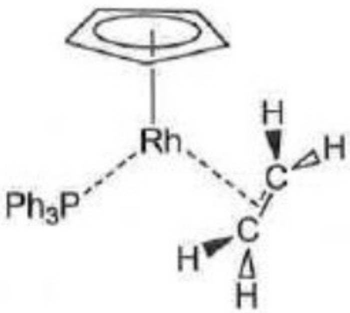
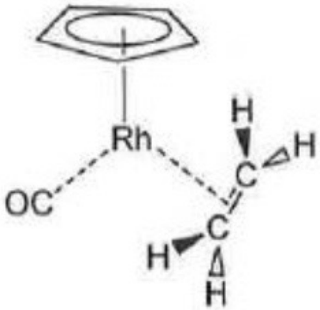
In the following molecules, which alkene ligand will rotate most rapidly? Why?

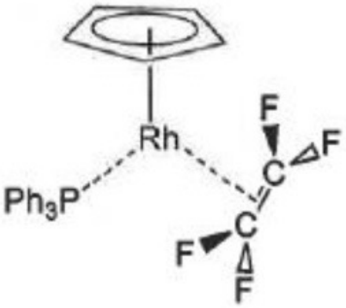


A

2

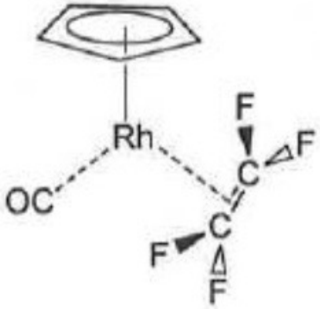


B



C

4



D

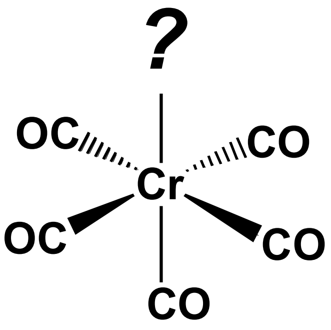
3

The more σ bonding and the less π back-bonding bonding the more will rotate (less strong M-C)

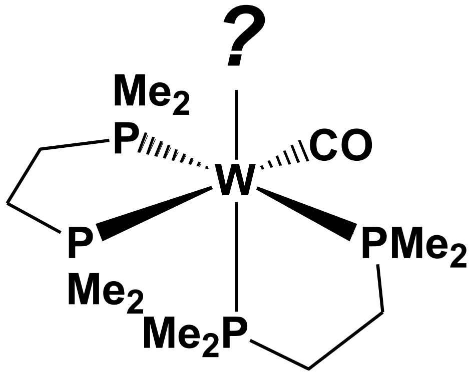
PPh3 increase back-donation in A and C, the Fluorinated olefine will increase back-donation in C and D

Problem: To which of the following (each with a single open coordination site) will **trifluoroethylene** bond to the most strongly? Why?

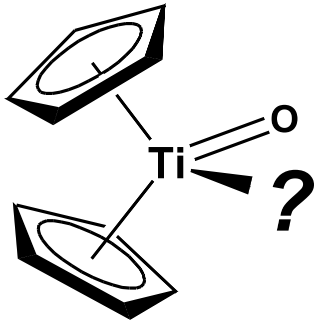
a)

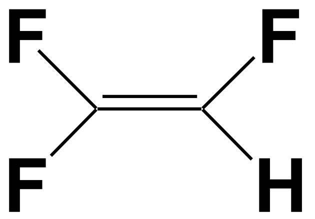


b)



c)



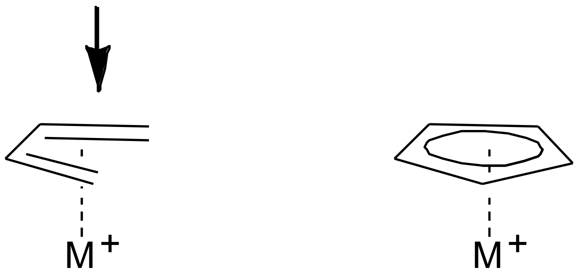


This electron-deficient alkene will favor π-backbonding and will coordinate the strongest to the most electron-rich metal, which is the W complex with the alkylated phosphine ligands. Third-row metals also usually have the strongest M-L bonding.

The Davies-Green-Mingos Rules: allow predictions of the direction of nucleophilic attack at 18-electron cationic metal complexes.

