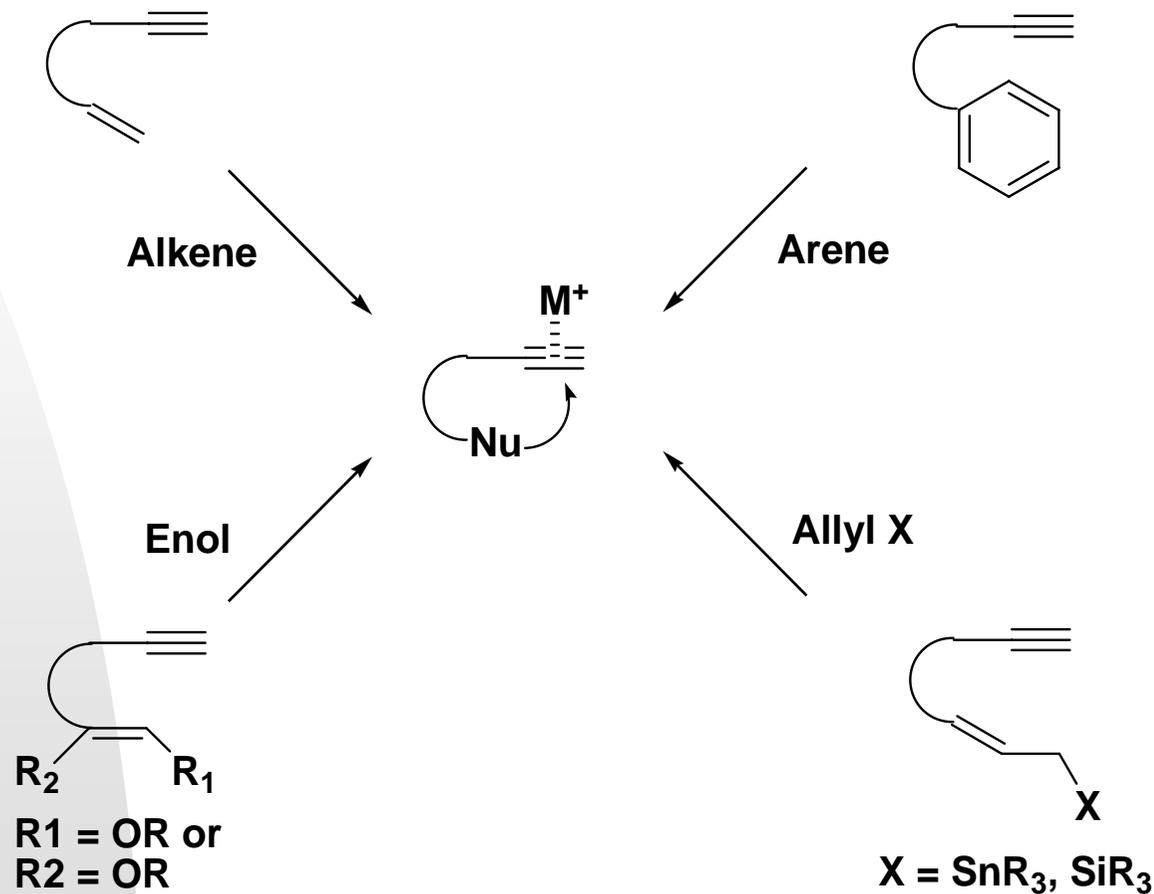
Skeletal Reorganization



Furstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* 1998, 120, 8305-8314.



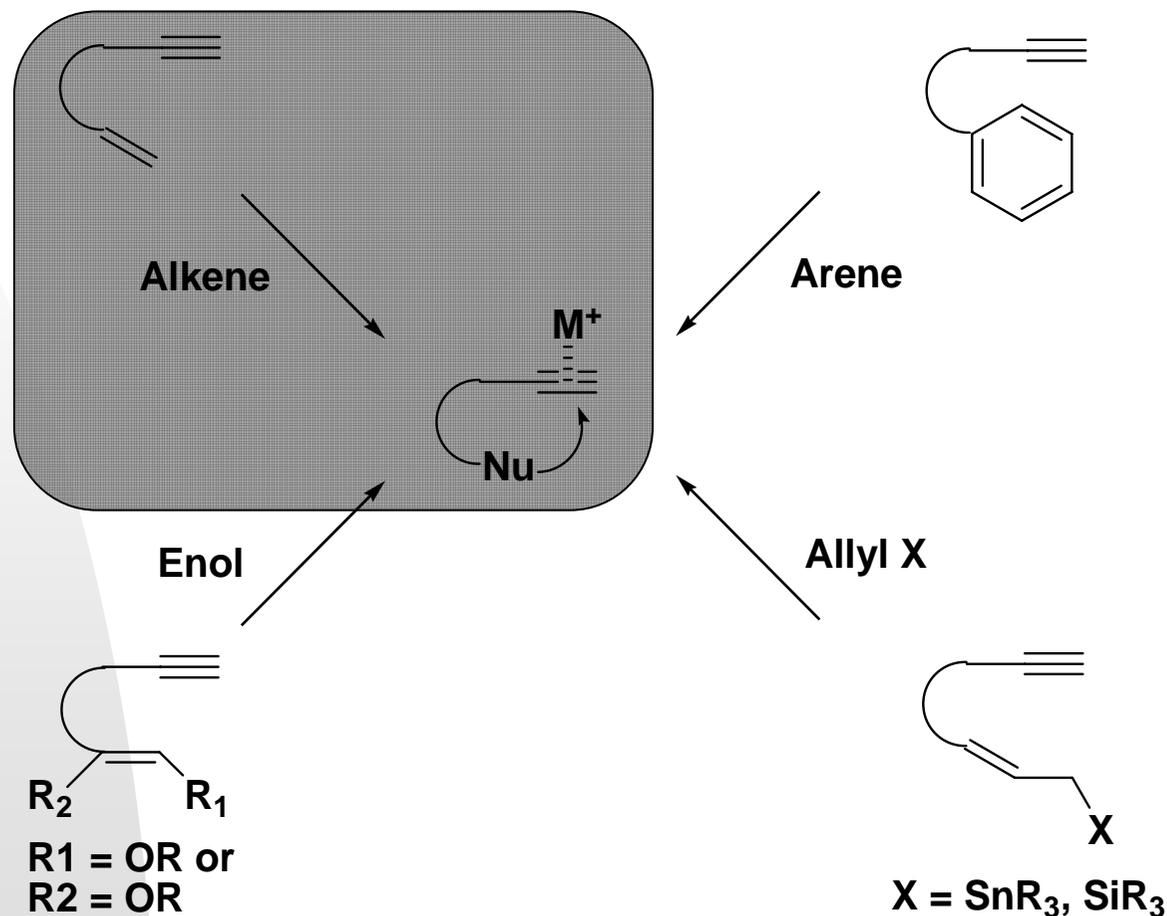
Cationic Alkyne Activation



$M = Ru(II), Ir(I), Pd(II), Pt(II), Pt(IV), Ag(I), Au(I), Au(III), Ga(III)$ et al



Cationic Alkyne Activation



$M = Ru(II), Ir(I), Pd(II), Pt(II), Pt(IV), Ag(I), Au(I), Au(III), Ga(III)$ et al



