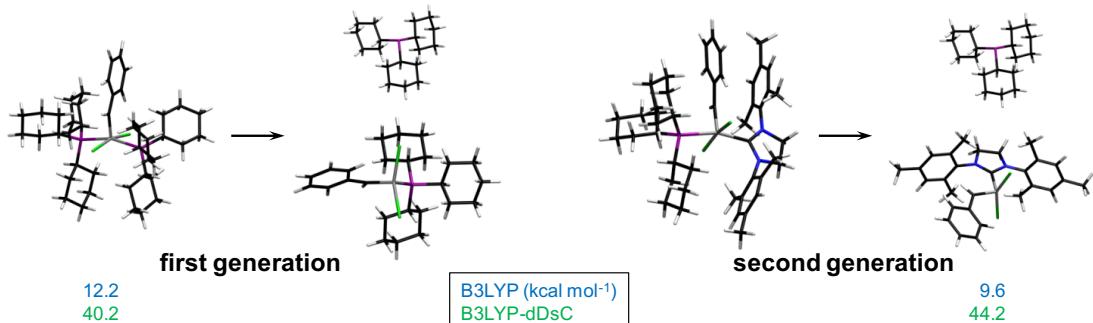


Question 1

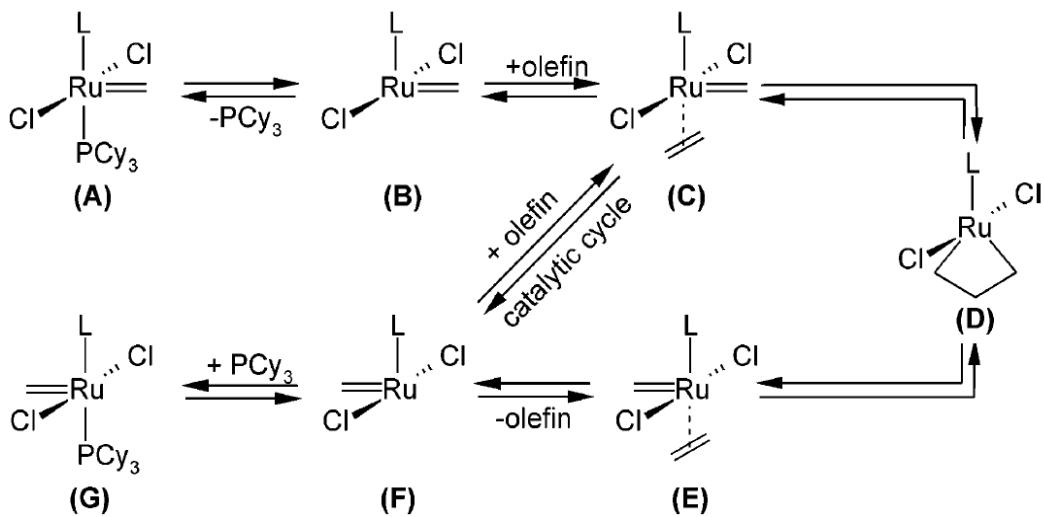
The performance of electronic structure methods for reaction mechanisms

Olefin metathesis catalyzed by ruthenium carbenes is a powerful tool for forming organic carbon-carbon double bond.



Give the cycle:

Scheme 1. Most Likely Mechanism for Olefin Metathesis by Grubbs-type Ruthenium Carbene Complexes



Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, 126, 3496-3510.

The ligand (L) differentiates first-generation and second generation of Grubbs catalysts. Changing the ligand from an organophosphine (Grubbs-I) to an N-heterocyclic carbene (NHC, Grubbs-II) dramatically increases the reactivity. After considering Figure 1, answer the following questions:

1. Can the increase in reactivity be attributed to a lower enthalpy of activation in Grubbs-II for the dissociation of the organophosphine ligand in the initiation step? Justify your answer and explain the computational data given in Figure 1.
2. Could you use CCSD(T) to verify your predictions?
3. Could you use M06-2X?