Sélectivité en catalyse moléculaire : Assistance de la chimie théorique

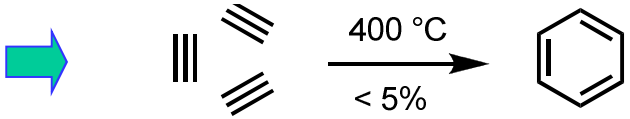
IIIème Journée de Simulation Numérique en Chimie à Paris-Sud

12 novembre 2014

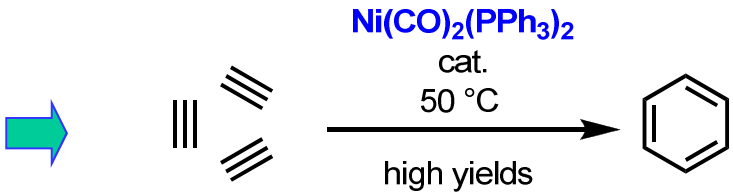
Vincent Gandon

Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182
Université Paris-sud

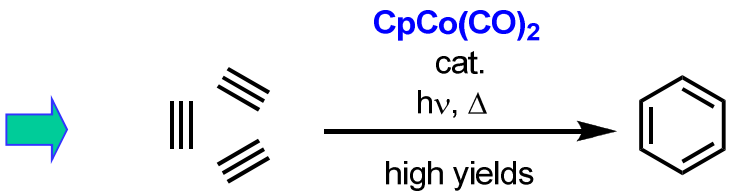
Metal-Catalyzed [2+2+2] Cycloaddition of Alkynes



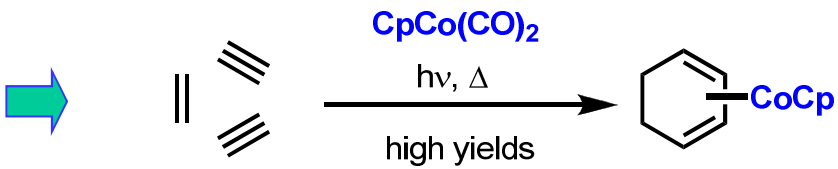
Thermal (Berthelot, 1866)



Catalytic (Reppe, 1948)

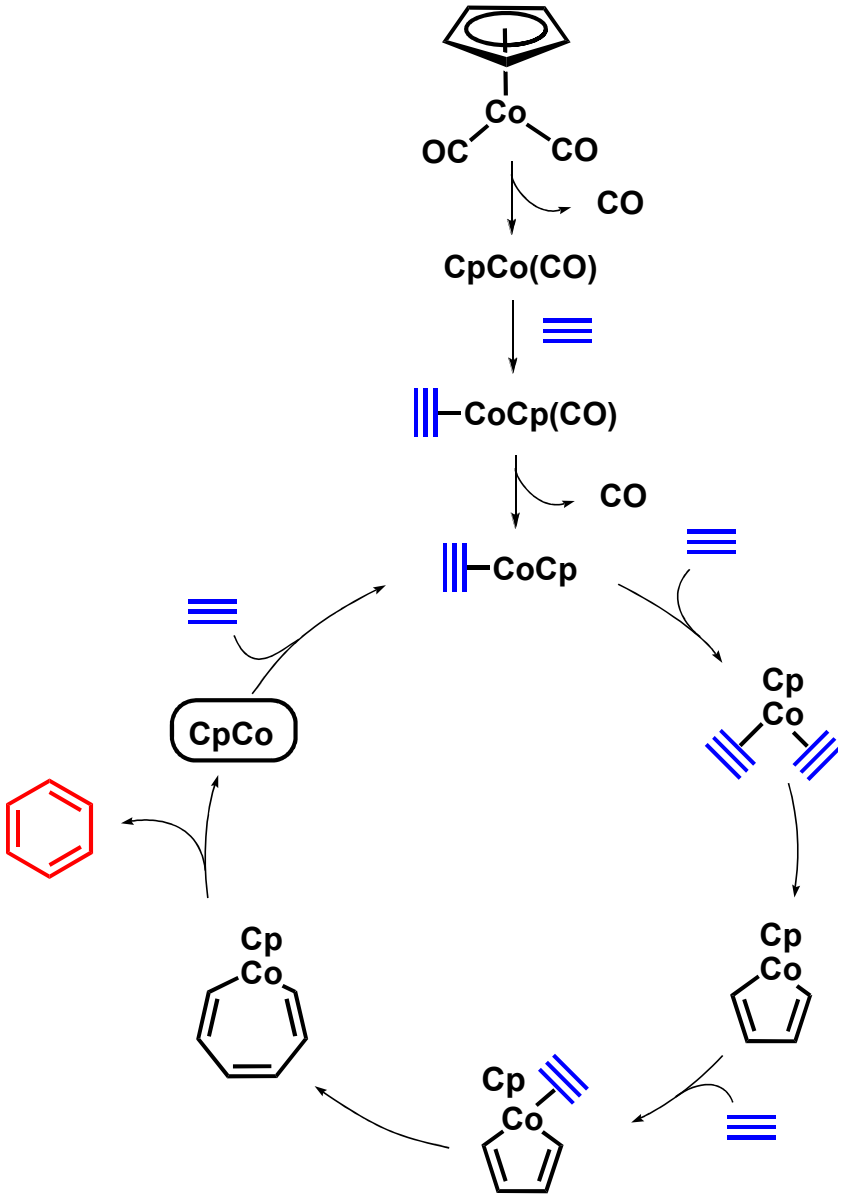


Catalytic (Vollhardt, 1970)

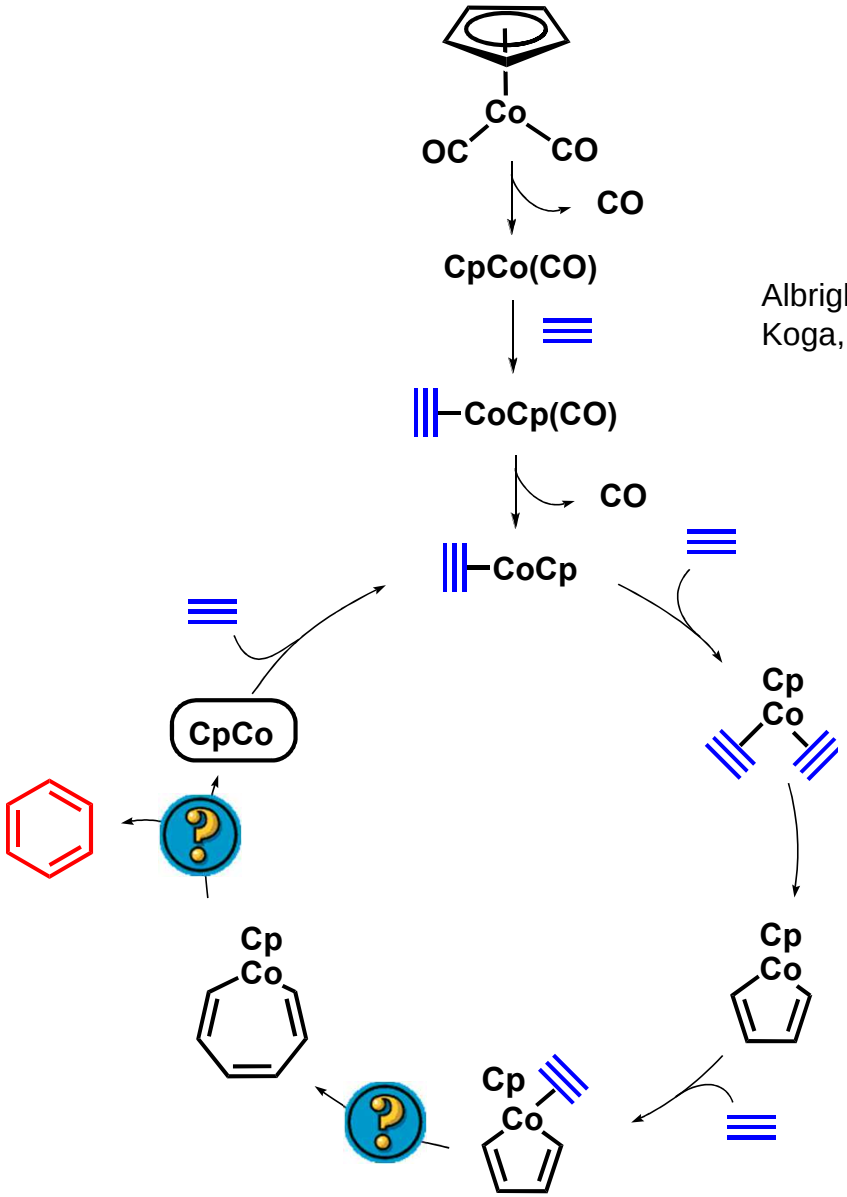


Stoichiometric (Vollhardt, 1970)

Cobalt-Catalyzed [2+2+2] Cyclotrimerization of Alkynes



Cobalt-Catalyzed [2+2+2] Cyclotrimerization of Alkynes

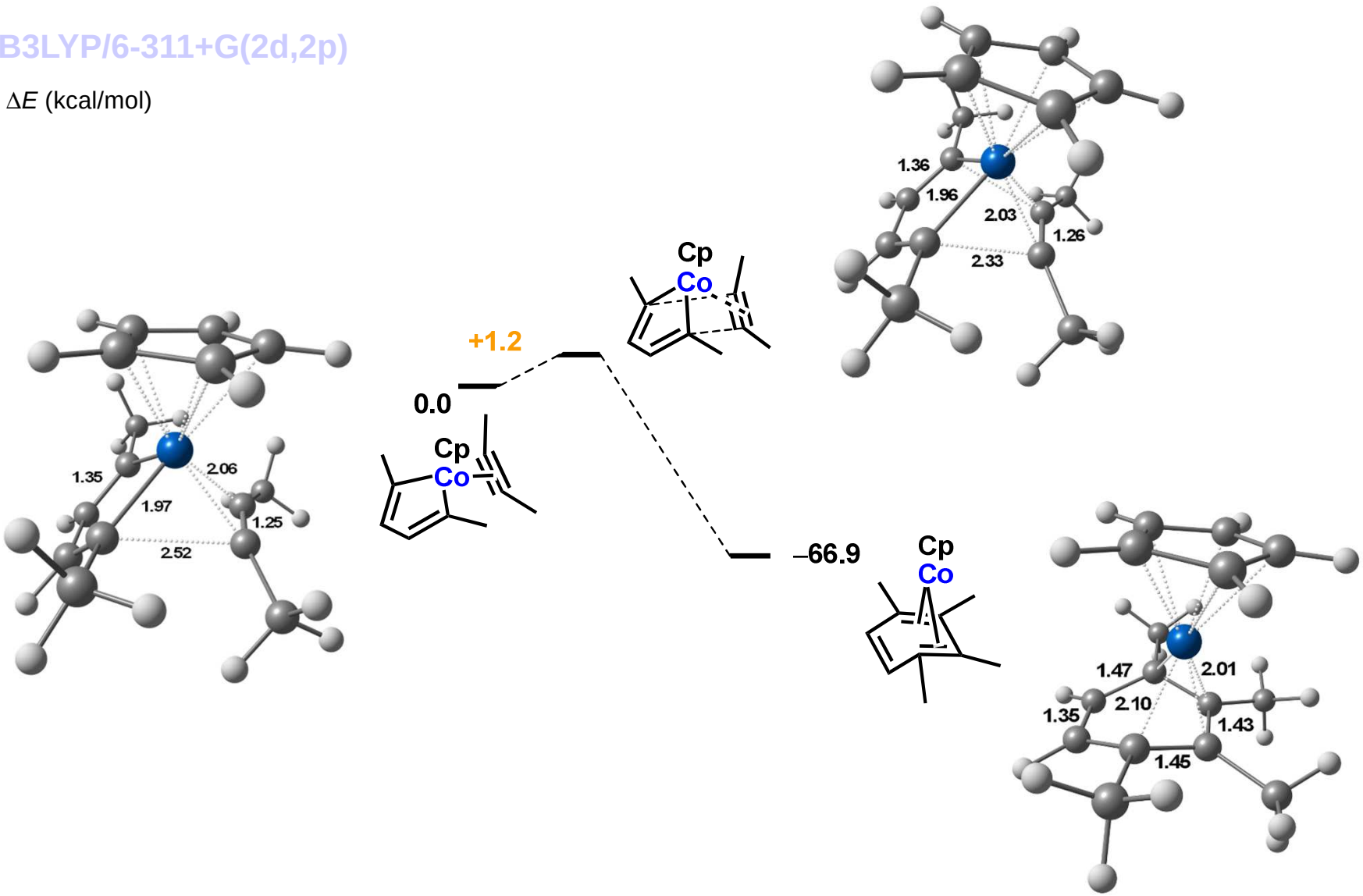


Albright, T. A. *J. Am. Chem. Soc*. **1999**, *121*, 6055
Koga, N. *Bull. Chem. Soc. Jpn*. **2005**, *78*, 781