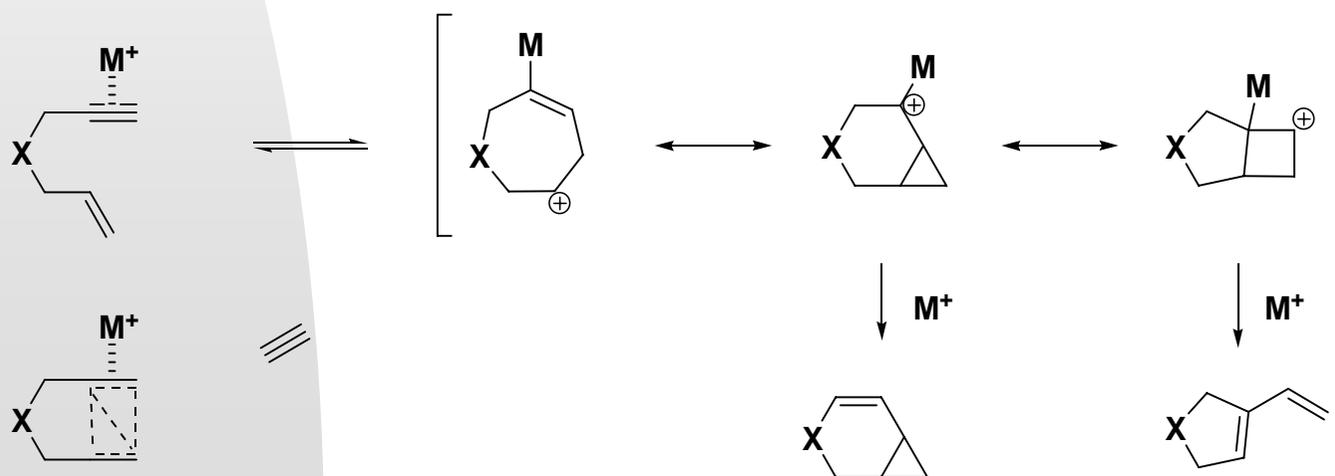
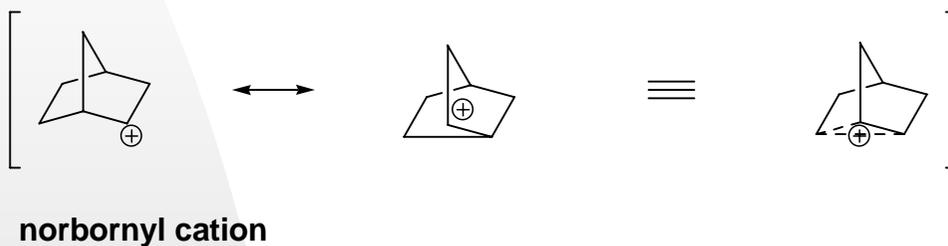
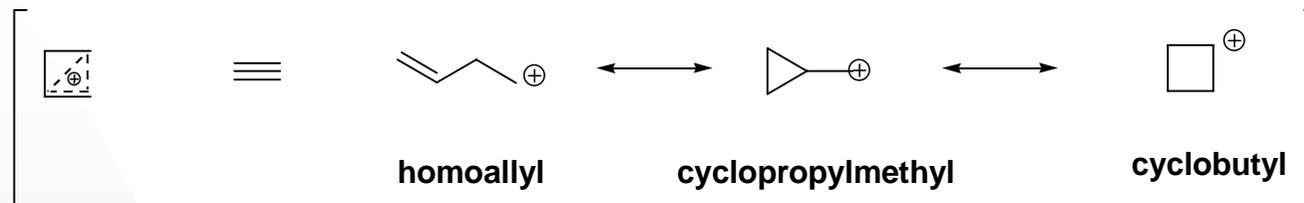
Non-classical Carbocation

- “In classical carbocations the positive charge is localized on one carbon atom or delocalized by resonance involving an unshared pair of electrons or a double or triple bond in the allylic position.”
- “In a non-classical carbocation, the positive charge is delocalized by a double or triple bond that is not in the allylic position or by a single bond.”

March, J. *Advanced Organic Chemistry*; 4th ed.; Wiley: New York, 1992, p312-326.

