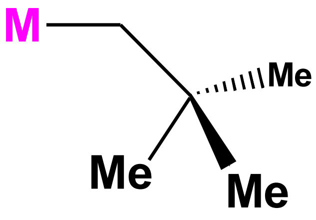
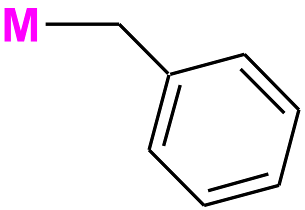
In order to prepare stable M-alkyl complexes one generally needs to stay away from alkyls with β-hydrogens (or avoid metals with empty coordination sites). Some common ligands used to <u>avoid</u> β-hydride elimination reactions are shown below.

$M—CH_3$

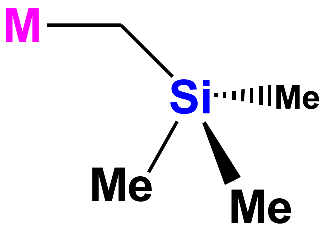
methyl



neopentyl



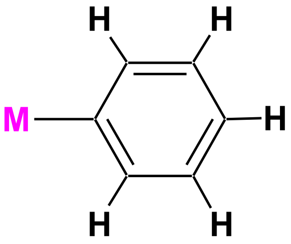
benzyl



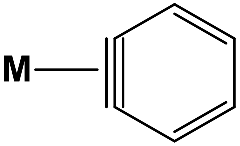
trimethylsilylmethyl

Problems:

a) Why doesn't a 16e- M-phenyl do a β-hydride elimination?

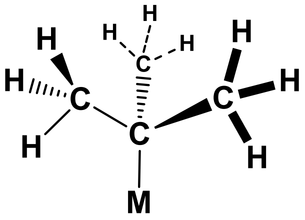


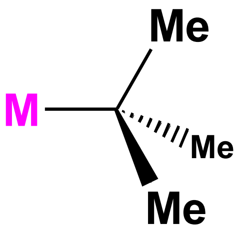
Because it generates a high-energy, thermodynamically unstable benzyne:



b) Would a 16 e- M-(*t*-butyl) complex be stable or not?

Extremely reactive to β-hydride eliminations due to the 9 β-H's present. At least 3 C-H bonds are in close contact with the metal center.





3) Alkene Insertion:

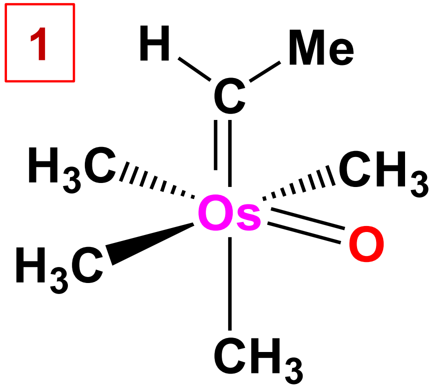
This is the reverse of β-hydride elimination (see earlier), often reversible, and is a crucial step in the polymerisation of alkene (see earlier).

Problem: **Based on DFT calculations, which complex is more electron-rich at the metal: $[W(CH_3)_7]^-$ or $W(CO)_6$?? Why?**

Although $[W(CH_3)_7]^-$ is formally W(+6) d^0, the anionic methyl groups are very strong σ-donors and will donate most of their negative charge (electron-density) to the W(+6) making the true positive charge on the W center far less than +6. DFT calculations on each complex demonstrate that the charge on the W(+6) atom in $[W(CH_3)_7]^-$ is +0.93, the same as +0.93 calculated for $W(CO)_6$, which is formally W(0), (d6) but electron density is delocalized into the CO orbitals.

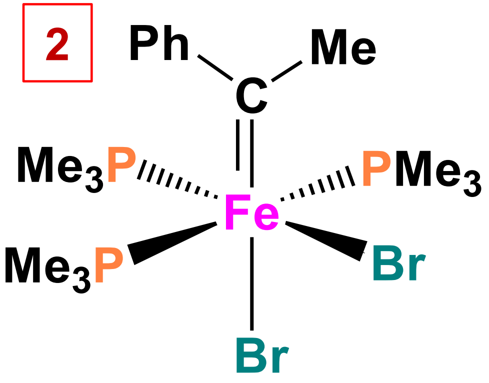
Problem: Order the following M=C complexes from the one with the highest $M{=}CR_2$ rotational barrier to the lowest. What factors affect the M=C rotational barrier? Identify each complex as either a **Fisher carbene** or a **Schrock alkylidene**.