Metal-Assisted [4+2] Cycloaddition

B3LYP/6-311+G(2d,2p)

ΔE (kcal/mol)

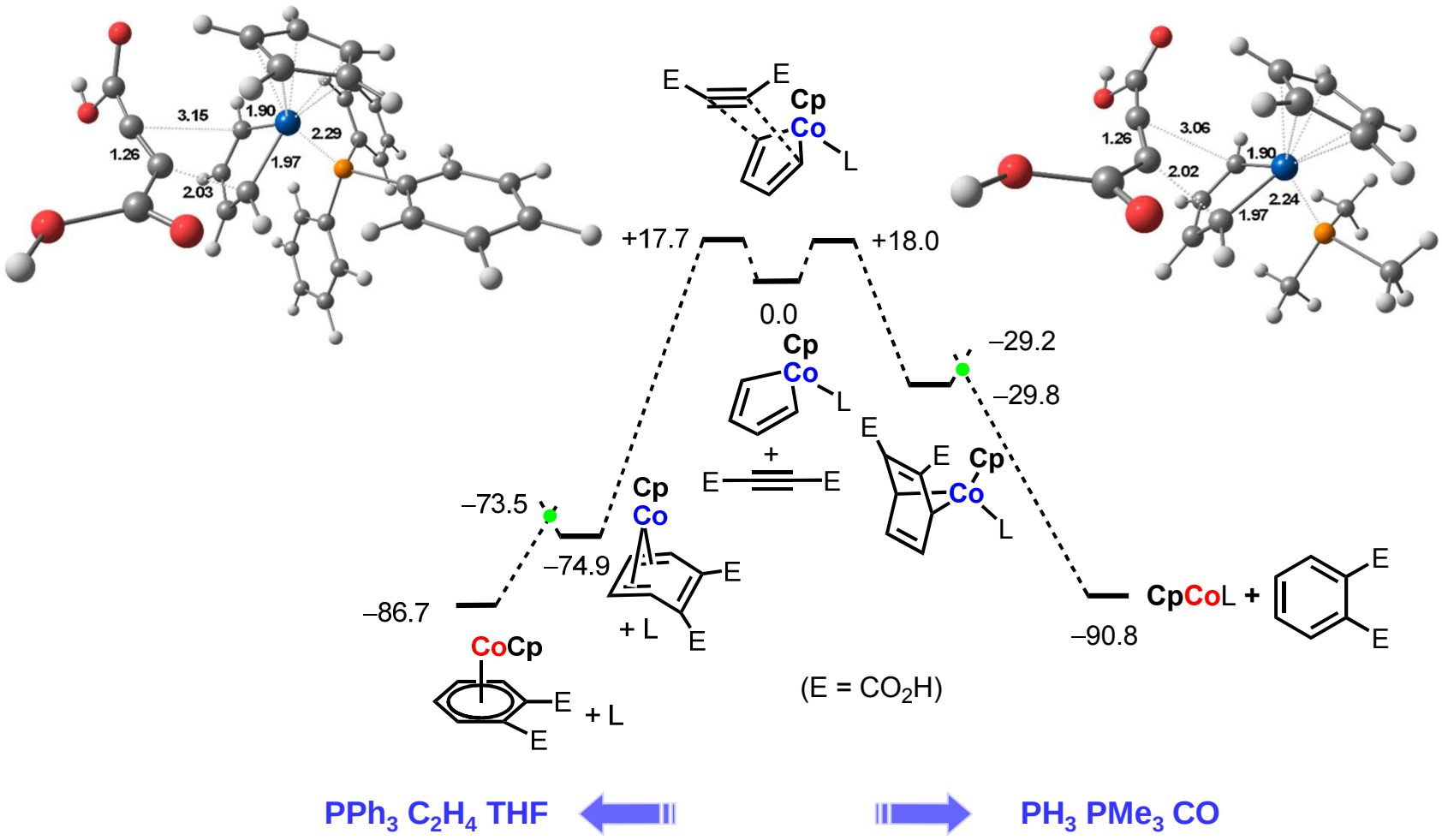


J. Am. Chem. Soc. **2007**, *129*, 8860

Unassisted [4+2] Cycloaddition

B3LYP/6-311+G(2d,2p)

ΔE (kcal/mol)

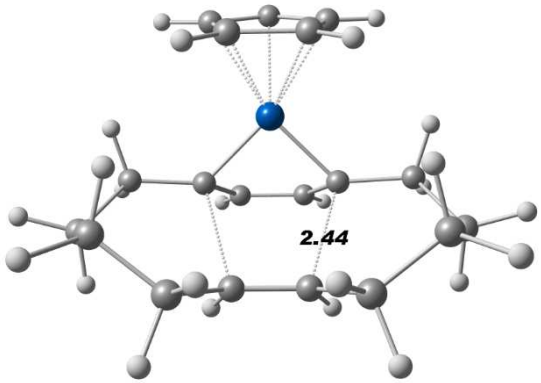


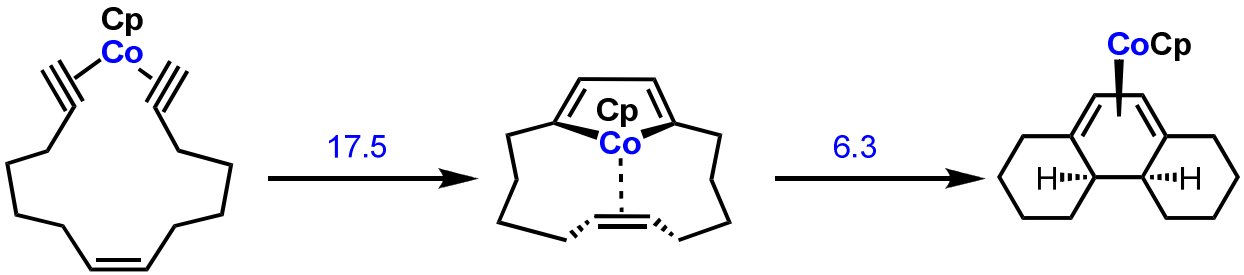
J. Am. Chem. Soc. **2007**, *129*, 8860

Tethered Systems

B3LYP/6-311+G(2d,2p)

ΔH_{298} (kcal/mol)





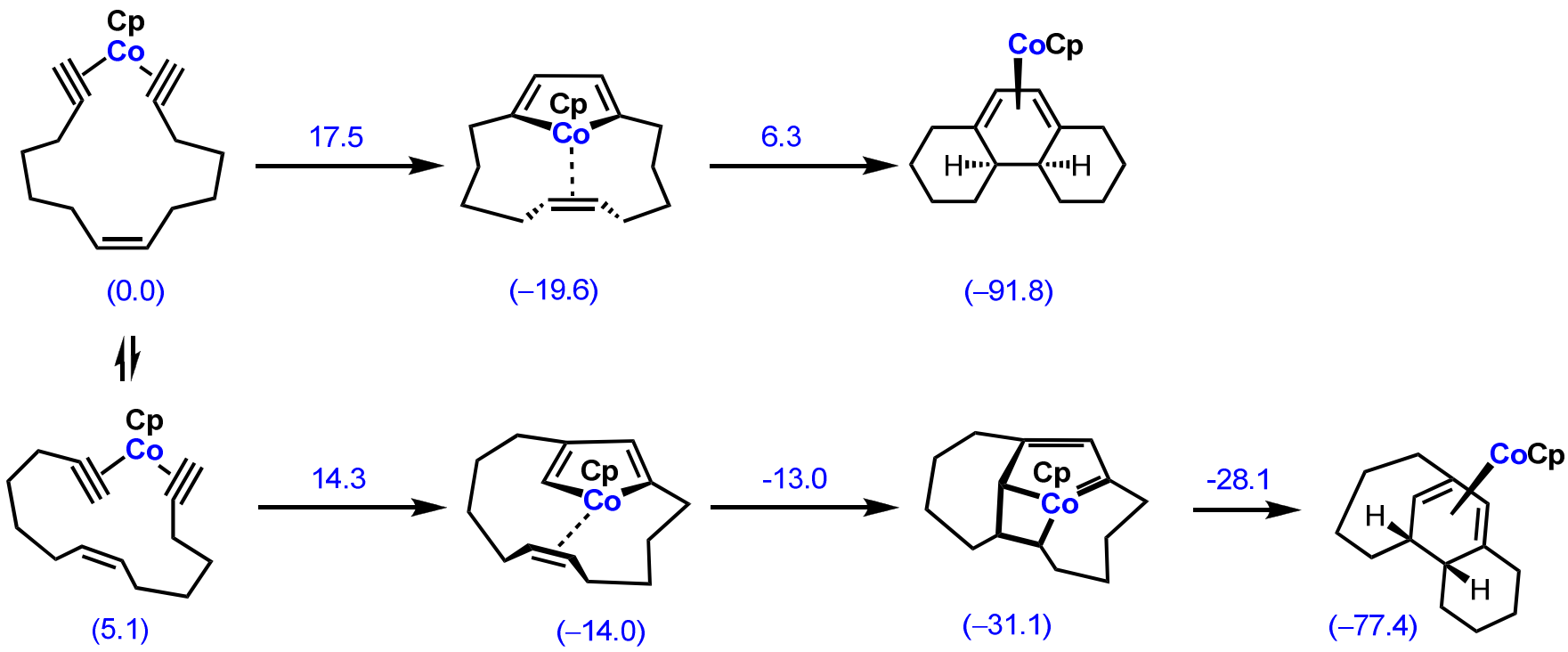
(0.0) (–19.6) (–91.8)

Chem. Eur. J. **2007**, *13*, 7466

Tethered Systems

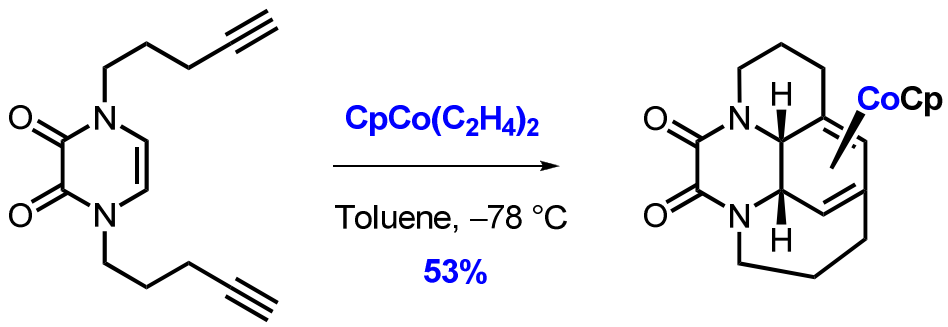
B3LYP/6-311+G(2d,2p)

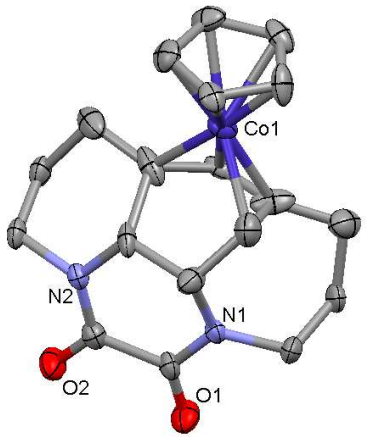
ΔH_{298} (kcal/mol)