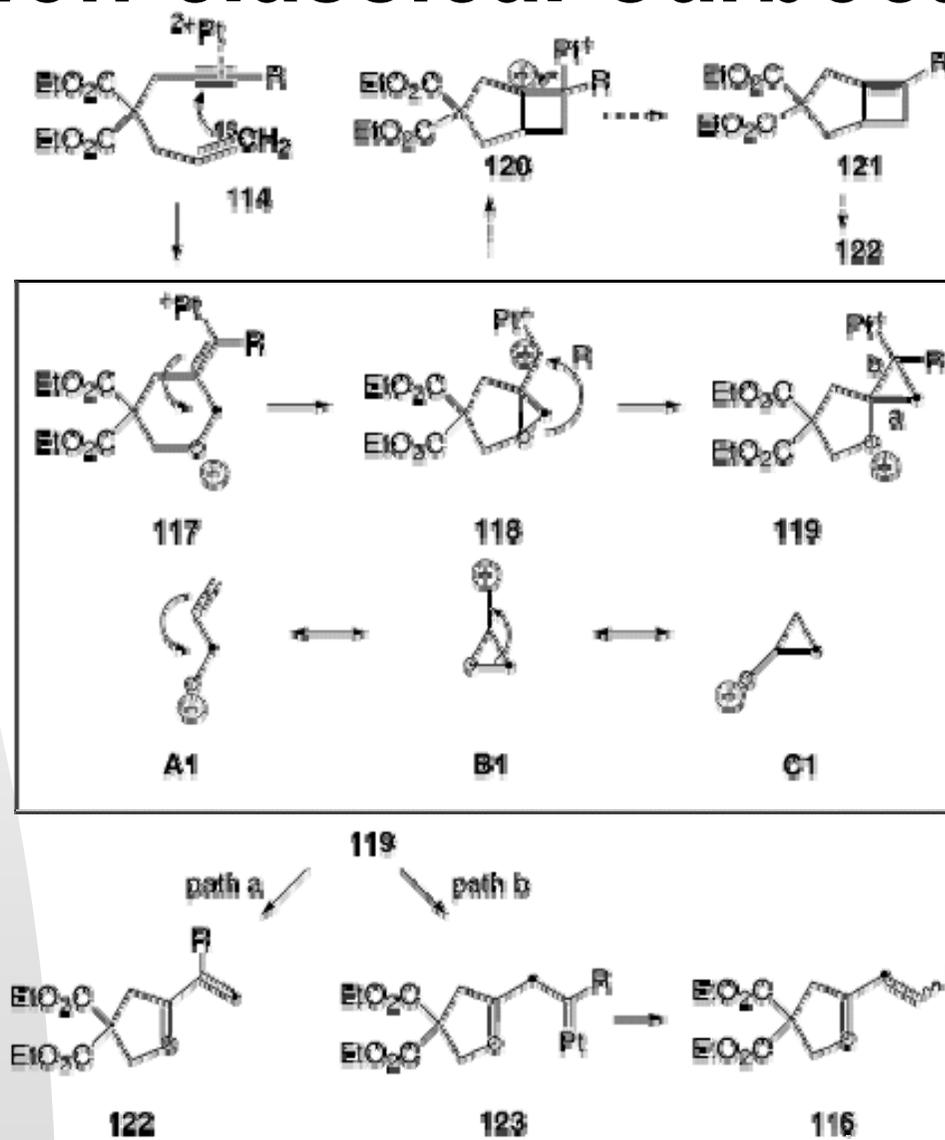


Non-classical Carbocation



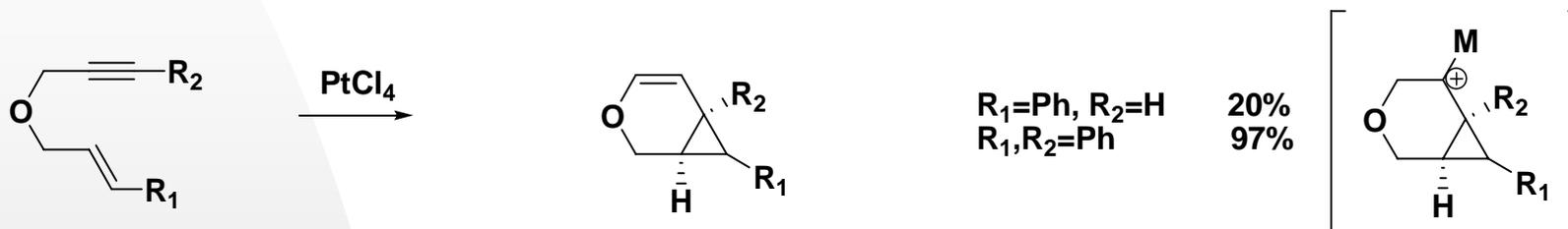


Non-classical Carbocation

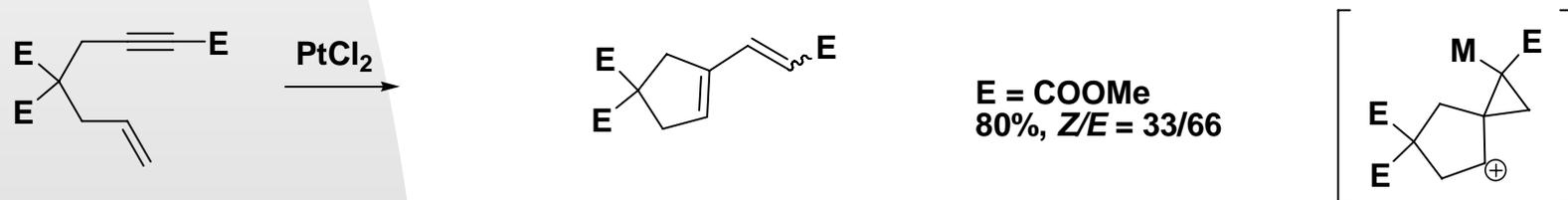




Skeletal Reorganization



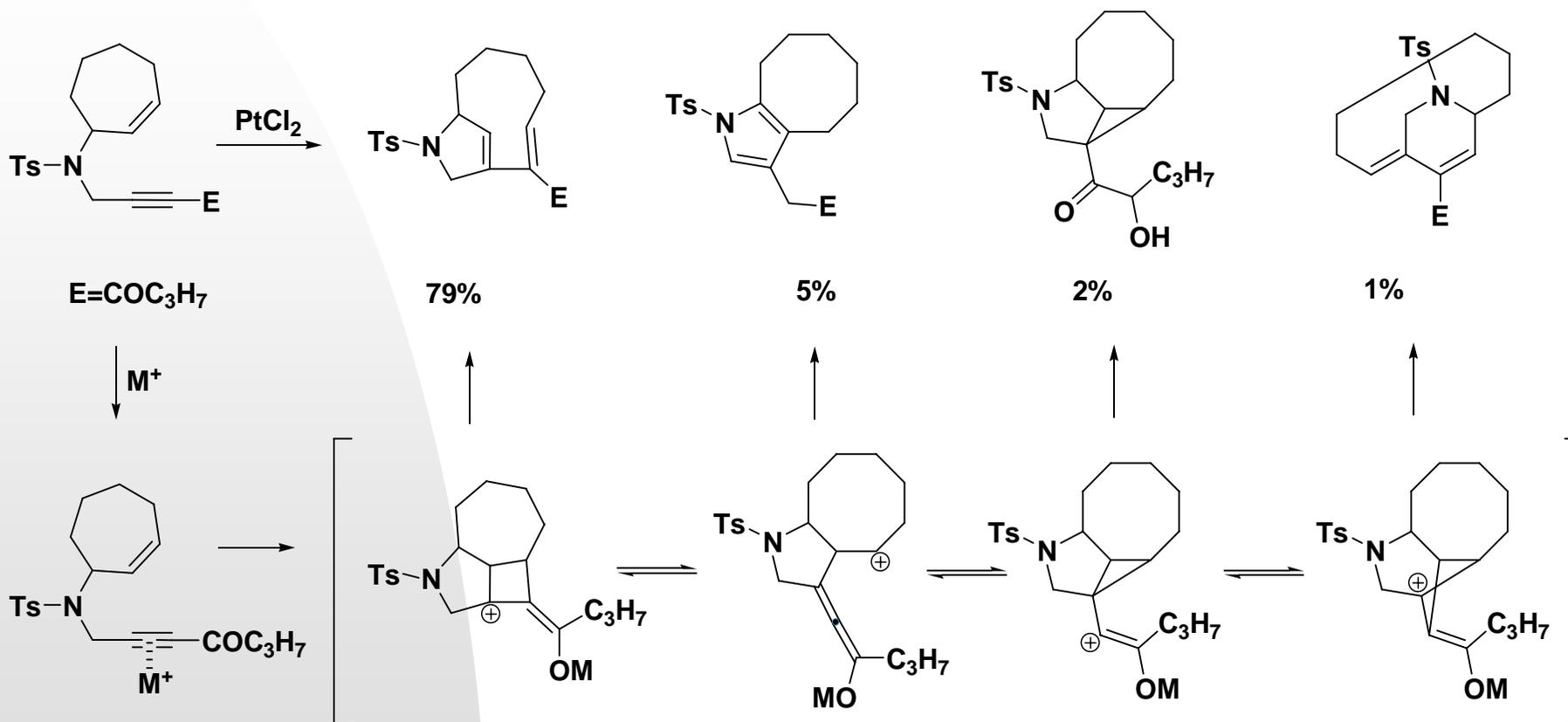
Blum, J.; Beer-Kraft, H.; Badrieh, Y. *J. Org. Chem.* 1995, 60, 5567-5569.



Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* 1996, 15, 901-903.



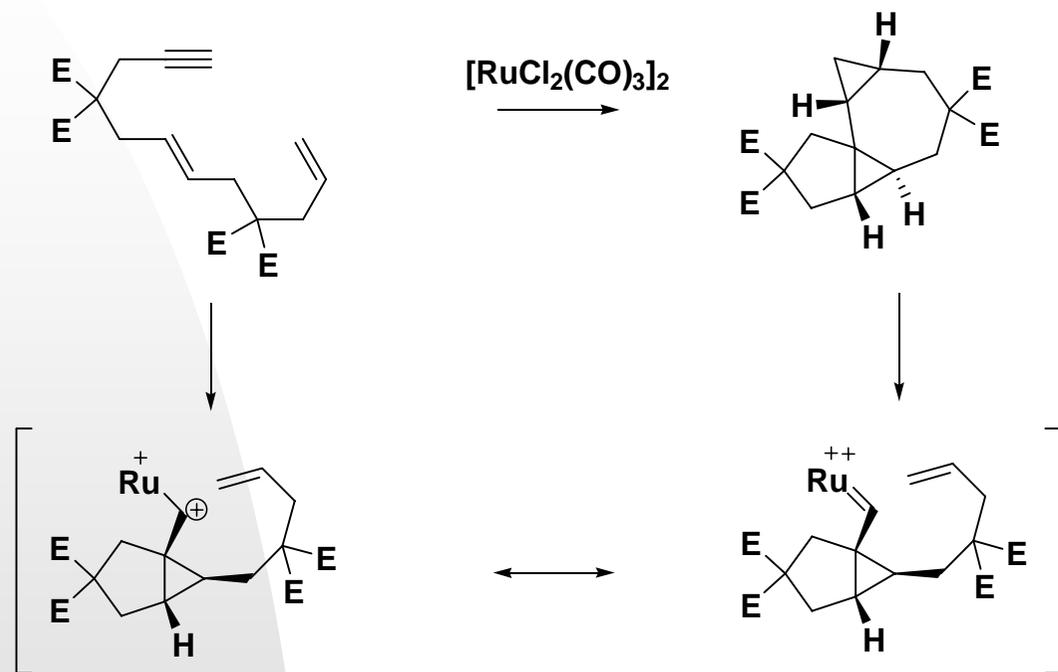
Skeletal Reorganization



Furstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* 1998, 120, 8305-8314.



