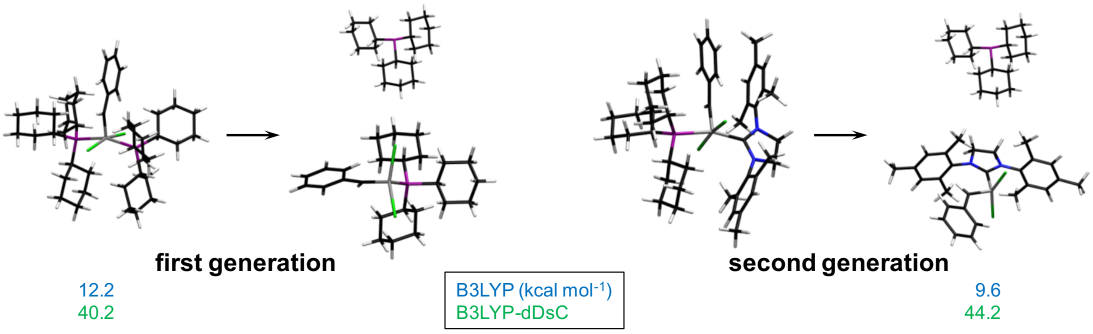
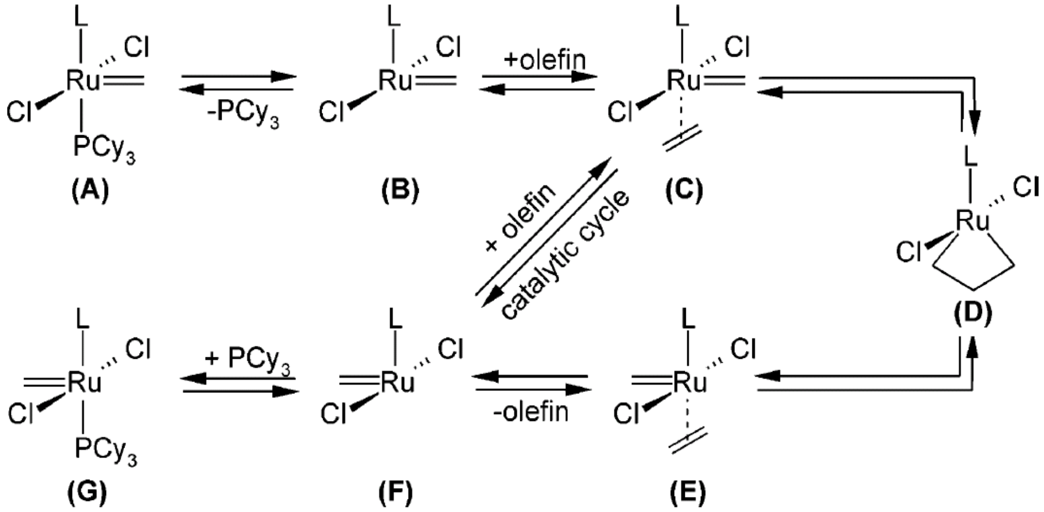
Question 1
The performance of electronic structure methods for reaction mechanisms

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.

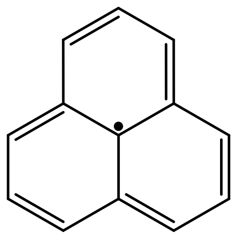
The ligand (L) differentiates first-generation and second generation of Grubbs catalysts. Changing the ligand from an organosphosphine (Grubbs-I) to an N-heterocyclic carbene (NHC, Grubbs-II) dramatically increases the reactivity. After considering Figure 1, answer the following questions:

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?

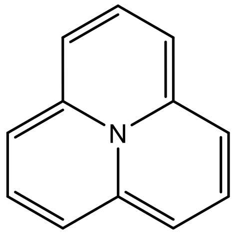
Question 2
Hydrocarbon radicals: challenges and opportunities for experimental and computational chemistry

The phenalenyl radical is a prototypical open-shell graphene fragment, proposed for use in organic molecular electronics.

9b-azaphenalene is a closed-shell analogue of the phenalenyl radical.