Chem. Eur. J. **2007**, *13*, 7466

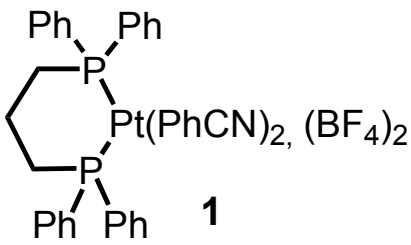
Tethered Systems



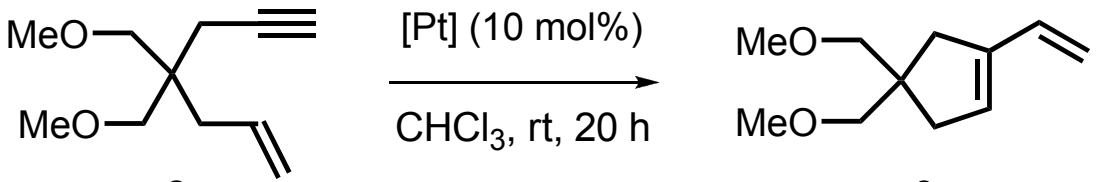


Chem. Eur. J. **2007**, *13*, 7466

Cycloisomerization of enynes: Pt(II)



1

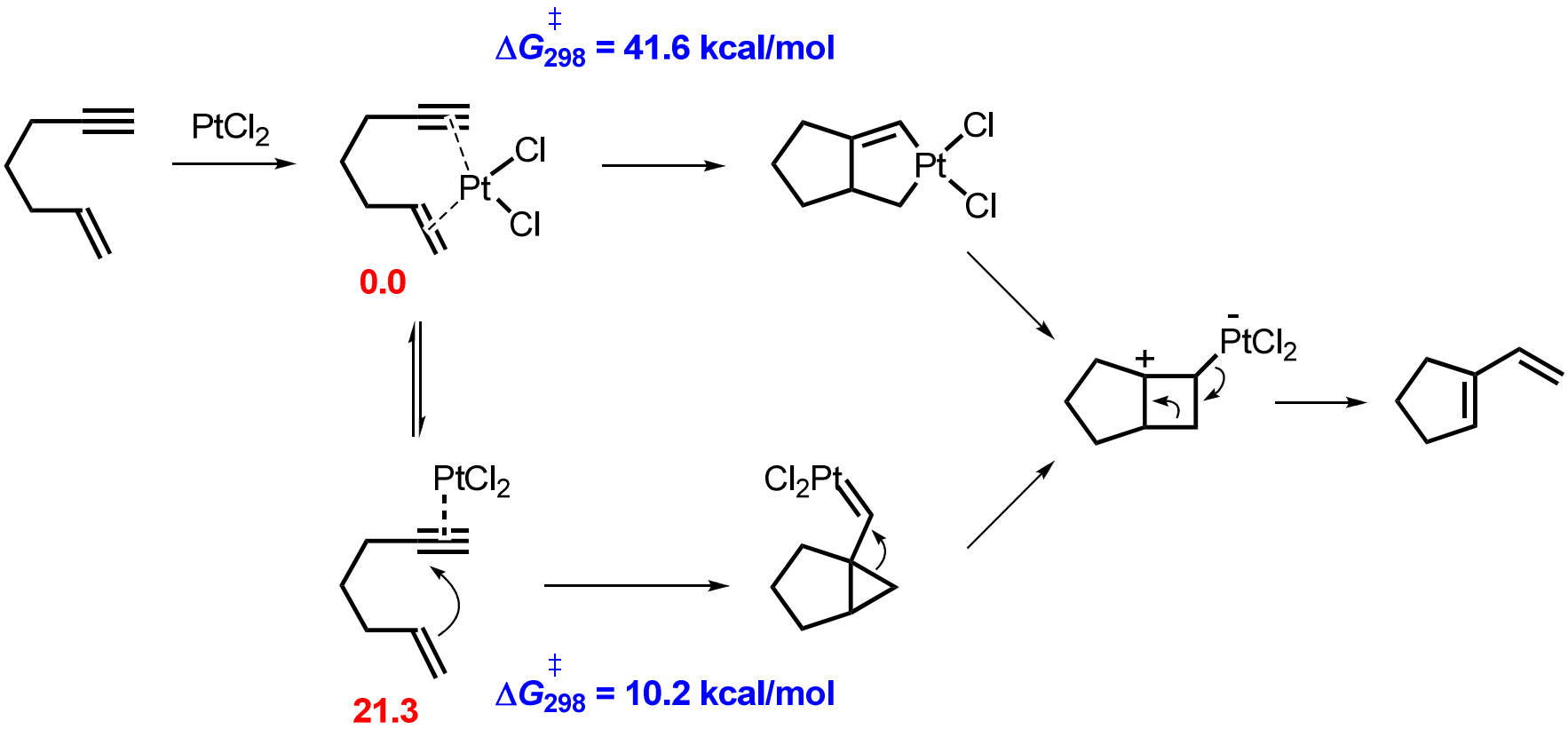


2 **3**

[Pt] = $PtCl_2$, 83%
[Pt] = **1**, 92%

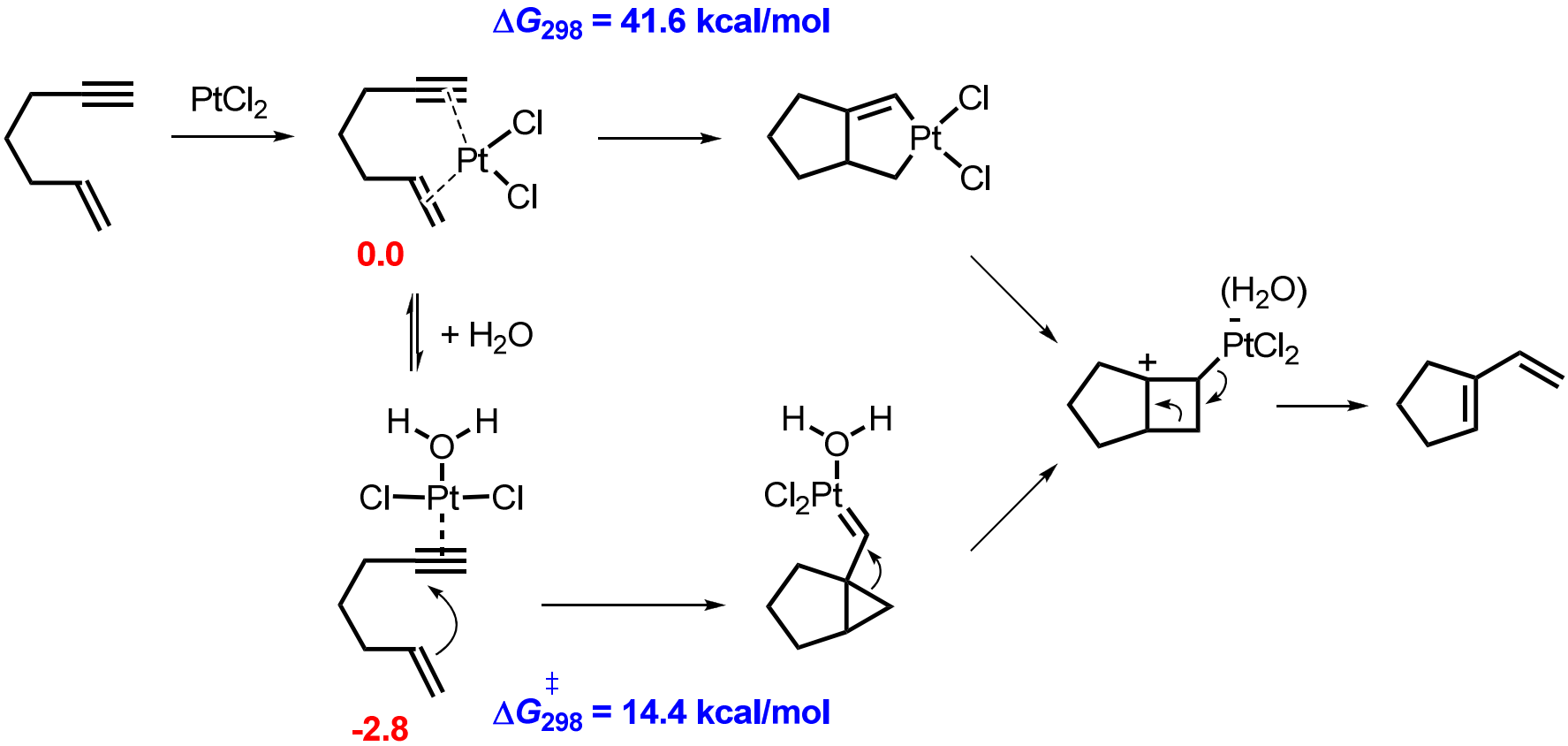
Cycloisomerization of enynes: Pt(II)

B3LYP/LANL2DZ(Pt)/6-31G(d,p)



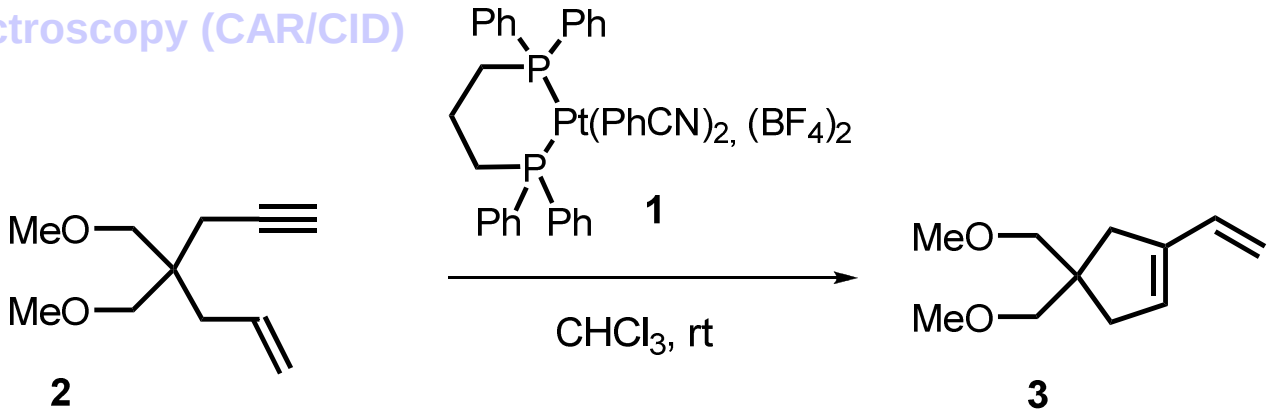
Cycloisomerization of enynes: Pt(II)

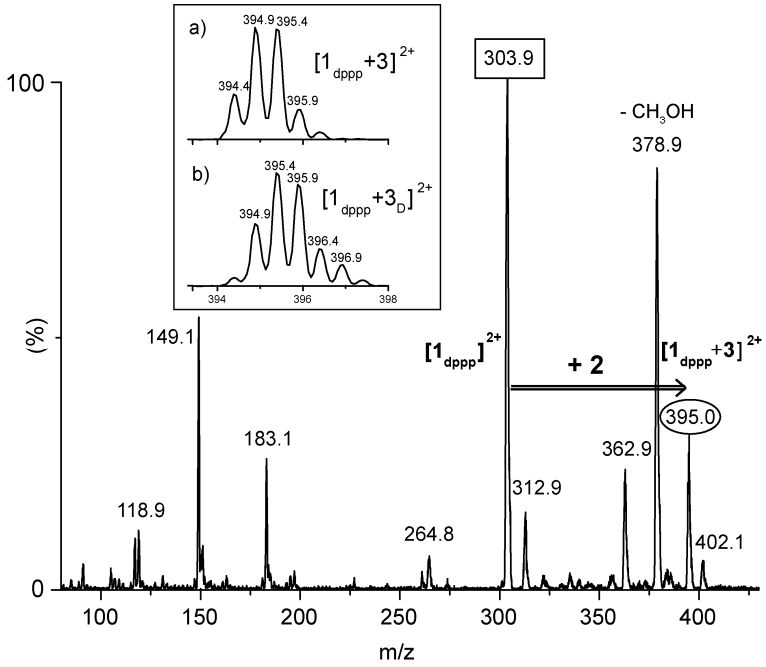
B3LYP/LANL2DZ(Pt)/6-31G(d,p)



Cycloisomerization of enynes: Pt(II)

Mass spectroscopy (CAR/CID)