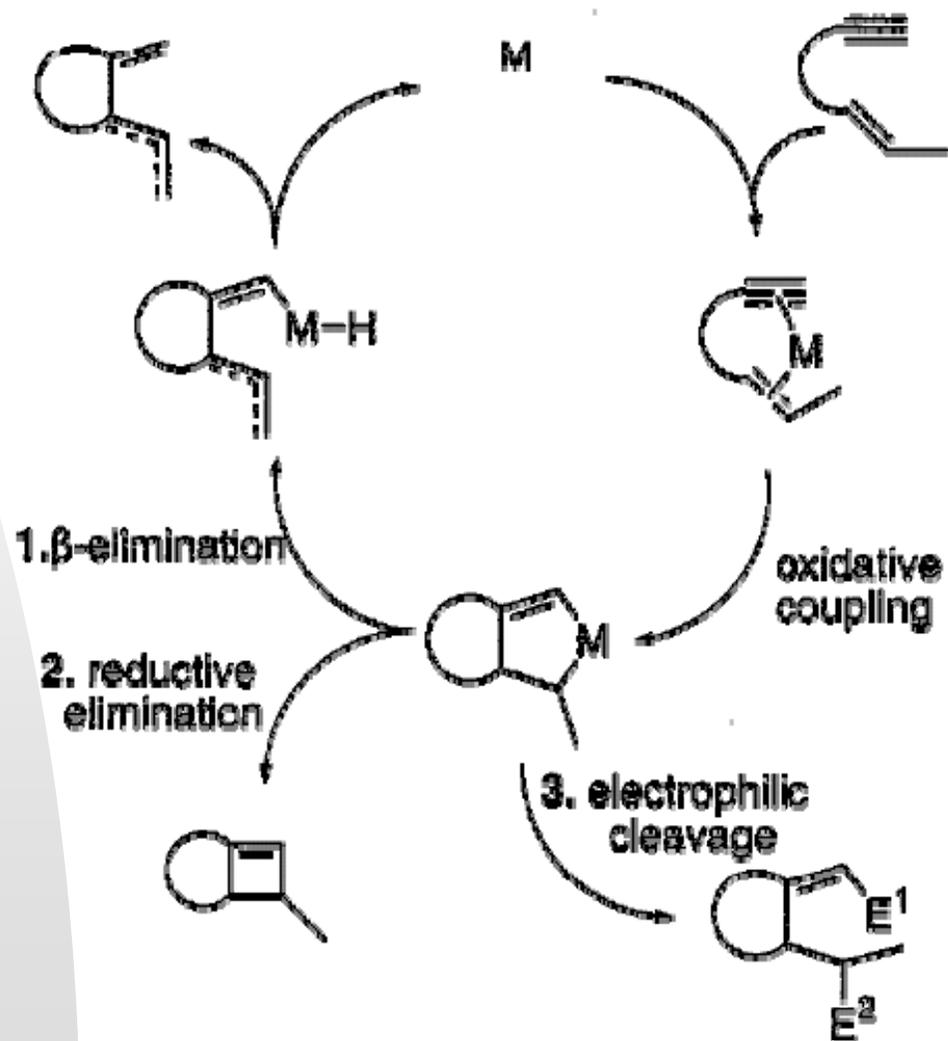
Carbenoid Character



Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* 1998, 120, 9104-9105.

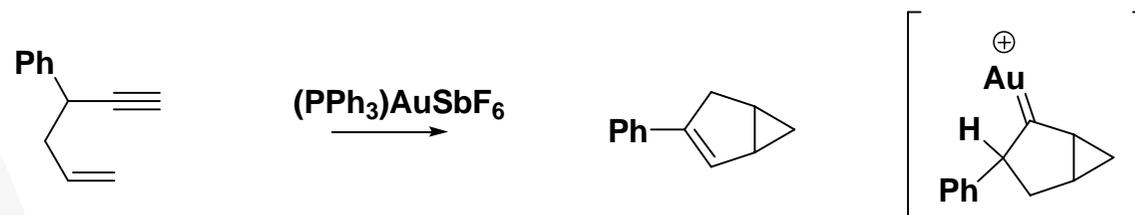


Metallacycle Pathway

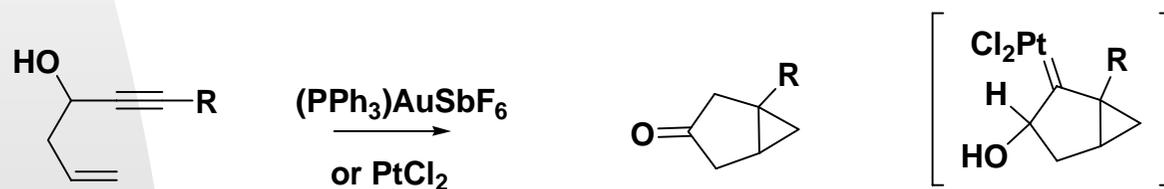




1,5-Enyne



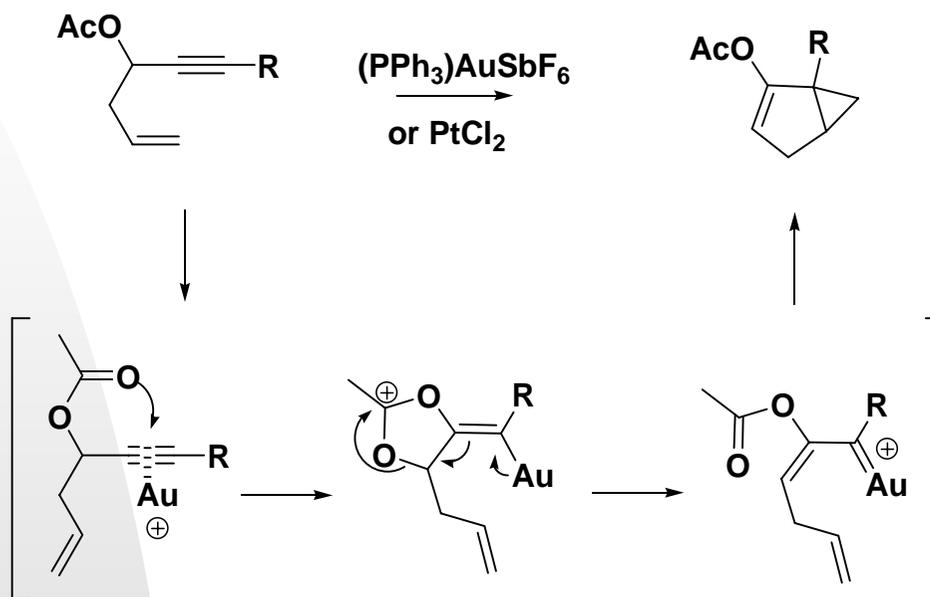
Luzung, M.R.; Markham, J.P; Toste, F.D. *J. Am. Chem. Soc.* 2004, 126, 10858-10859.



Mamane, V.; Gress, T.; Krause, H.; Furstner, A. *J. Am. Chem. Soc.* 2004, 126, 8654-8655.
Harrak, Y.; Malacria, M. et al. *J. Am. Chem. Soc.* 2004, 126, 8656-8657.