Phenalenyl



9b-azaphenalene

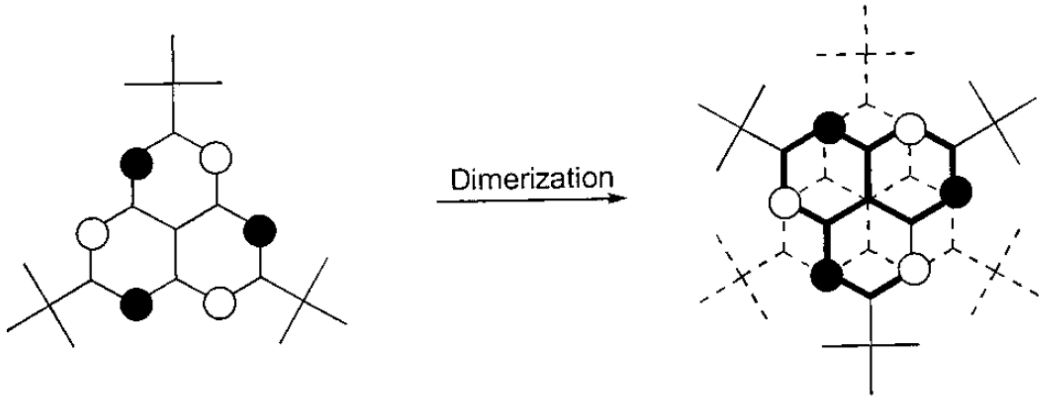


Figure 1 Experimentally studied stacked phenalenyl dimer. Koutentis, P. A.; Chen, Y.; Cao, Y.; Best, T. P.; Itkis, M. E.; Beer, L.; Oakley, R. T.; Cordes, A. W.; Brock, C. P.; Haddon, R. C. *J. Am. Chem. Soc.* 2001, *123*, 3864.

1. Which physical forces dominate the interaction of the phenalenyl-radical dimer? - What about 9b-azaphenalene? Which dimer is bound more strongly?
2. Why is only the X-ray structure of 2,5,8-^{t}Bu-phenalenyl-radical available, but not of the unsubstituted molecule?
3. Which computational levels would you choose to compute the interaction energy profile of 9b-azaphenalene? - Would you expect that the same methods are accurate for the phenalenyl stacked dimer?

Bonus 1: If you remove one electron from the phenalenyl-radical dimer (giving a doublet, cationic dimer) - do you expect the interaction energy to increase or to decrease?

Bonus 2: What do you expect is the spin state of the phenalenyl-radical dimer? How would you verify your prediction (experimentally and/or computationally)? Which external variable could play a role?

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The performance of electronic structure methods for reaction mechanisms

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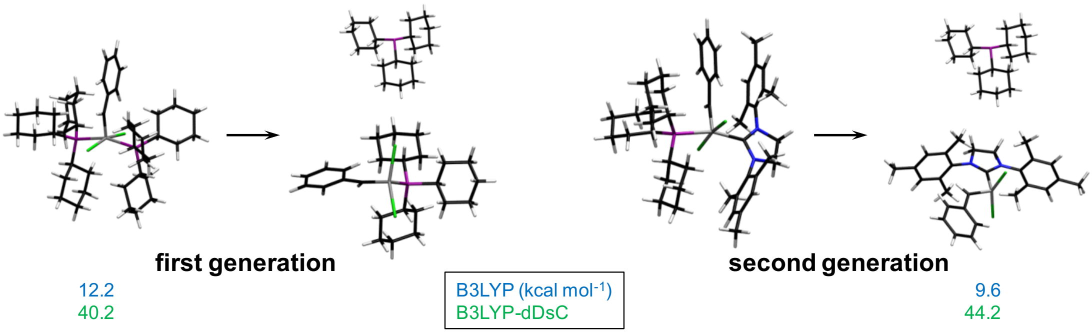