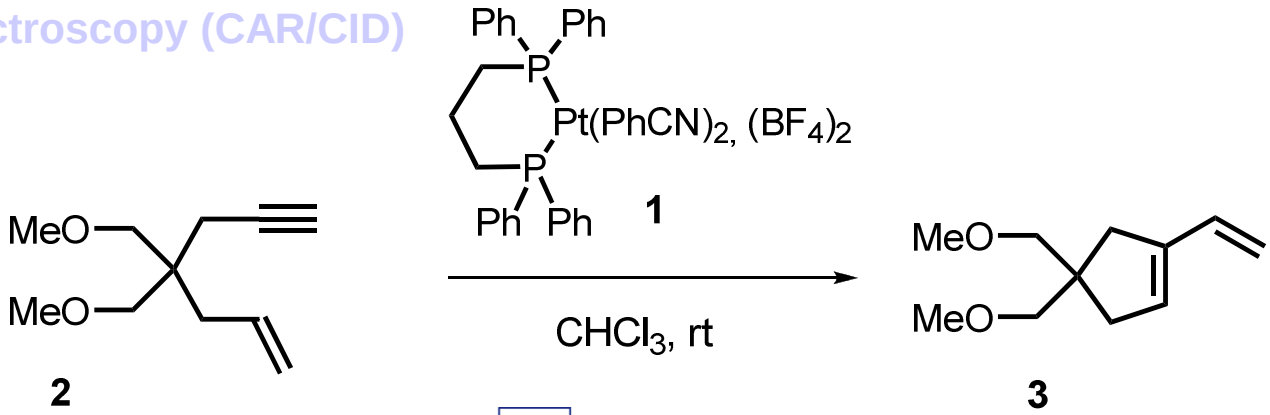


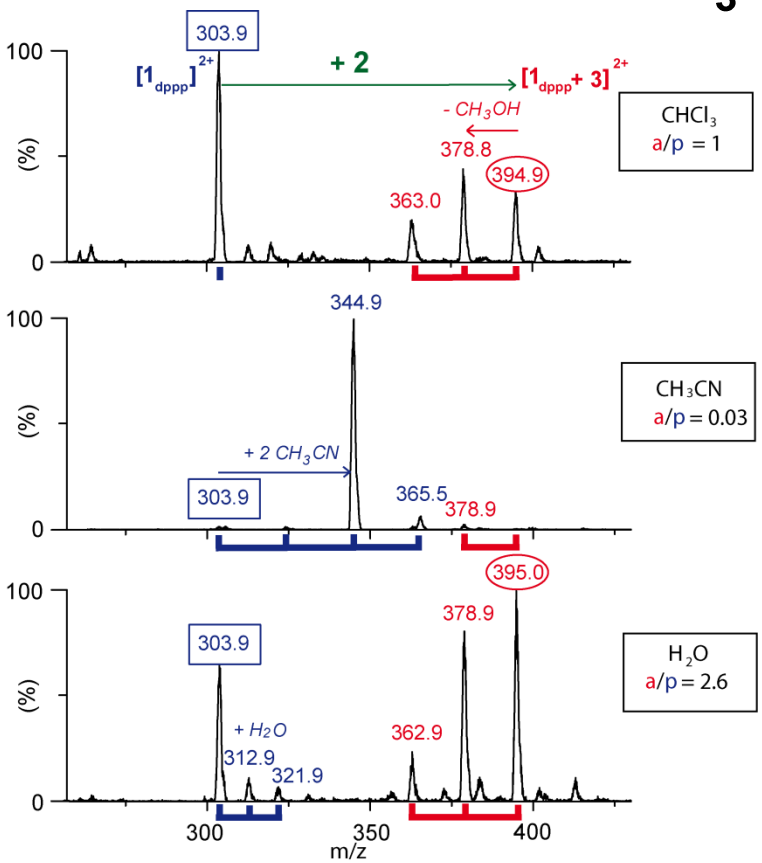


Electrospray ionization tandem mass spectrometric experiments.
Consecutive CAR/CID sequences (Collision-Activated Reaction, Collision-Induced Dissociation)

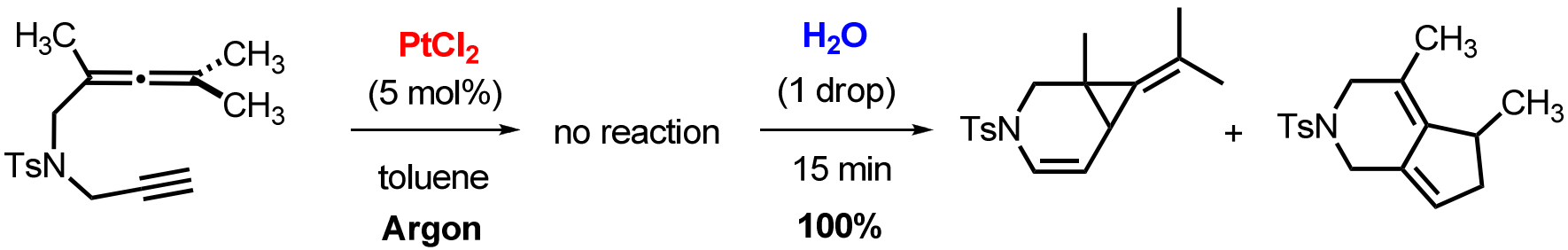
Cycloisomerization of enynes: Pt(II)

Mass spectroscopy (CAR/CID)



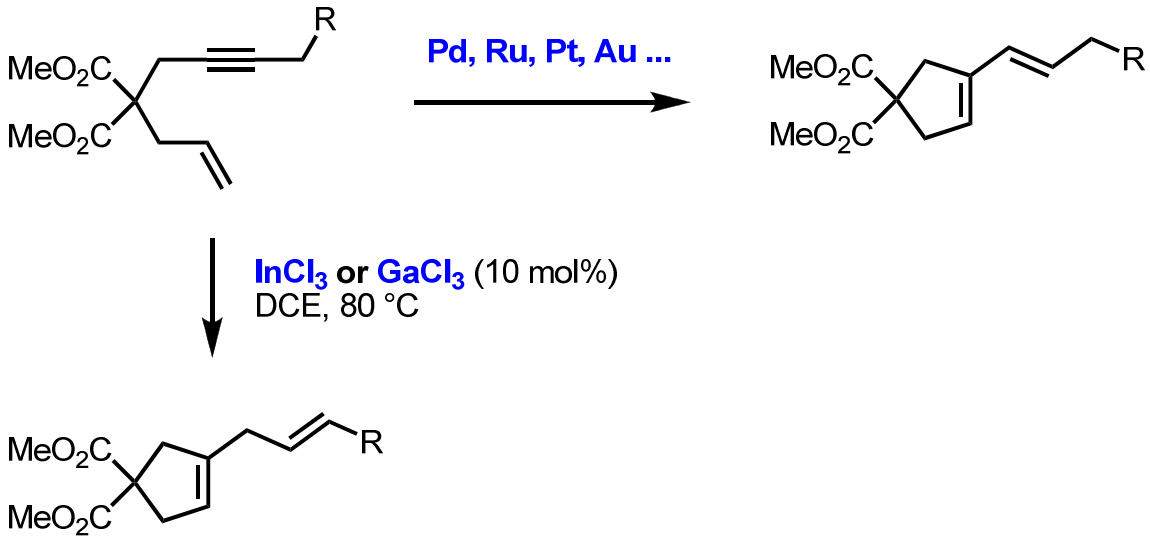


Cycloisomerization of enynes: Pt(II)



ChemCatChem **2009**, *1*, 138
Chem. Sci. **2011**, *2*, 2417

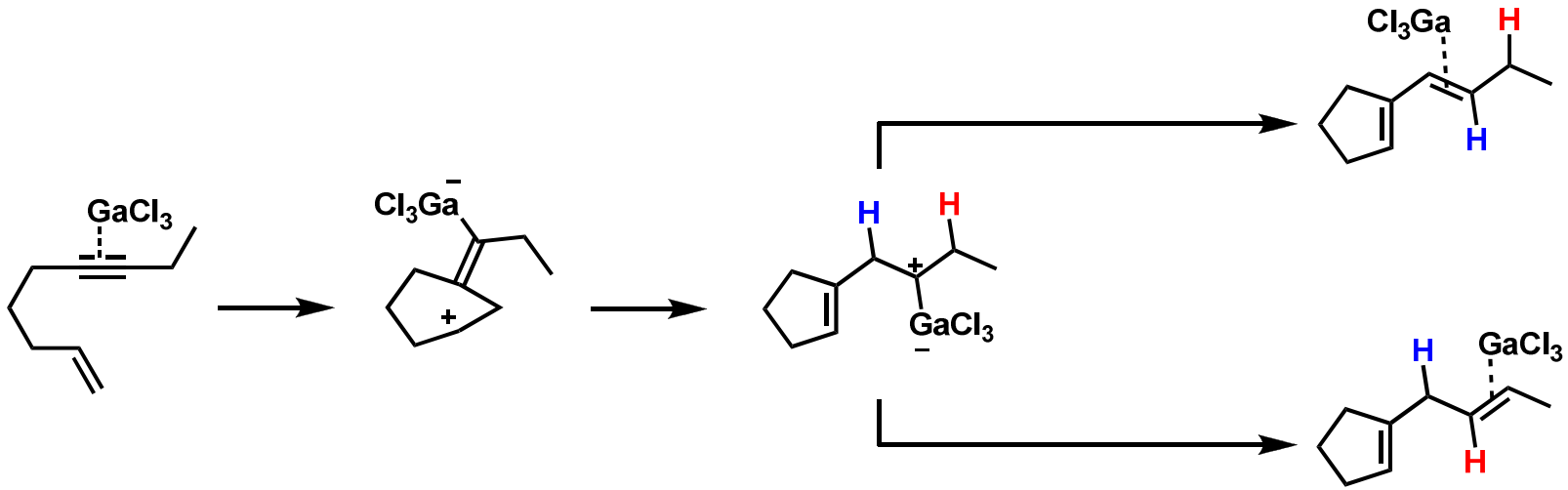
Cycloisomerization of enynes



Chatani, *Org. Lett.* **2006**, *8*, 2155

Cycloisomerization of enynes

B3LYP/LANL2DZ(Ga)/6-31G(d)



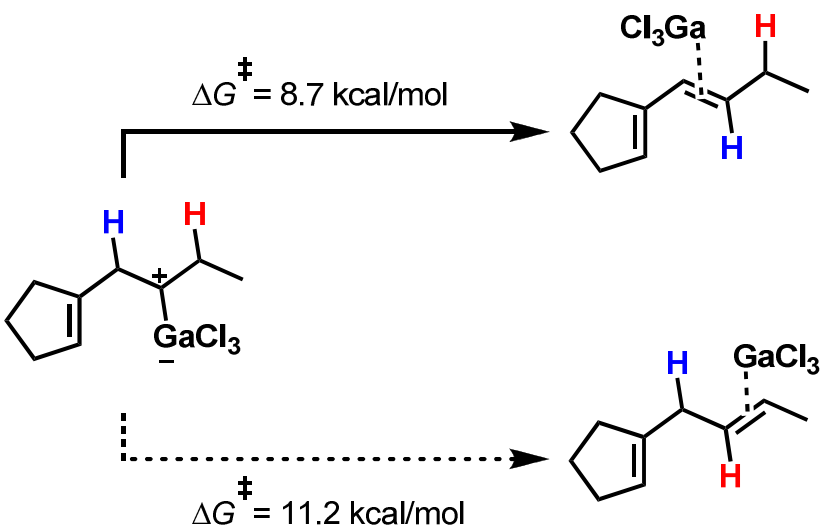
Yu, *A. J. Org. Chem*. **2014**, *3*, 842
Yu, *J. Org. Chem*. **2014**, *79*, 3809
Yu, *J. Org. Chem*. **2012**, *77*, 8527

