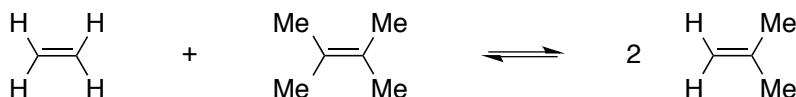
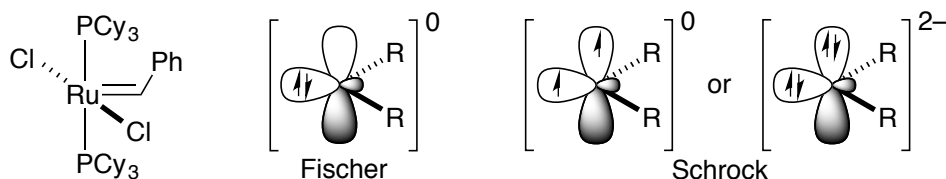


Created by Richard L. Lord, Grand Valley State University (lordri@gvsu.edu), Vanessa McCaffrey, Albion College (vmccaffrey@albion.edu), and Sabrina G. Sobel, Hofstra University (sabrina.g.sobel@hofstra.edu) and posted on VIPEr (www.ionicviper.org) on December 28, 2016. Copyright 2016. This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

1. A salt metathesis, or double replacement, reaction involves cations and anions being swapped in two compounds. The reaction below is an example of an olefin metathesis reaction. Define what is meant by olefin metathesis. Why is olefin metathesis an important reaction?



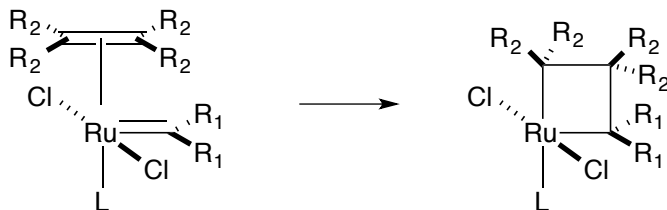
2. One of the most well-known catalysts for this transformation is the Grubbs catalyst that earned the Nobel prize in 2005 (shown below). This catalyst features a Ru=C bond that is also known as a carbene. When a carbene engages in double bonding with a metal center, it can be classified as a σ -donor and π -acceptor (Fischer carbene) or as a σ - and π -donor (Schrock carbene with neutral (left) and ionic (right) donor schemes shown). Based on the oxidation state and d -electron count of the Ru center in this complex, briefly explain whether you think this is a Fischer- or Schrock-type carbene.



3. The Ru complex in problem 2 is known as the first-generation Grubbs catalyst. Count electrons for this complex assuming the carbene is Fischer-type, then redo the count assuming it is a Schrock-type carbene. Does your assumption about the type of carbene change your conclusion about the overall electron count?

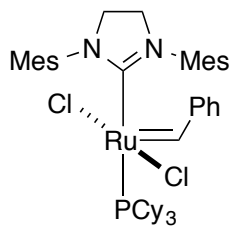
4. The first mechanistic step is proposed to be phosphine exchange with an incoming olefin. This reaction could take place by associative (I_a) or dissociative (I_d) interchange. Predict whether the I_a or I_d mechanism would be favored based on electron counting arguments.

5. An important intermediate in this mechanism is the ruthenacyclobutane intermediate. Push arrows to show how this species forms, and explain how it facilitates the reaction shown in 1.



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6. A class of carbenes related to Fischer-type carbenes, but which are much weaker π -acceptors (and therefore typically only have a Ru–C single bond), are N-heterocyclic carbenes (NHCs). The second-generation Grubbs catalyst that is shown below replaces one of the phosphines with a NHC ligand. How does the electron donation / formal charge of this ligand compare to the Ru=C carbene present in both this and the first-generation catalyst?



7. Based on your answer to 5, does your prediction of associative/dissociative olefin binding based on electron counting change for the second-generation catalyst?

8. Where do you think a NHC ligand would fall on the *trans* effect series relative to a phosphine? Briefly justify your answer based on a comparison of the σ -donor and π -acceptor character of both ligand classes.