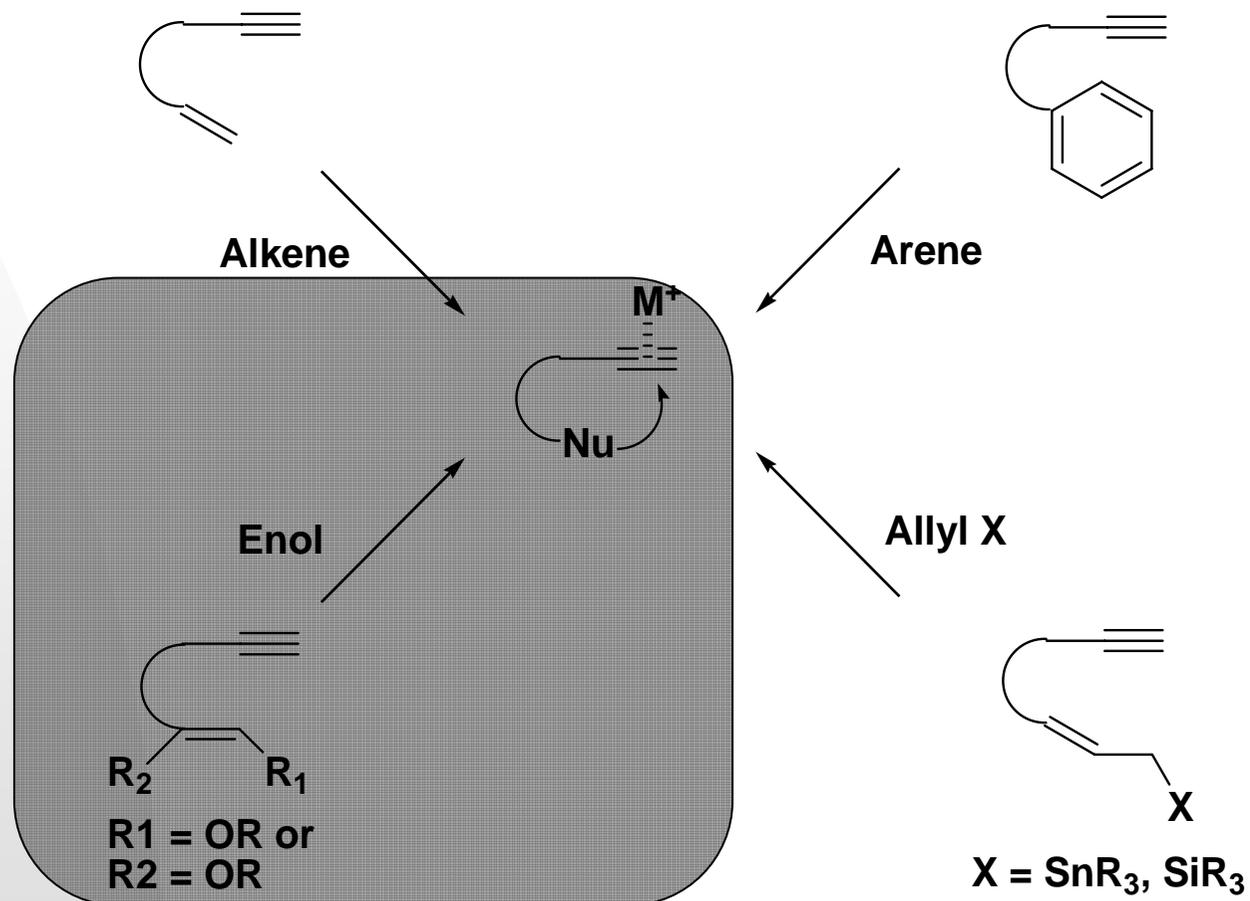
1,2-Acetate Migration



Mamane, V.; Gress, T.; Krause, H.; Furstner, A. *J. Am. Chem. Soc.* 2004, 126, 8654-8655.
Harrak, Y.; Malacria, M. et al. *J. Am. Chem. Soc.* 2004, 126, 8656-8657.



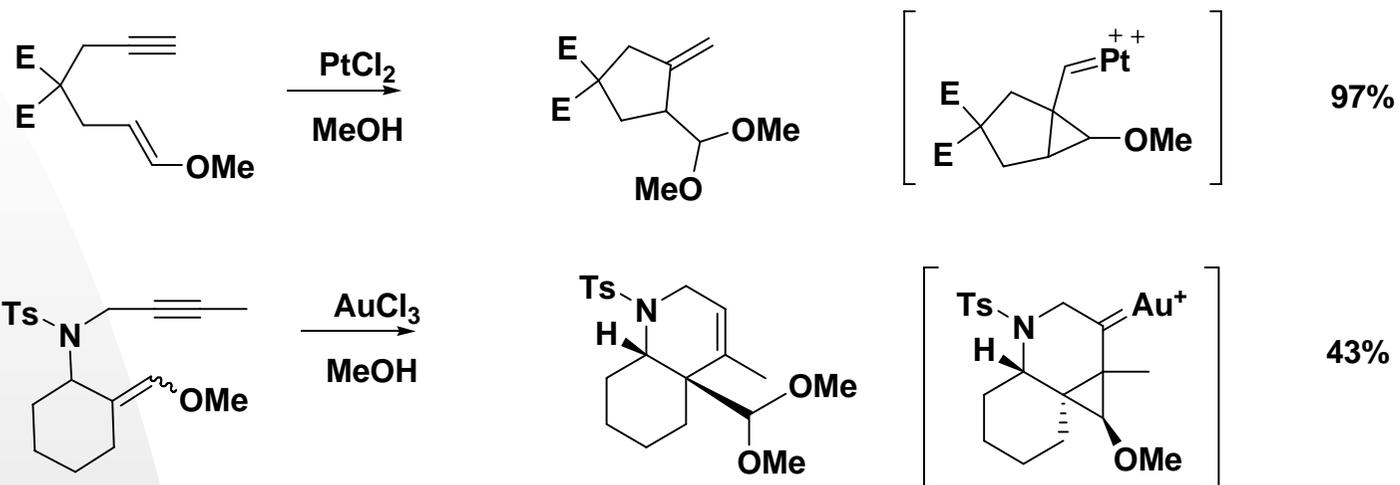
Cationic Alkyne Activation



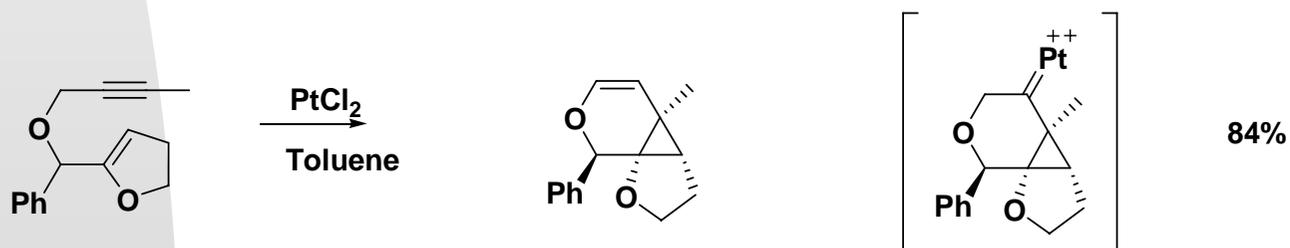
$M = Ru(II), Ir(I), Pd(II), Pt(II), Pt(IV), Ag(I), Au(I), Au(III), Ga(III)$ et al



Enol Ether as Nucleophile



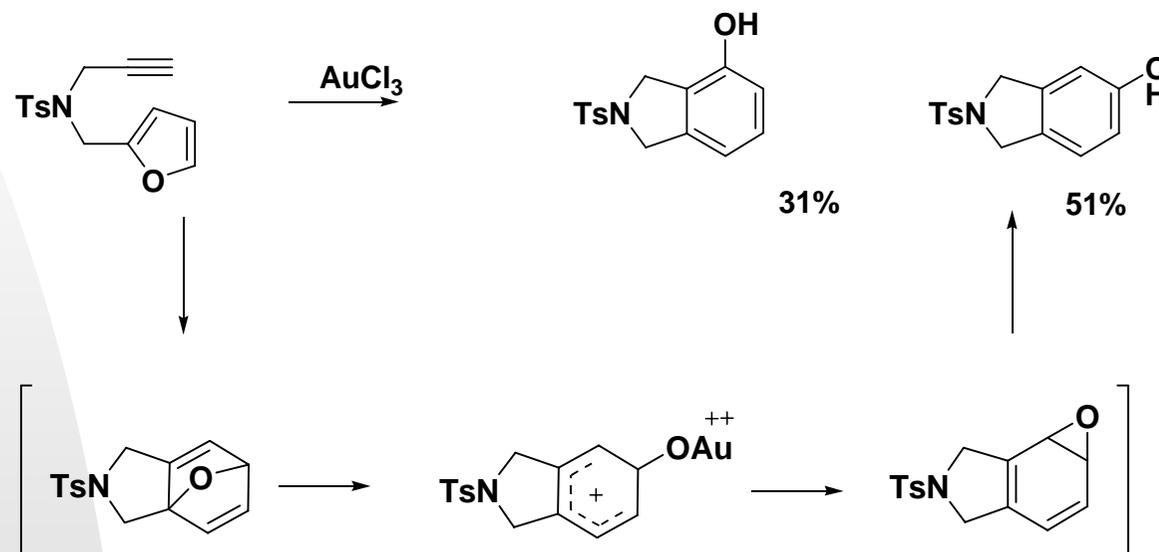
Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* 2003, 9, 2627-2635.



Nevado, C.; Ferrer, C.; Echavarren, A. M. *Org. Lett.* 2004, 6, 3191.