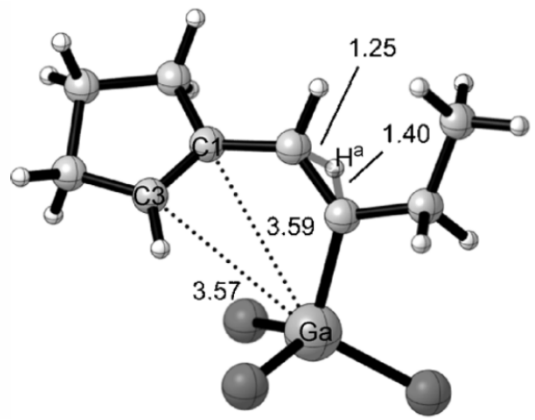
V1

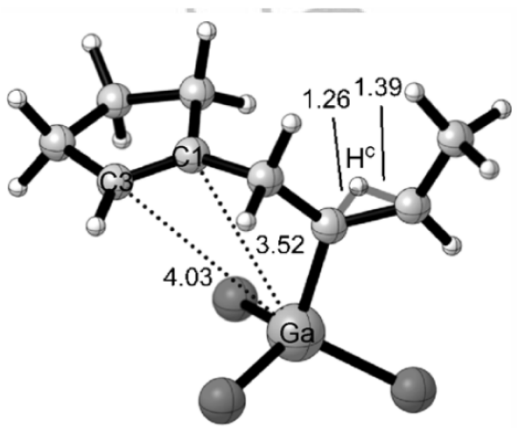
Cycloisomerization of enynes

B3LYP/LANL2DZ(Ga)/6-31G(d)

ΔG_{298} (kcal/mol)







Yu, *A. J. Org. Chem.* **2014**, *3*, 842
Yu, *J. Org. Chem.* **2014**, *79*, 3809
Yu, *J. Org. Chem.* **2012**, *77*, 8527

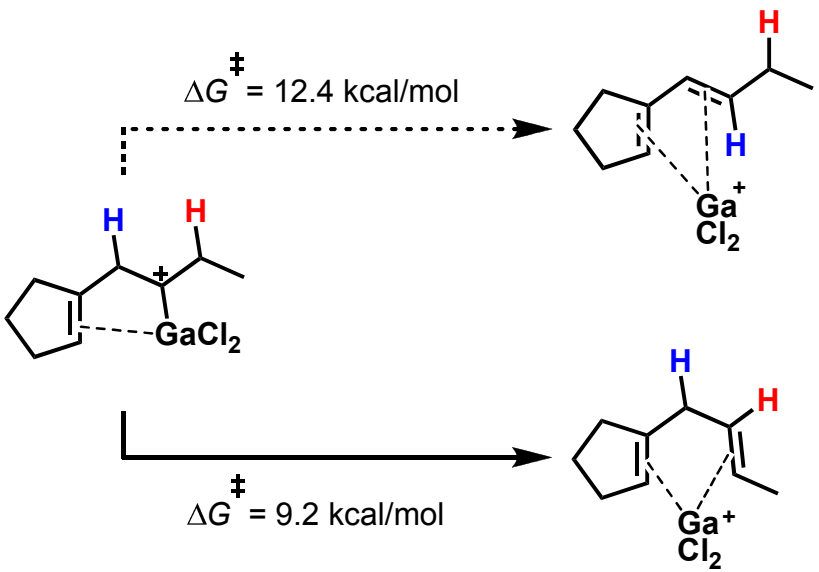
Diapositive 18

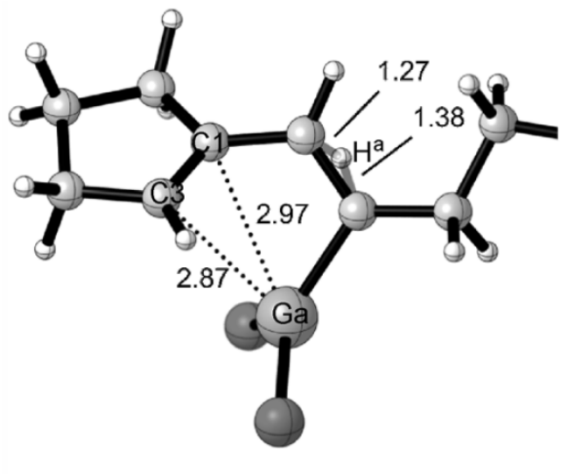
V1 le trans nonconj est écrit cis dans le papier !
Vincent; 10/11/2014

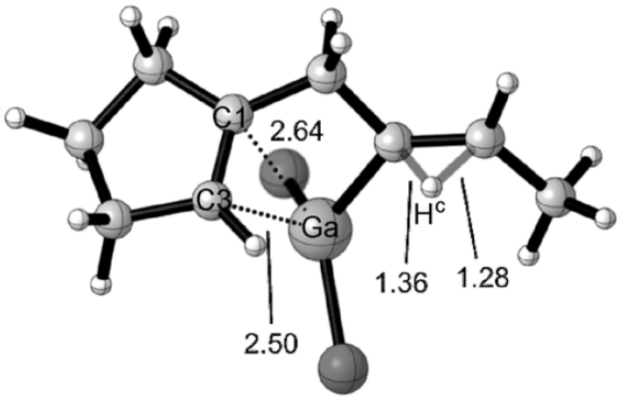
Cycloisomerization of enynes

B3LYP/LANL2DZ(Ga)/6-31G(d)

ΔG_{298} (kcal/mol)



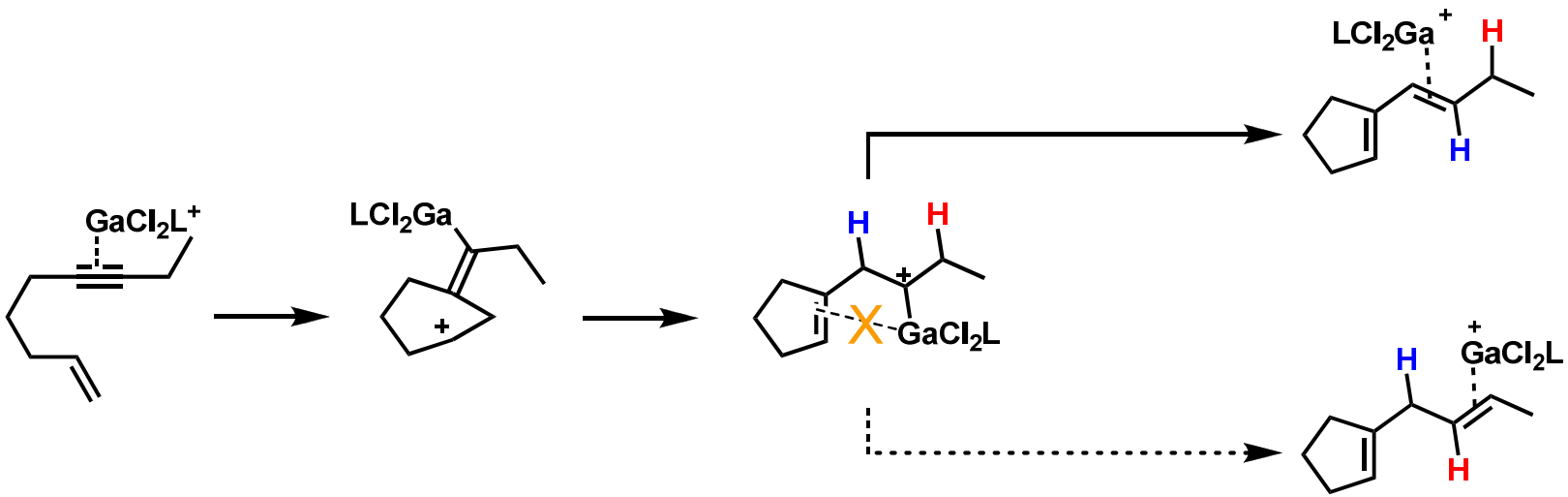




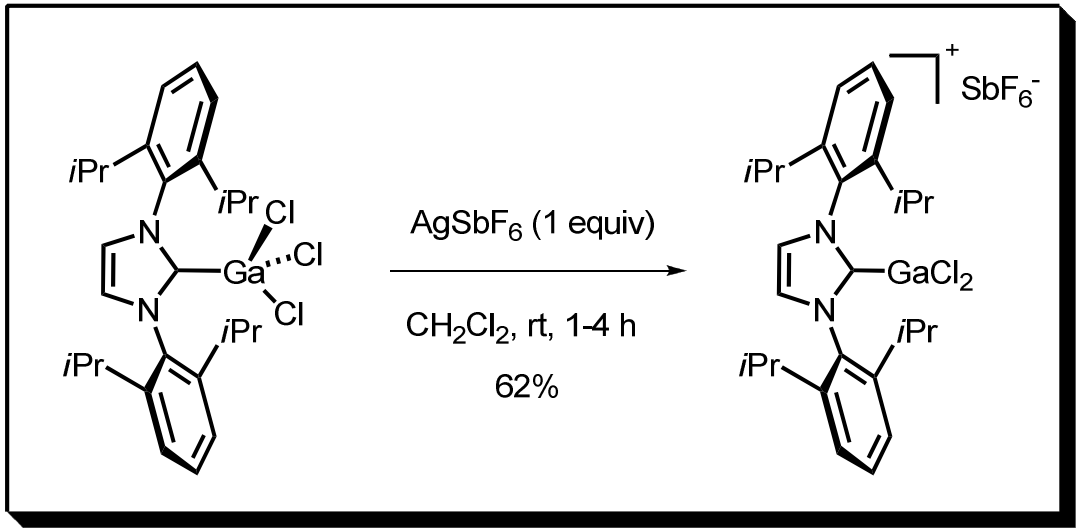
Yu, *A. J. Org. Chem.* **2014**, *3*, 842
Yu, *J. Org. Chem.* **2014**, *79*, 3809
Yu, *J. Org. Chem.* **2012**, *77*, 8527

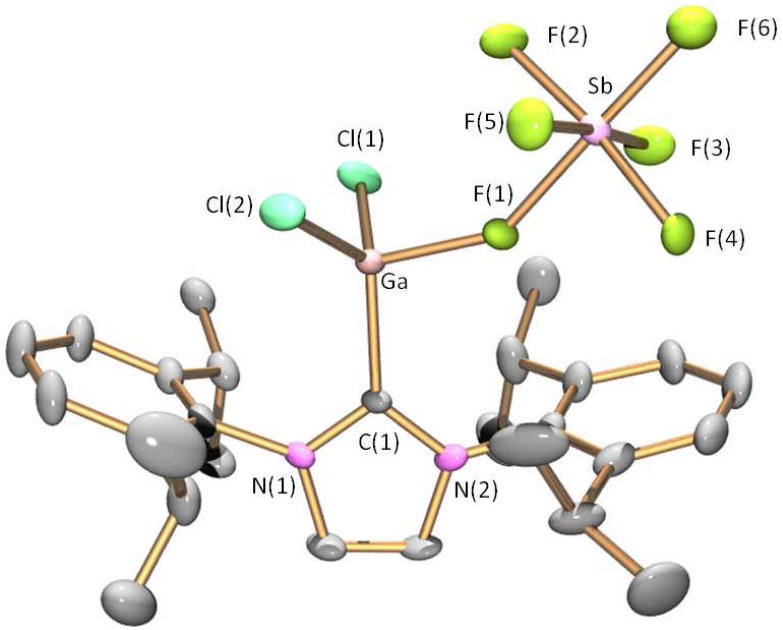
Cycloisomerization of enynes

B3LYP/LANL2DZ(Ga)/6-31G(d)