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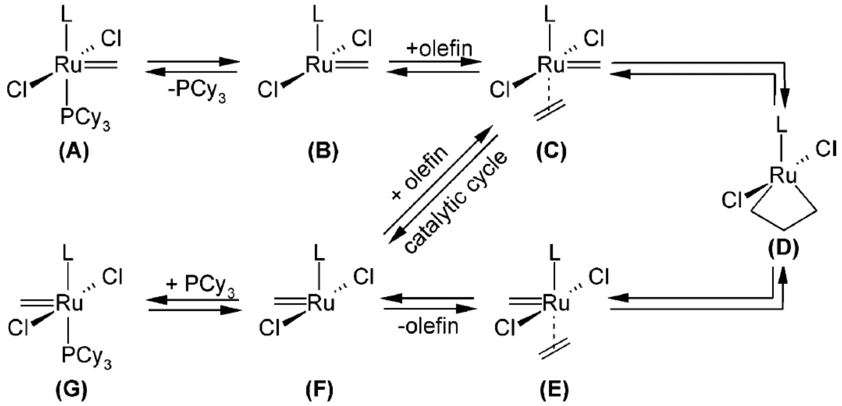
Scheme 1. Most Likely Mechanism for Olefin Metathesis by Grubbs-type Ruthenium Carbene Complexes



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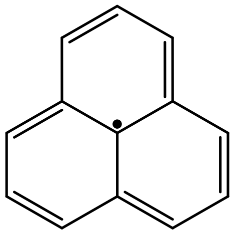
The ligand (L) differentiates first-generation and second generation of Grubbs catalysts. Changing the ligand from an organosphosphine (Grubbs-I) to an N-heterocyclic carbene (NHC, Grubbs-II) dramatically increases the reactivity. After considering Figure 1, answer the following questions:

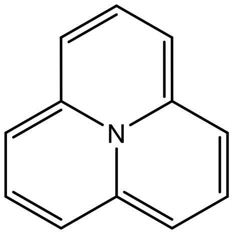
1. Can the increase in reactivity be attributed to a lower enthalpy of activation in Grubbs-II for the dissociation of the organophosphine ligand in the initiation step? Justify your answer and explain the computational data given in Figure 1
   For the bulky ligands dispersion interactions are important. Therefore, B3LYP is not reliable and only the B3LYP-dDsC values should be interpreted. According to these computations, the activation energy is higher in the second generation catalysts, excluding the hypothesis that the second generation catalysts are more active because of a facilitated initiation step.
2. Could you use CCSD(T) to verify your predictions?
   CCSD(T) is a computationally very expensive method and is therefore very difficult to apply to such big systems.
3. Could you use M06-2X?
   M06-2X captures a large part of the dispersion energy around equilibrium distances and is computationally approximately equally expensive as B3LYP-dDsC. Indeed, M06-2X would give reasonable results for the reactions in question.

Question 2
Hydrocarbon radicals: challenges and opportunities for experimental and computational chemistry

The phenalenyl radical is a prototypical open-shell graphene fragment, proposed for use in organic molecular electronics.
9b-azaphenalene is a closed-shell analogue of the phenalenyl radical.