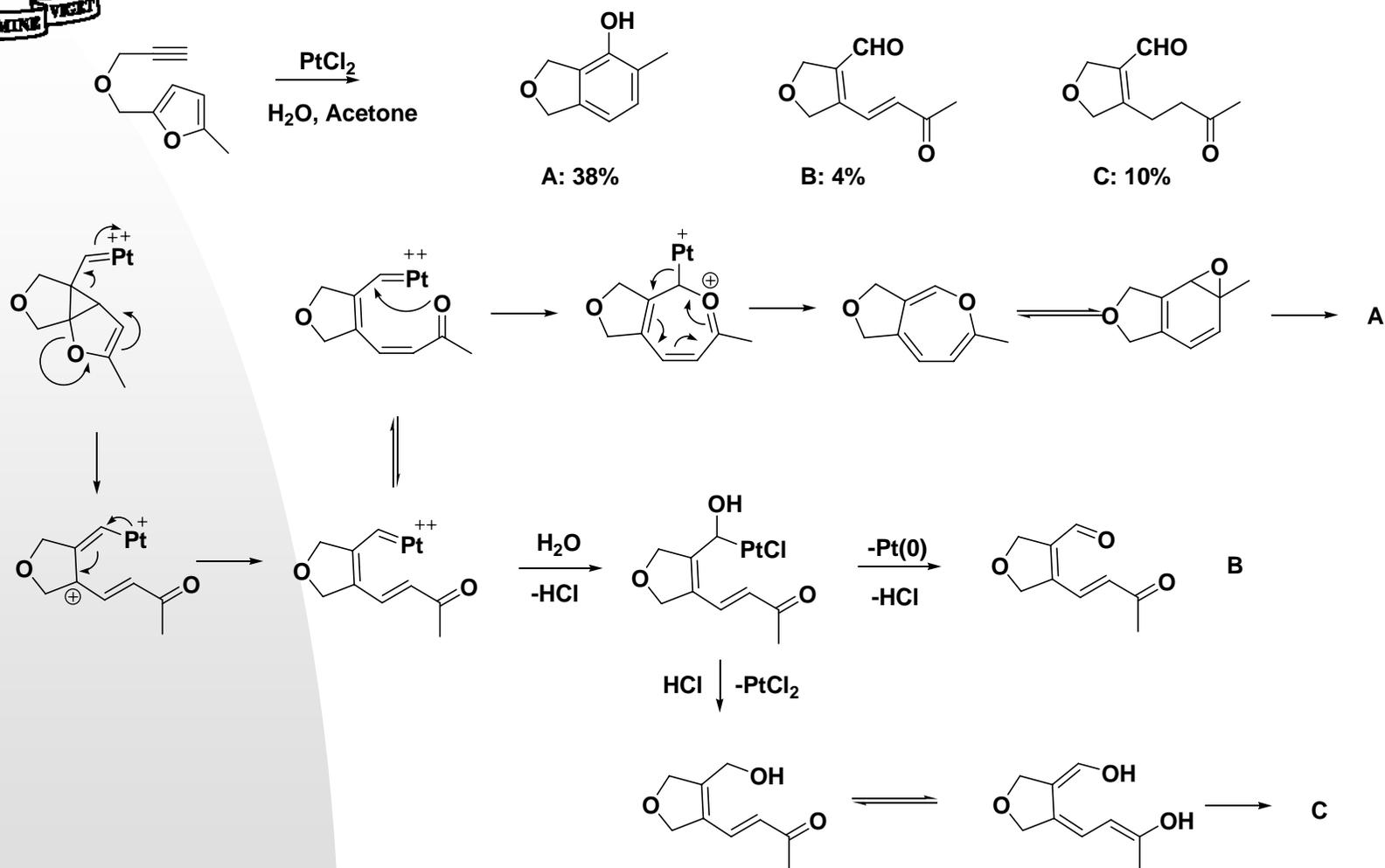
Furan as Nucleophile



Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* 2000, 122, 11553-11554.



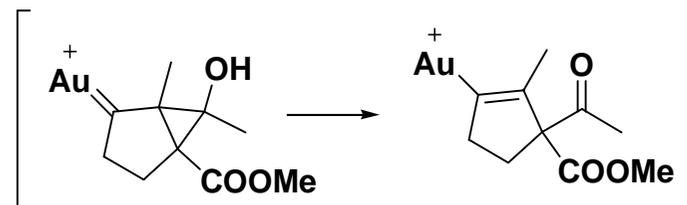
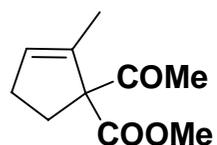
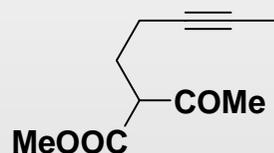
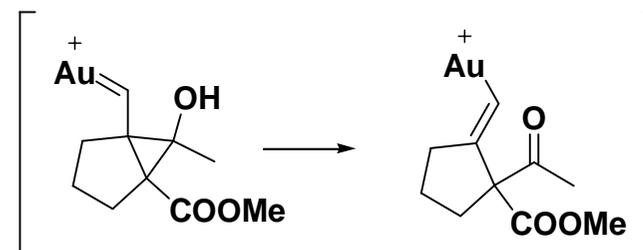
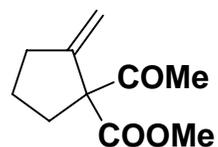
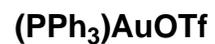
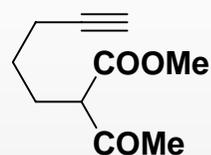
Furan as Nucleophile



Martin-Matute, B.; Nevado, C.; Cardenas, D. J., Echavarren, A. M. *J. Am. Chem. Soc.* 2003, 125, 5757-5766.



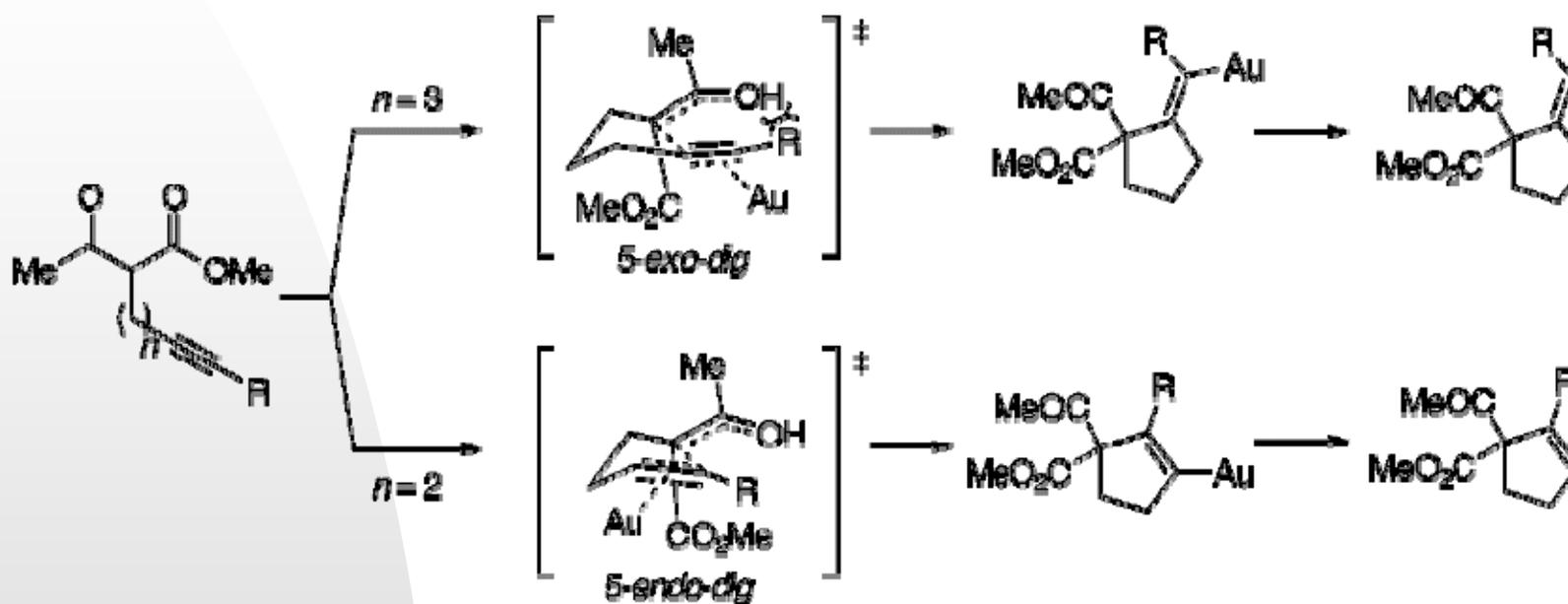
β -Ketoester as Nucleophile



Kennedy-Smith, J. J.; Staben, S. T.; Toste, F.D. *J. Am. Chem. Soc.* 2004, 126, 4526-4527.
Staben, S.T.; Kennedy-Smith, J. J.; Toste, F.D. *Angew. Chem. Int. Ed.* 2004, 43(40), 5350-5352.