Cationic Gallium(III) Complexes

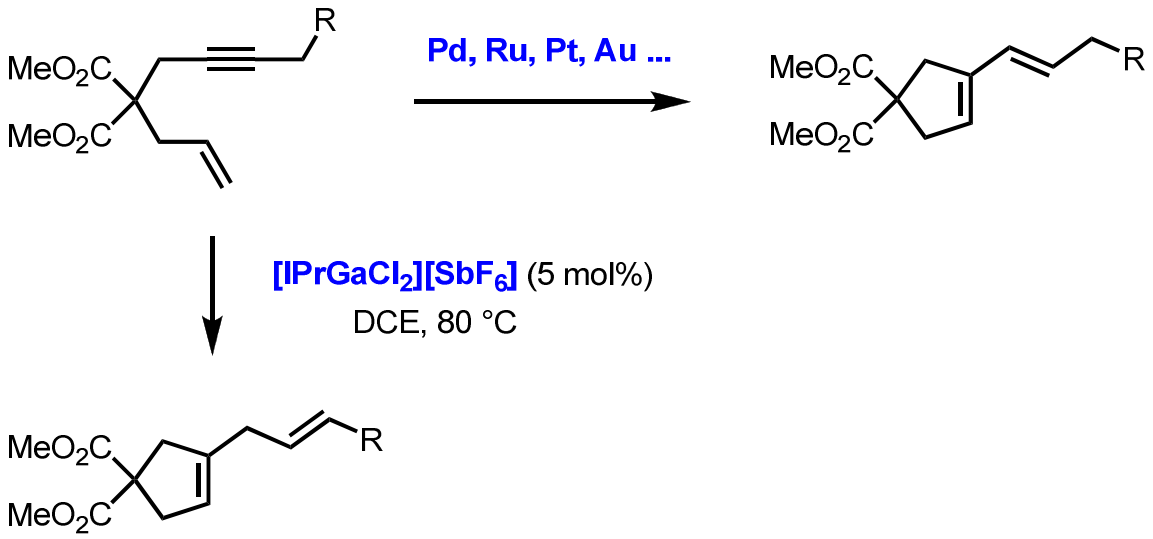




Ga-F(1) 1.920(4) Å
Sb-F(1) 1.987(1) Å
Sb-F(2,3,4,5,6)$_{av}$ 1.87 Å

Inorg. Chem. **2013**, *52, 11493*
Inorg. Chem. **2013**, *52, 506*
Organometallics **2014**, *33*, 594

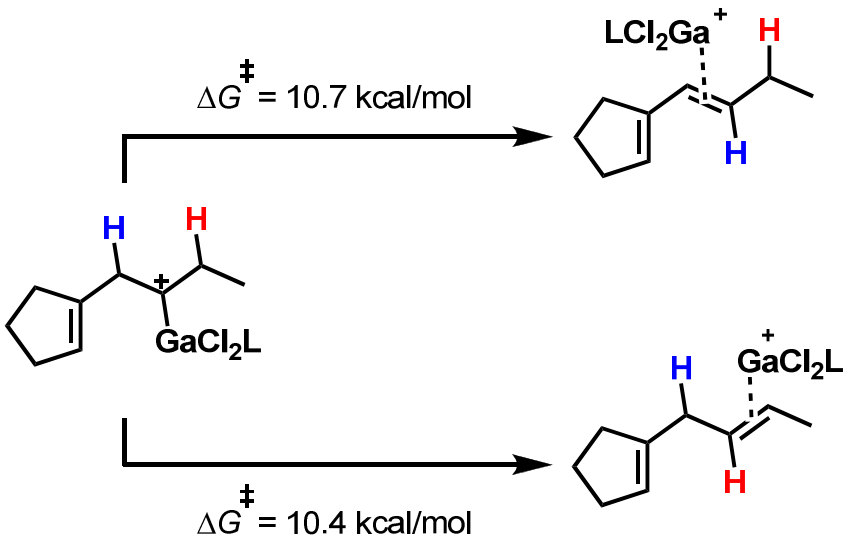
Cycloisomerization of enynes

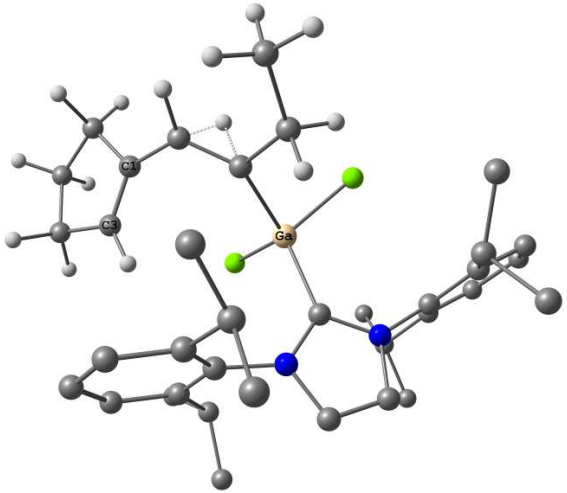


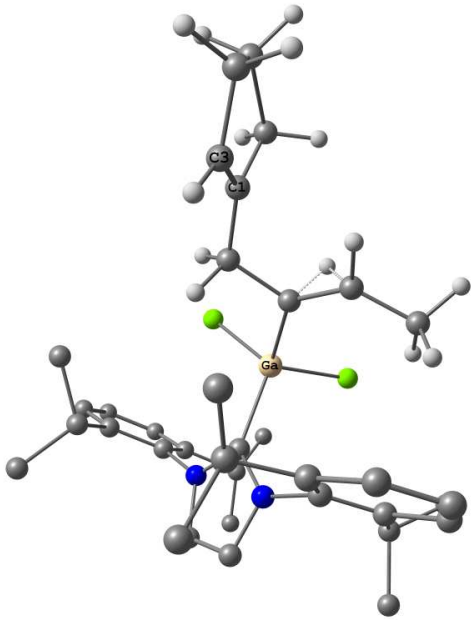
Cycloisomerization of enynes

B3LYP/6-31G(d)

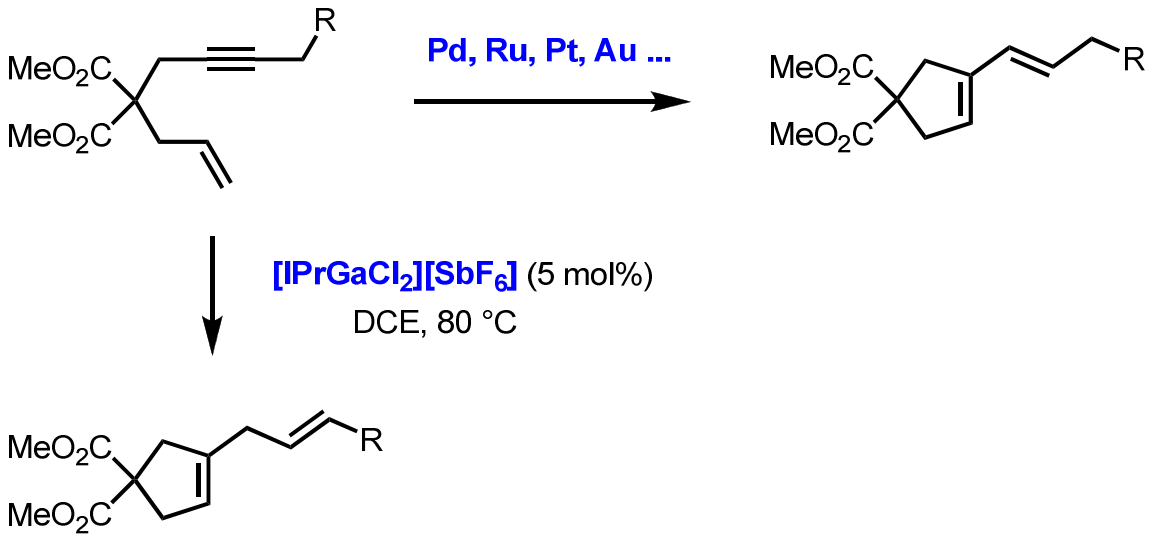
ΔG_{298} (kcal/mol)







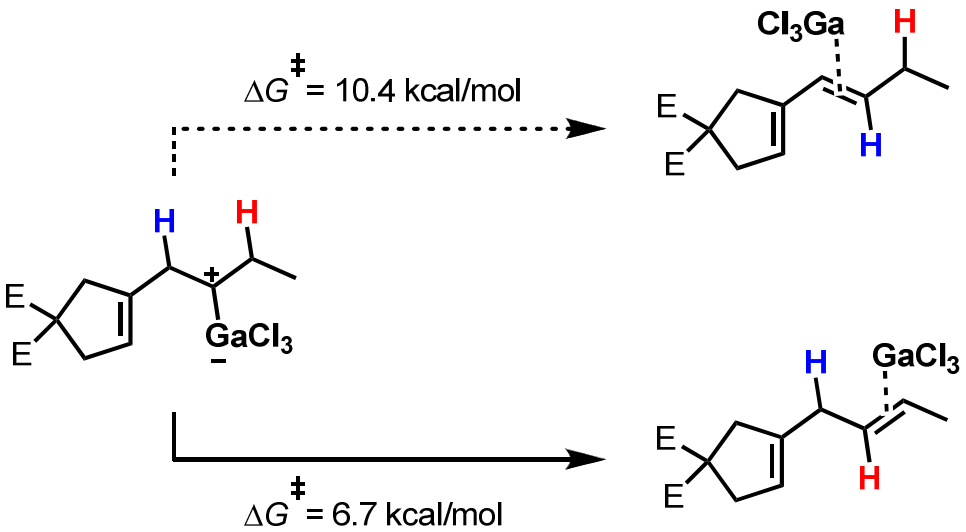
Cycloisomerization of enynes



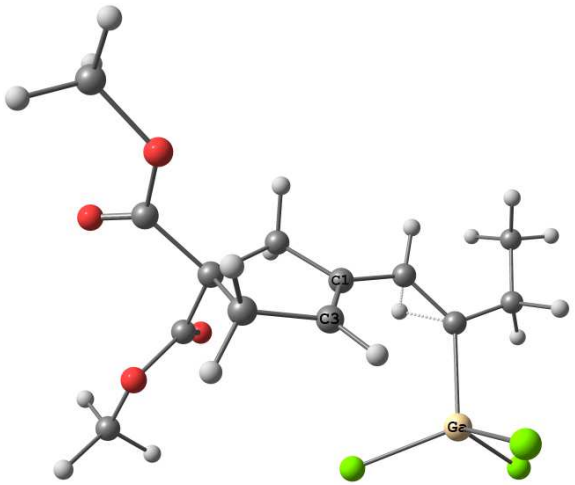
Cycloisomerization of enynes

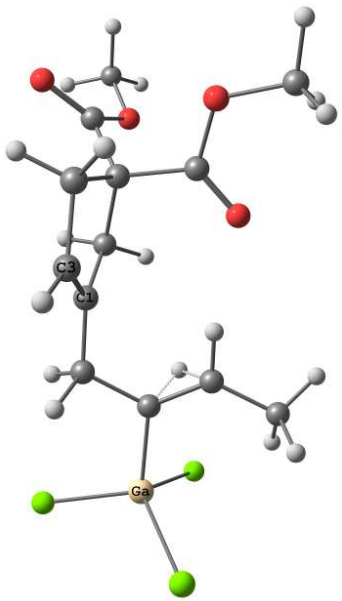
B3LYP/6-31G(d)

ΔG_{298} (kcal/mol)



(E = CO_2Me)