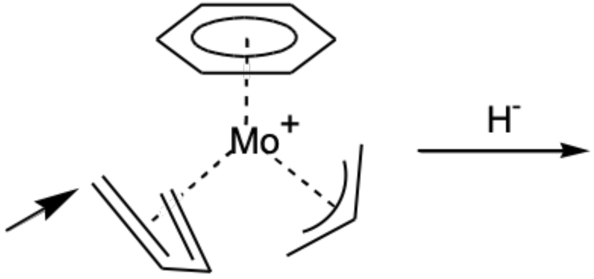
Rule 1. Nucleophilic attack occurs preferentially at EVEN coordinated polyenes (polyenes before polyenyls)

Apply rule 1 before rule 2

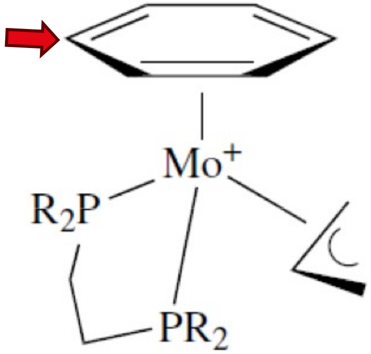


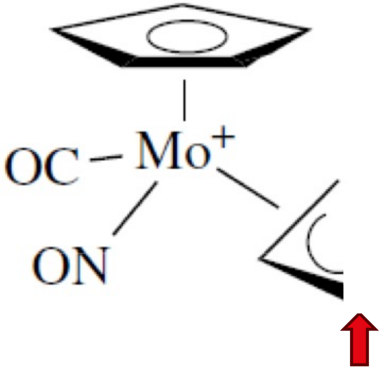
Rule 2. Nucleophilic attack occurs preferentially at OPEN coordinated polyenes before closed.

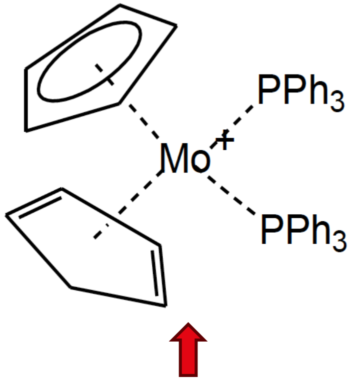
Rule 3. For EVEN OPEN polyenes, nucleophilic attack always occurs at the terminal carbon atom, For ODD OPEN polyenyls, attack at the terminal carbon occurs only if L_nM^+ is strongly electron withdrawing.



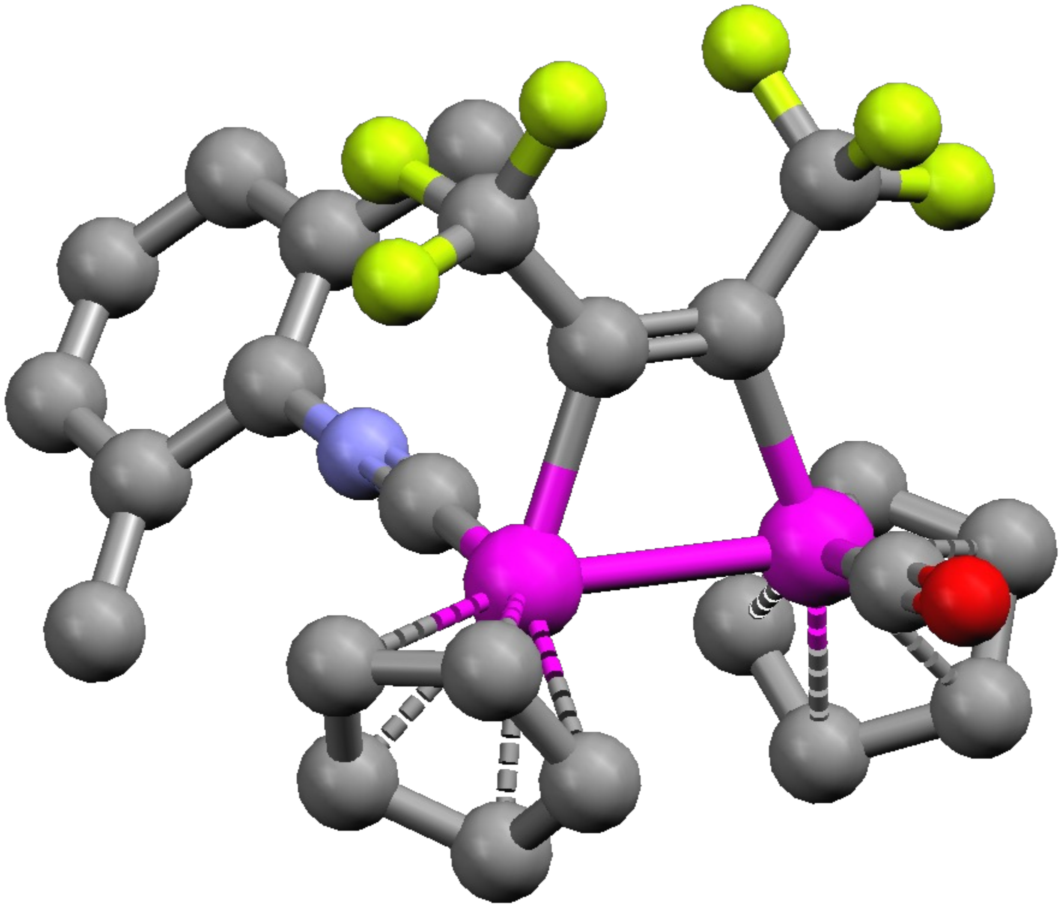
Problem: Predict nucleophilic attack using The Davies-Green-Mingos Rules