Phenalenyl



9b-azaphenalene

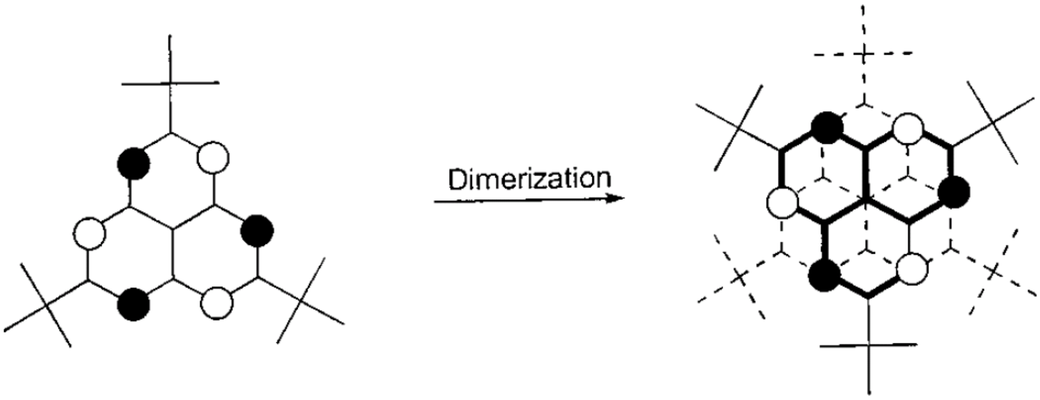


Figure 2 Experimentally studied stacked phenalenyl dimer. Koutentis, P. A.; Chen, Y.; Cao, Y.; Best, T. P.; Itkis, M. E.; Beer, L.; Oakley, R. T.; Cordes, A. W.; Brock, C. P.; Haddon, R. C. *J. Am. Chem. Soc.* 2001, *123*, 3864.

1. Which physical forces dominate the interaction of the phenalenyl-radical dimer? - What about 9b-azaphenalene? Which dimer is bound more strongly?
   The interaction energy of the stacked phenalenyl-radical dimer is composed of two important contributions: Dispersion and a weak multi-center covalent bond, whereas the dimer of 9b-azaphenalene is bound only by dispersion. Therefore, the phenalenyl-radical dimer is more strongly bound than the 9b-azaphenalene dimer.
2. Why is only the X-ray structure of 2,5,8-^{t}Bu-phenalenyl-radical available, but not of the unsubstituted molecule?
   The unsubsituted phenalenyl-radical dimerizes to give a σ-bound closed-shell dimer and not the more interesting (stacked) π-dimer. The bulky ^{t}Bu groups disfavor the σ-dimer much more than the π-dimer, for which the steric clash can be largely avoided, as indicated in Figure 1.
3. Which computational levels would you choose to compute the interaction energy profile of 9b-azaphenalene? - Would you expect that the same methods are accurate for the phenalenyl stacked dimer?
   9b-azaphenalene dimer is a dispersion bound complex. Therefore, numerous methods could be used to describe well the interaction energy profile, e.g., any kind of dispersion corrected DFT or MP2-type wave function method. CCSD(T) would be ideal, but at the limit of computational feasibility.
   All the mentioned methods are based on a single-reference, which is not a good approximation for the singlet- phenalenyl dimer at long-distance, where the triplet and singlet states are degenerate. Therefore, to obtain an accurate interaction energy profile for the singlet state, a multi-reference treatment is necessary, but since dispersion is equally important, perturbation

theory based dynamical correlation needs to be included; methods such as CASPT2 or MRMP2 are typical choices.

Bonus 1: If you remove one electron from the phenalenyl-radical dimer (giving a doublet, cationic dimer) - do you expect the interaction energy to increase or to decrease?

Even though one electron is removed from the multicenter-bonding orbital, the cation is bound more strongly than the neutral dimer, because the electrostatic and polarization interaction energy make up the partial loss of the weak covalent bond.

Bonus 2: What do you expect is the spin state of the phenalenyl-radical dimer? How would you verify your prediction (experimentally and/or computationally)? Which external variable could play a role?

Two radicals are expected to couple to a singlet state. However, since the covalent interaction is only weak, at elevated temperatures (T > 180 K) the thermal energy is enough to overcome the coupling. --It is not so clear to me if at the higher temperature only the spin-coupling is lost or the dimerization does not occur anymore and how this would be experimentally distinguished (as a weakly coupled triplet is essentially equivalent to two doublets for ESR) and I did not see any computations on the triplet--

Experimentally, ESR/EPR spectra or measuring the magnetic field strength of the sample (e.g., with SQUID) as a function of the temperature, gives direct information about the spin-state.

Computationally, the spin-state splitting (singlet-triplet gap) including thermal corrections to the dimerization energy are necessary to predict the spin-state.

Main sources

Tian, Y.-H.; Kertesz, M. *J. Am. Chem. Soc.*, *132*, 10648-10649. (computational study, see SI for the aza-derivative)

Small, D.; Zaitsev, V.; Jung, Y.; Rosokha, S. V.; Head-Gordon, M.; Kochi, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 13850-13858. („main“ study of the pi-dimer)

Small, D.; Rosokha, S. V.; Kochi, J. K.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 11261-11267. (sigma-dimerization, where the loss of aromaticity is discussed)