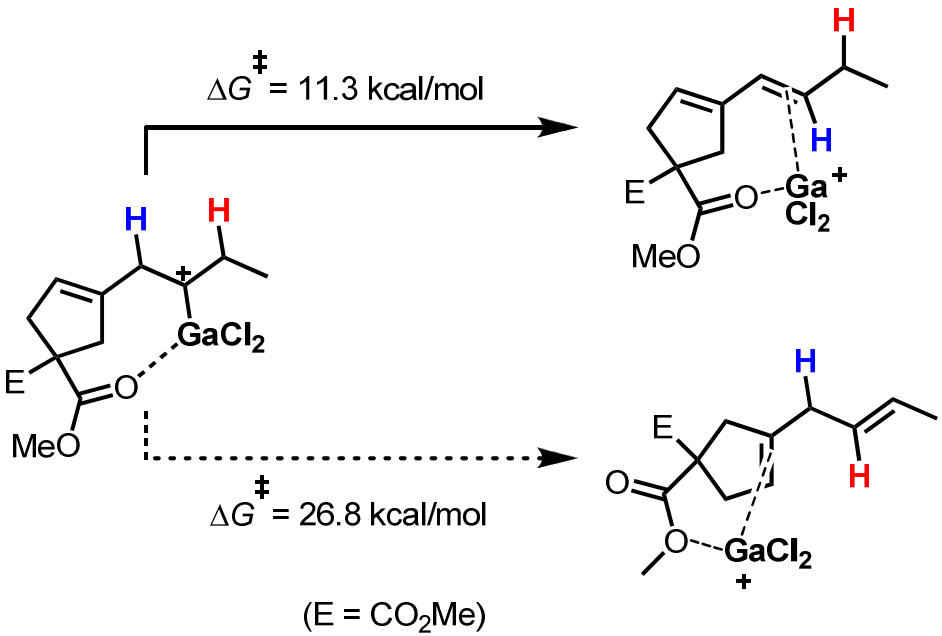


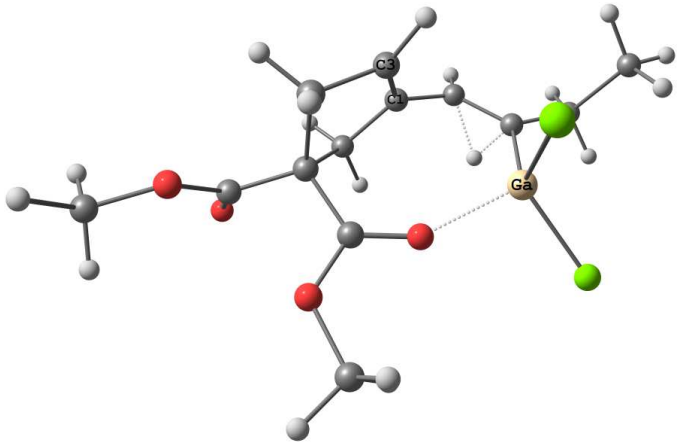


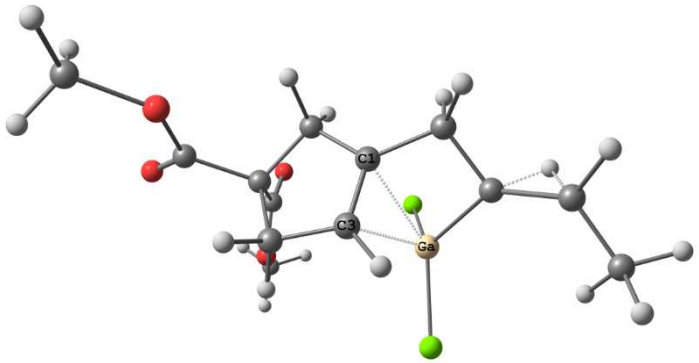
Cycloisomerization of enynes

B3LYP/6-31G(d)

ΔG_{298} (kcal/mol)



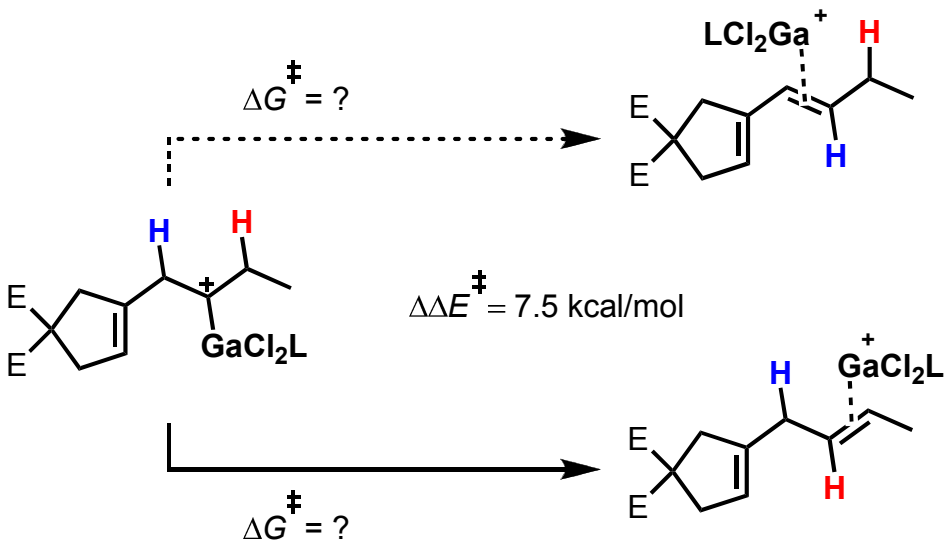




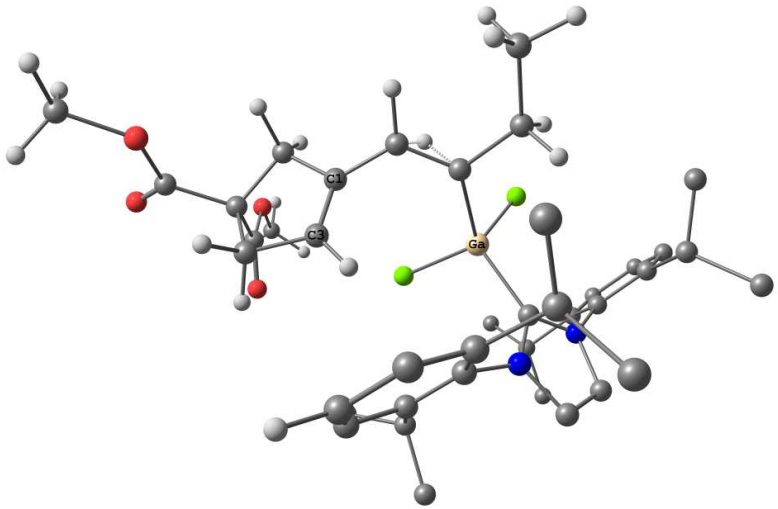
Cycloisomerization of enynes

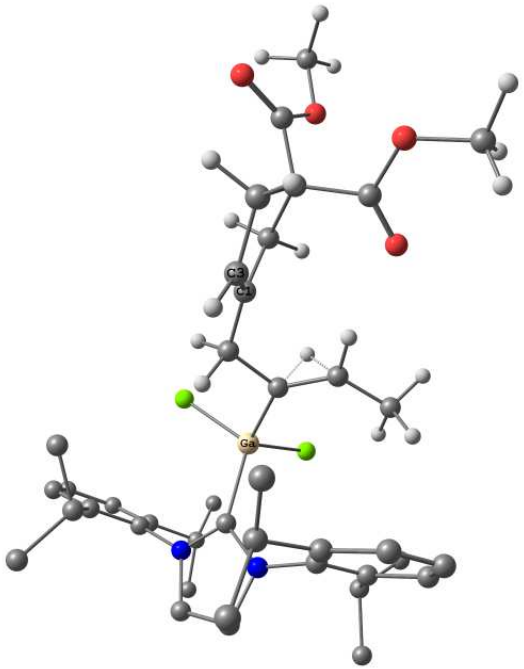
B3LYP/6-31G(d)

ΔG_{298} (kcal/mol)



(E = CO_2Me)





Acknowledgements

Bogdan Iorga (ICSN)
Etienne Derat (P6)
Tom Albright (Houston)
Jeremy Harvey (Bristol)
CRIHAN

UNIVERSITÉ PARIS SUD
Comprendre le monde, construire l'avenir®

Agence Nationale de la Recherche ANR

ICSN

cnrs

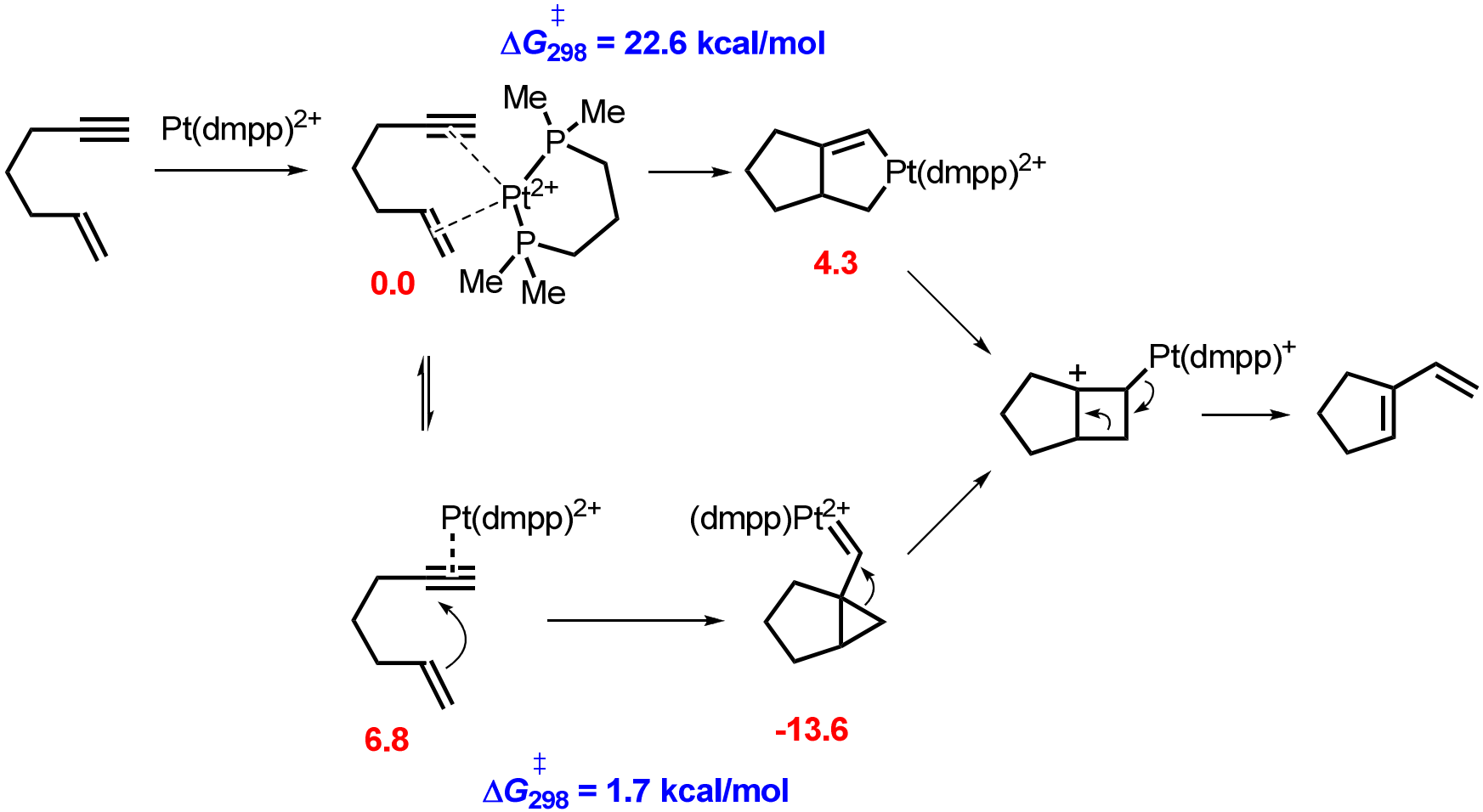
ICMMO

IUF

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE
MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE