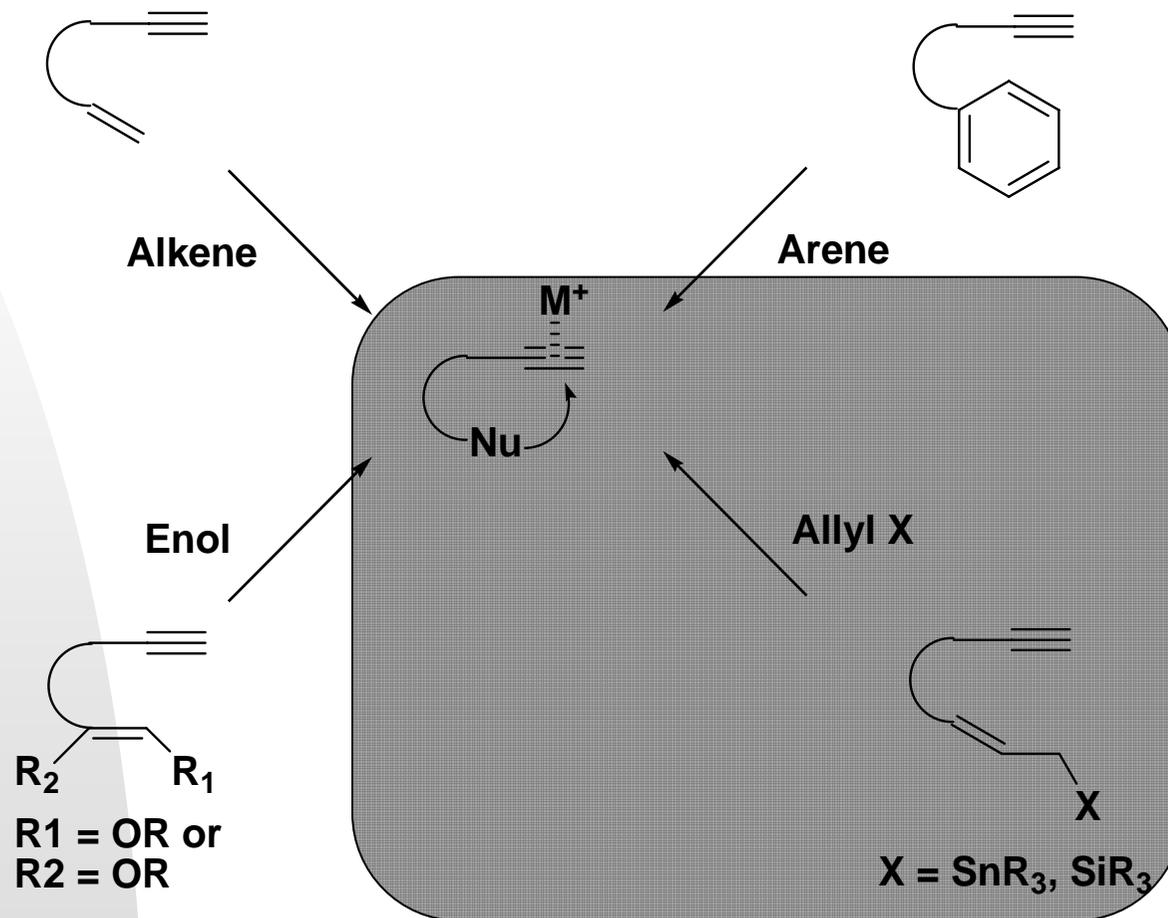
β -Ketoester as Nucleophile



Staben, S.T.; Kennedy-Smith, J. J.; Toste, F.D. *Angew. Chem. Int. Ed.* 2004, 43(40), 5350-5352.



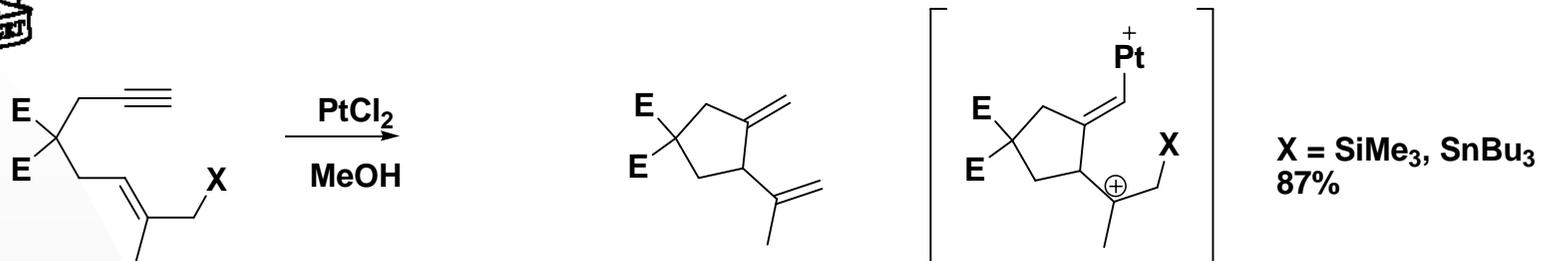
Cationic Alkyne Activation



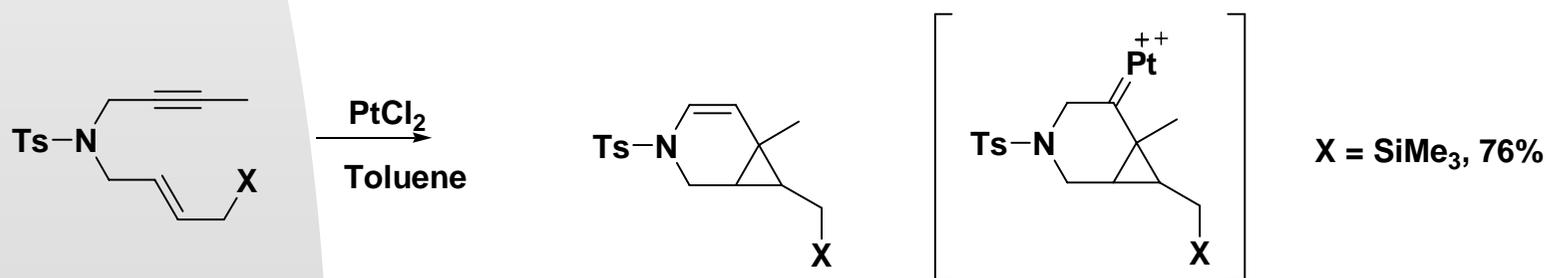
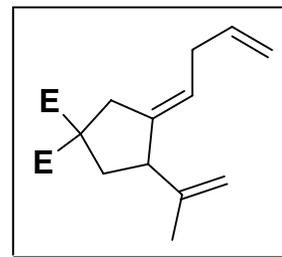
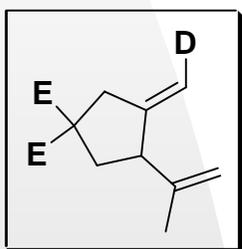
$M = Ru(II), Ir(I), Pd(II), Pt(II), Pt(IV), Ag(I), Au(I), Au(III), Ga(III)$ et al