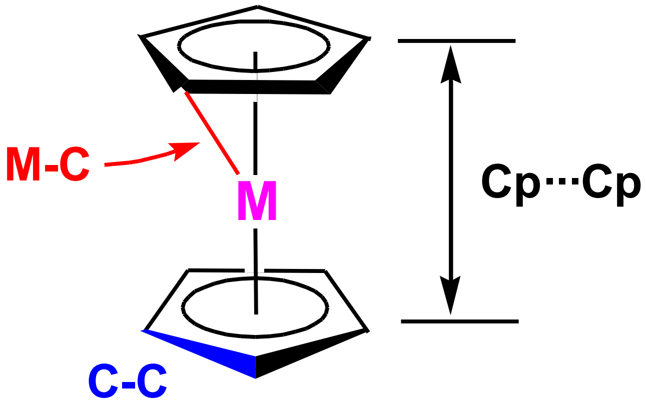
Problem: The $Cp_2Rh_2[\mu\text{-}(CF_3C{\equiv}CCF_3)](CO)(C{\equiv}N\text{-}R)$ complex shown below has a Rh-Rh bond distance of 2.67 Å, strongly indicating a covalent bond between the rhodium atoms. How would you electron count this complex to accommodate a Rh-Rh covalent bond?



The electron-withdrawing CF_3 groups will make the alkyne a good π-acceptor – good enough to oxidize each Rh center by one e- to put them in the Rh(II) oxidation state and make a reduced dianionic alkyne that now has a C=C:

Rh(II)	d^7
$[CF_3C{=}CCF_3]^{2-}$	2e-
Cp^-	6e-
L (CO or CNR)	2e-
Rh-Rh	1e-
Total:	18e-

Structural Features

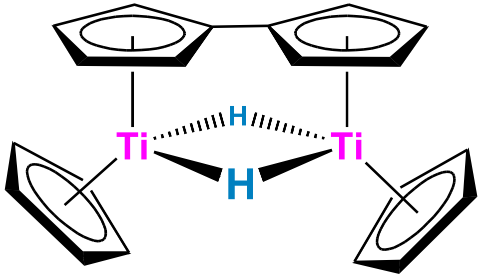


M	M-C	Cp…Cp	C-C
Fe	2.04	3.29	1.42
$[Fe]^+$	2.07	3.40	1.40
Ru	2.19	3.64	1.43
Os	2.19	3.61	1.45
Co	2.10	3.44	1.41
$[Co]^+$	2.03	3.24	1.42
Ni	2.18	3.63	1.41

The changes in the neutral Fe, Co, Ni metallocenes are a direct result of going from 18e- (Fe) to 19e- (Co) to 20e- (Ni) counts. The extra electrons for the Co and Ni complexes are going into M-Cp antibonding orbitals, which are delocalized and progressively weaken the M-Cp bonding, leading to the increase in bond distances. This even though the metal's covalent radius is *decreasing* as going from Fe to Ni.

Problem: Explain why the Fe-C distance *lengthens* for $[Cp_2Fe]^+$,
while the Co-C distance *shortens* for $[Cp_2Co]^+$.

The Fe-C distance increases since you are removing a Fe-Cp bonding electron, which weakens the Fe-Cp bonding. Due to the symmetry of the Cp rings, all the Fe d^6 orbitals have some sort of bonding interaction with the Cp ring. The highest occupied Fe orbitals are π-backbonding into empty Cp π* orbitals. The electron removed from Cp_2Co to make $[Cp_2Co]^+$ is in an antibonding orbital (19e-), so that strengthens the Co-Cp bonding.



Problem: Electron-count this Ti_2 complex and define if diamagnetic or paramagnetic How the complex should be drawn after discovering that is diamagnetic?