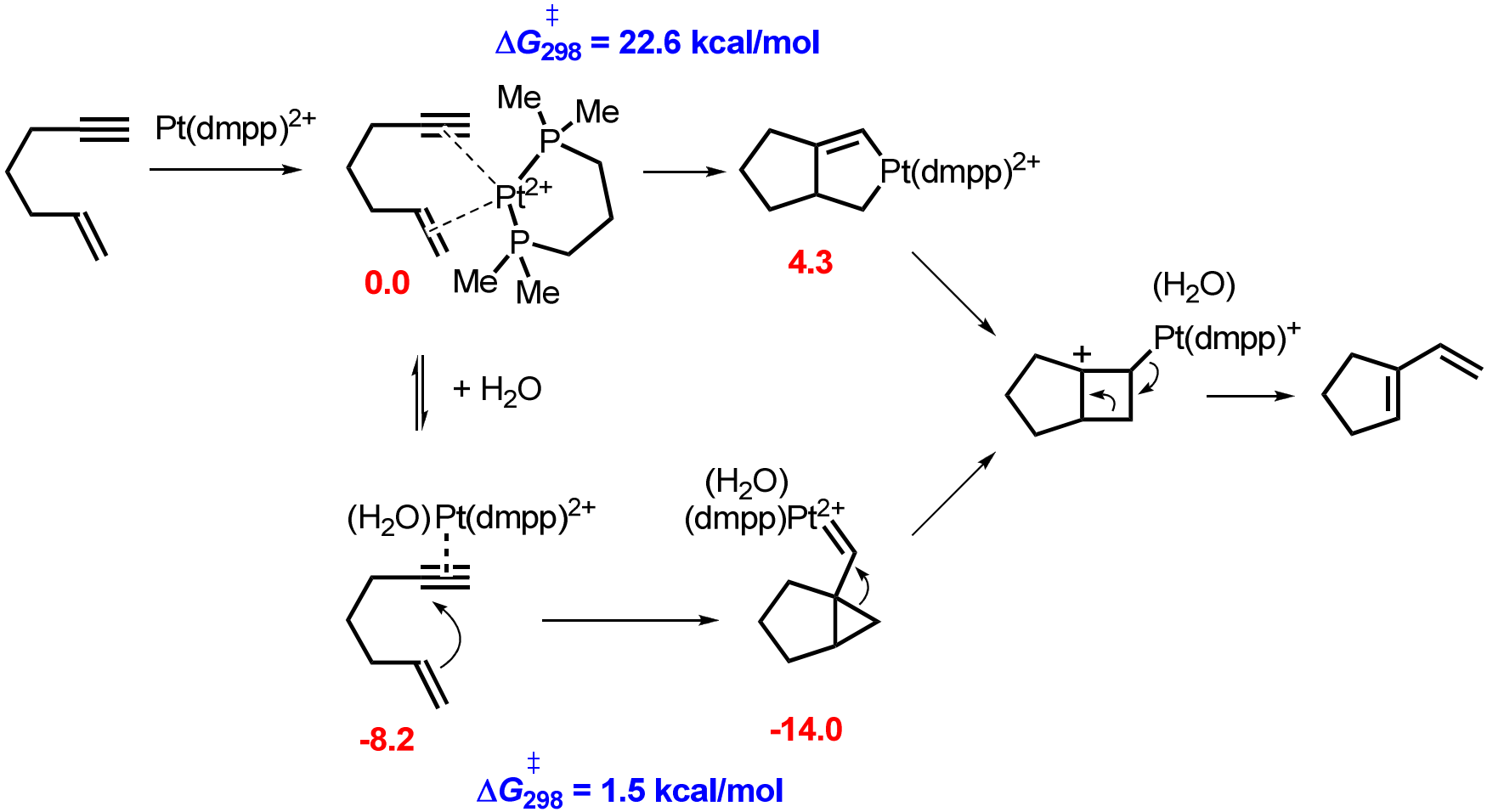
Cycloisomerization of enynes: Pt(II)

B3LYP/LANL2DZ(Pt)/6-31G(d,p)



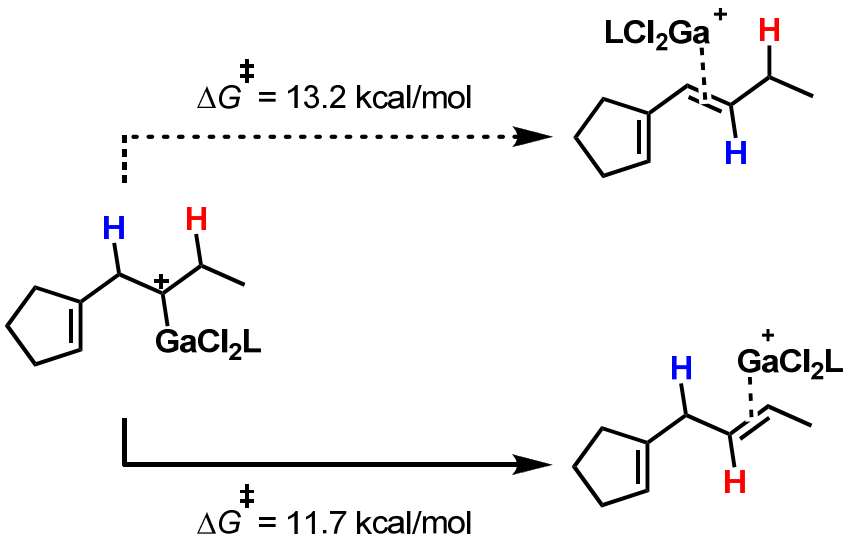
Cycloisomerization of enynes: Pt(II)

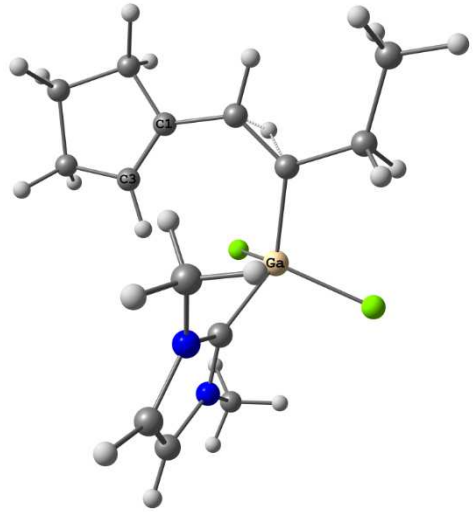
B3LYP/LANL2DZ(Pt)/6-31G(d,p)

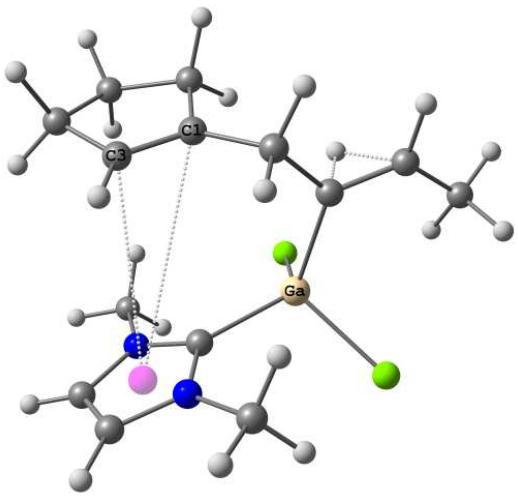


Cycloisomerization of enynes

B3LYP/6-31G(d)

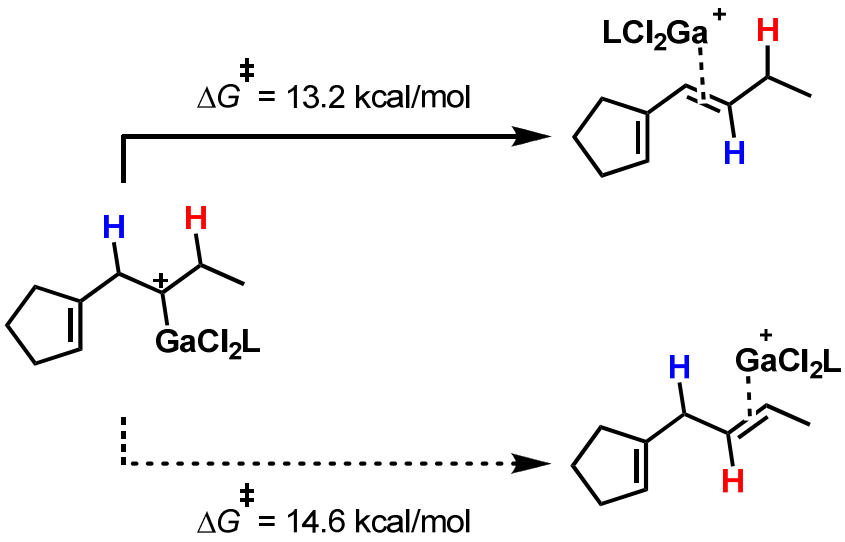


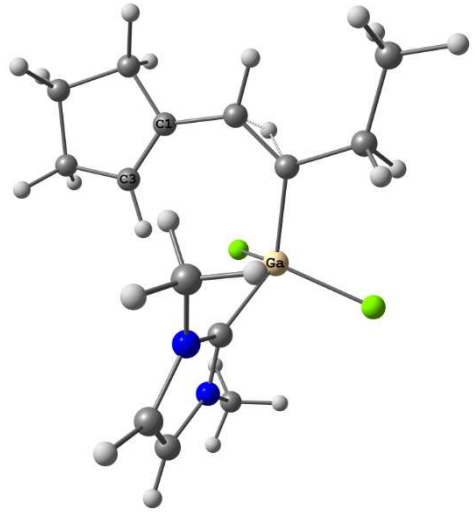


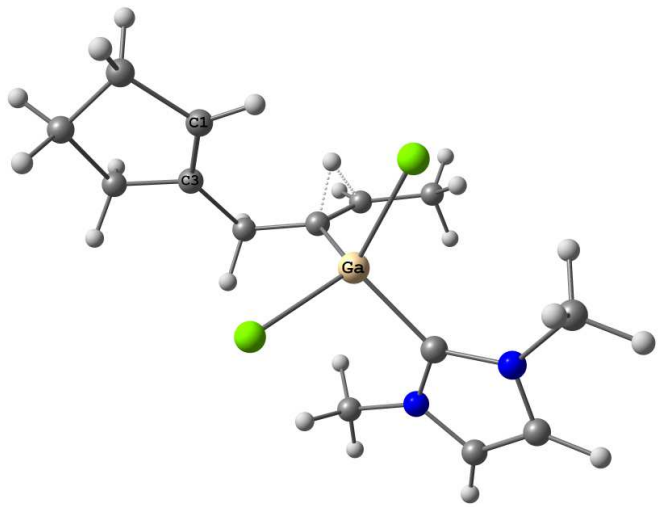


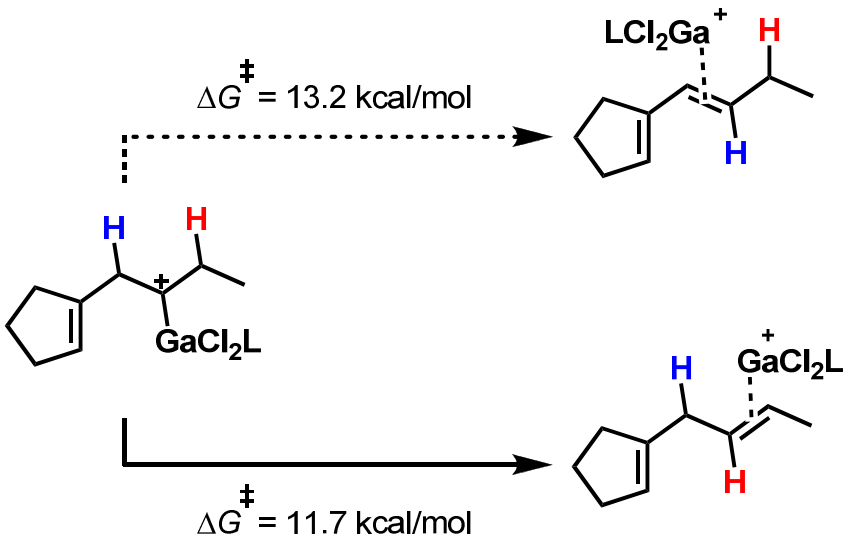
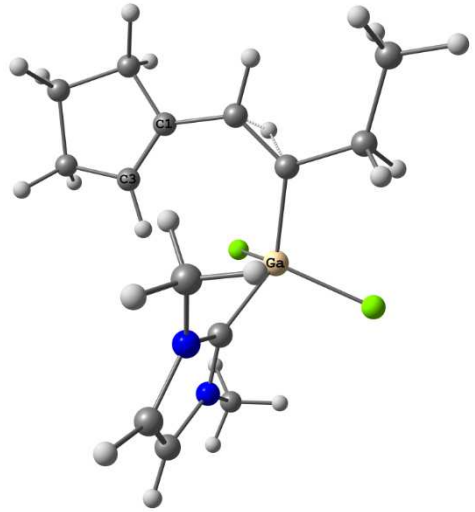
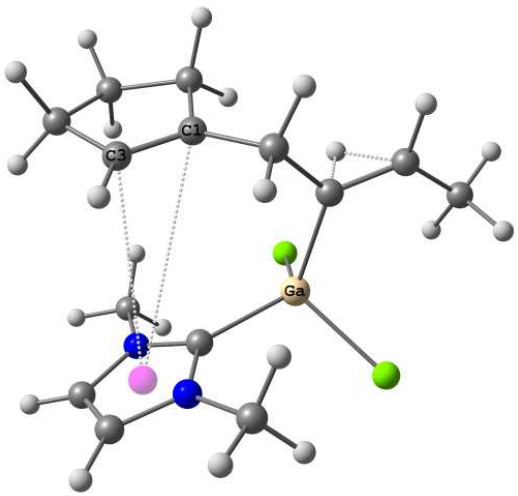
Cycloisomerization of enynes

B3LYP/6-31G(d)







Cycloisomerization of enynes

B3LYP/6-31G(d)