Allyl Silane/Tin



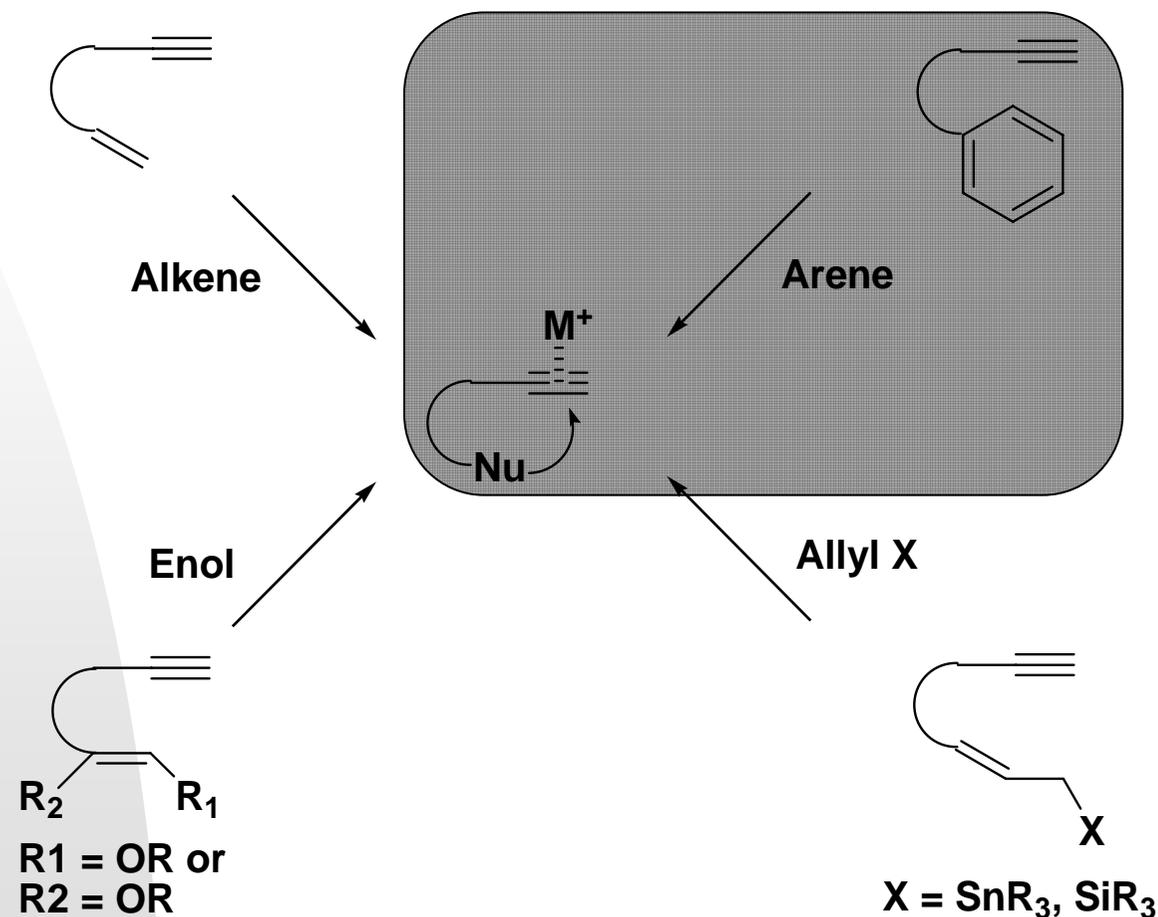
Fernandez-Rivas, C.; Mendez, M.; Echavarren, A. M. *J. Am. Chem. Soc.* 2000, 122, 1221-1222.



Furstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* 2000, 122, 6785-6786.



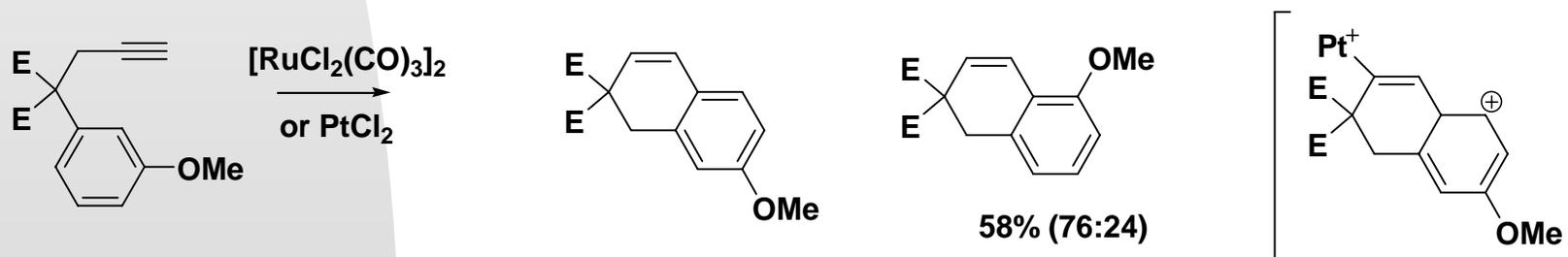
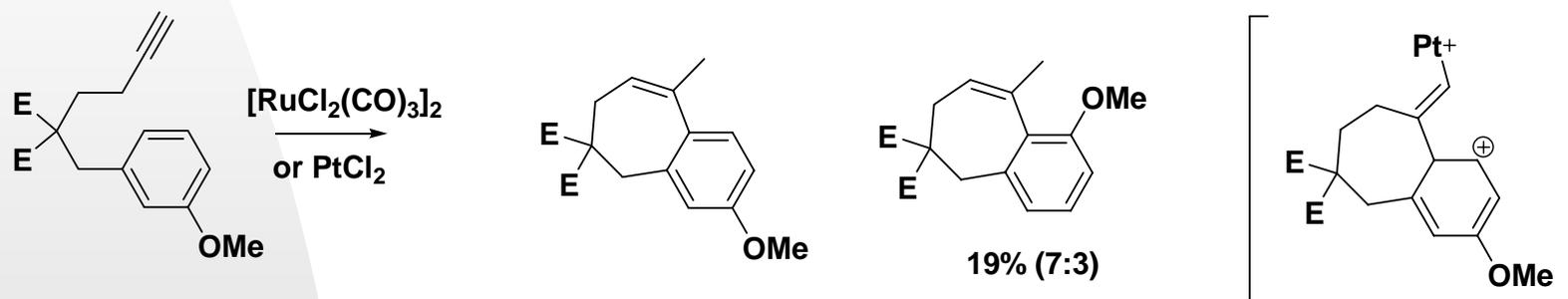
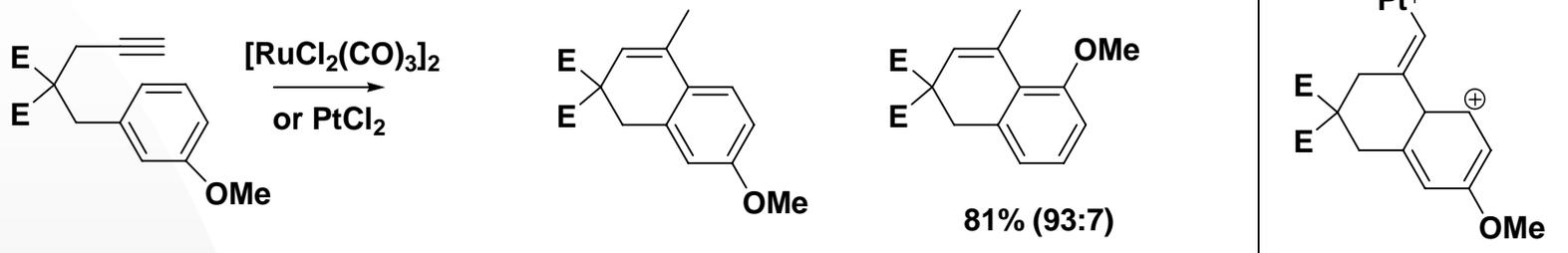
Cationic Alkyne Activation



$M = Ru(II), Ir(I), Pd(II), Pt(II), Pt(IV), Ag(I), Au(I), Au(III), Ga(III)$ et al



Arene as Nucleophile



Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* 2000, 65, 4913-4918.



Cationic Alkyne Activation