a) 1



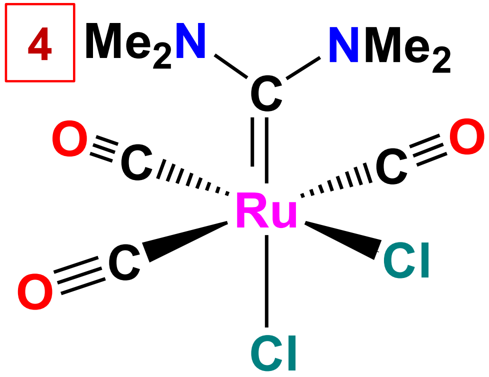
Os(+8), d^0: Schrock Alkylidene

b) 2



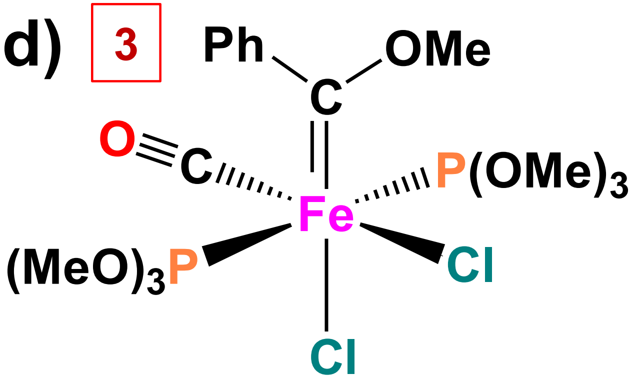
Fe(+2), d^6: Fisher carbene; most electron-rich metal with most π-backbonding to carbene. Ph is weak p-donator on carbene.

c) 4



Fe(+2), d^6: Fisher carbene; most electron-deficient; least π-backbonding to carbene. Strongest π-donors on carbene.

d) 3

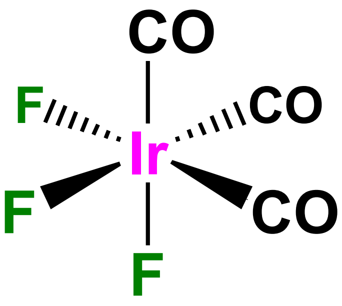


Fe(+2), d^6: Fisher carbene; less electron-rich metal with less π-backbonding to carbene. More π-donating groups on carbene

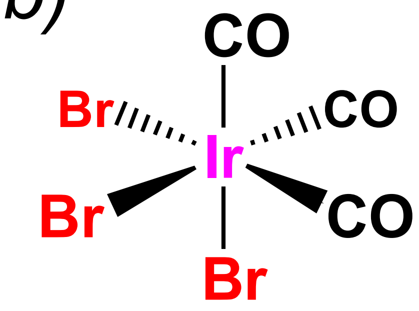
Problem: Which of the following metal carbonyl compounds will have the highest νCO stretching frequency in the IR? Why? Will this be the most electron-rich or deficient compound?

Fluorides (F^-) are very electronegative and very poor donors to all but metals in very high oxidation states. Most of the negative charge will stay localized on the F^- ligands resulting in a higher positive charge on the Ir(+3) center. This will contract and lower the energy of the Ir d-orbitals resulting in less π-back-bonding to the CO's

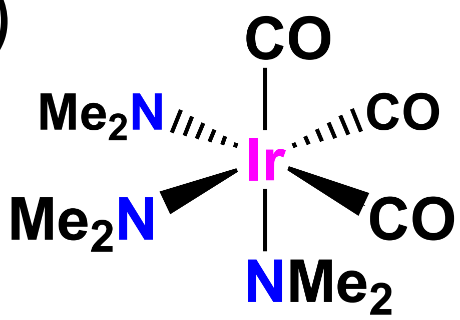
a)



b)



c)



The HIGHEST CO stretching frequency refers to the most electron-deficient (poor) complex that has the worst donor ligands, highest positive charge, and/or most electronegative metal centers.

Problem: Order the following phosphines from strongest to weakest σ donor:

$P(OEt)_3$ PPh_3 PPr_3 PCl_3 $PPh(OMe)_2$

The strongest σ-donor has the most alkyl groups, which are considered to be donating to the phosphorus center (actually the least electron-withdrawing). The more electronegative (electron-withdrawing) groups attached to the P center, the more positive charge on the P center and the more contracted and lower the energy of the P lone pair. This makes it a poorer σ-donating group.

$PPr_3 > PPh_3 > PPh(OMe)_2 > P(OEt)_3 > PCl_3$

Pr= propyl