The complex is paramagnetic as drawn.
Since is diamagnetic should be drawn with a Ti-Ti bond

Ti(3+)	d^1
$2Cp^-$	12e-
$2\mu\text{-}H^-$	2e-
	15e-
Ti-Ti	1e-
Total:	16e-

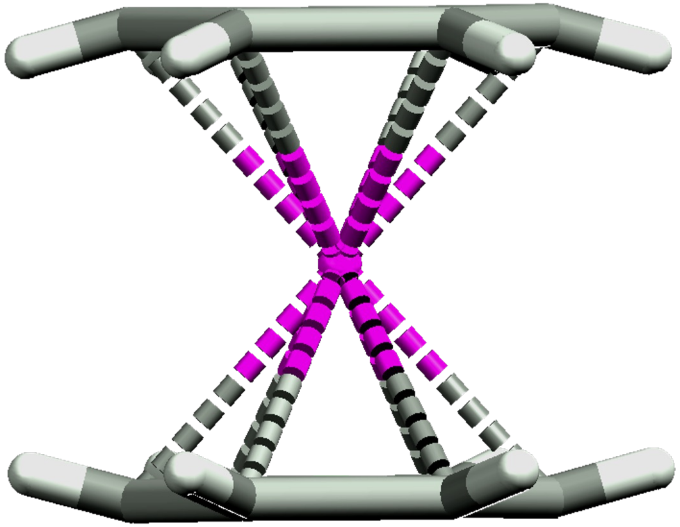
Diamagnetic with a covalent Ti-Ti single bond.

π-Backbonding

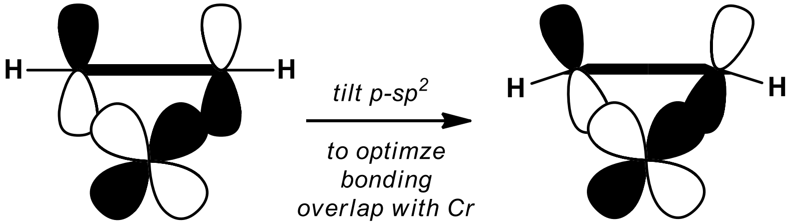
π-backdonation plays a relatively important role in arene bonding and chemistry. Arenes tend to favor metals in low oxidation states and often generate surprisingly stable complexes. $Cr(C_6H_6)_2$, for example, is kinetically inert to most substitution reactions, no doubt due to its 18 e- configuration, but also due to the mix of π-bonding and backbonding.

Remember that CO is far, far stronger π-backbonding ligand.

Problem: The crystal structure of $[Cr(C_6H_6)_2]^+$ clearly shows that the hydrogen atoms on the benzene distinctly lean in towards the metal center. Explain why.

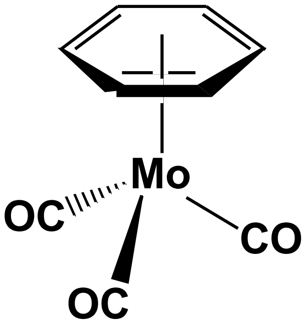


In order to get good overlap with the contracted Cr d-orbitals, the p-orbitals on the benzene ring have to cant or tilt towards the Cr center. When this happens, the sp^2-hybridized C-H bond also has to tilt to follow the reorientation of the pure carbon p-orbital to get better overlap with the Cr orbitals. This is shown schematically below showing just two C-H carbons on the arene interacting with the Cr:

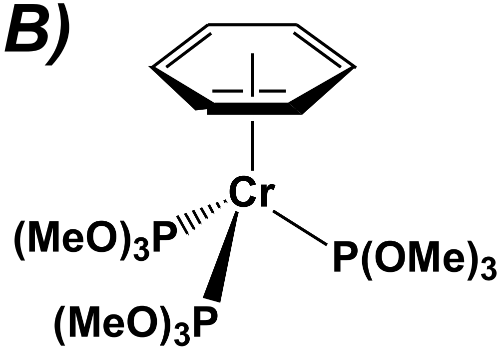


Problem: In which of the following complexes should the η^6-benzene ligand coordinate the strongest? Why??

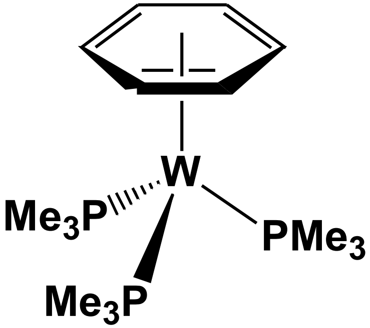
A)



B)



C)



π-backbonding is fairly important to stabilize the arene-metal bonding, so the most electron-rich metal should π-backbond the most to the arene and have the strongest overall bonding. Third-row metals also form the strongest M-L bonds.