1. For Vaska's complex, $[IrCl(CO)(PPh_3)_2]$ which among the given activities will decrease the CO stretching frequency of the coordinated CO ligand from 1967 cm^{-1} to lower value(s)? Justify your answer.

(i) Replacing both PPh_3 by PMe_3

(ii) Oxidative addition by MeI

(iii) Replacing Cl^- by CH_3^-

(iv) Replacing Cl^- by CH3CN (cationic complex)

The correct options are (i) and (iii) where electron density on the metal gets increased by the activity.

2. 18. (i) The IR spectra of the following 18-electron complexes, $[Ir(CO)_6]^{3+}$ (X), $[Ir(CO)_3]^{3-}$ (Y), and $Ir_4(CO)_{12}$ (Z), were measured and compared with free CO. Match the complexes with the correct CO stretching frequency (i) to (iv): (i) 2060 and 2020 cm^{-1}; (ii) 1642 cm^{-1}; (iii) 2143 cm^{-1};(iv) 2254 cm^{-1}. Note that the text of this exercise has been changed !!

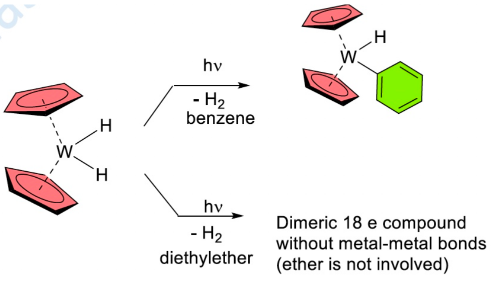
Free CO (iii)

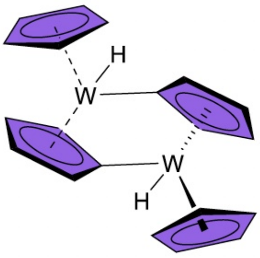
X (iv) only donation increases C-O bonding order and frequency

Y (ii) most electron-rich metal

Z(i) electron-rich metal with multiple binding modes (bridging and terminal)

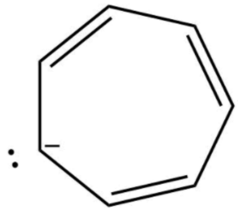
3. UV irradiation of the given tungsten hydride in presence of benzene results in the reductive elimination of H_2 and oxidative addition of benzene leading to the formation a new compound as shown. In the presence of diethylether as solvent, a similar reaction happens resulting in the formation of a dimeric 18 e compound without metal-metal bonds. Predict the structure of this new compound.





4. Draw the structures of the 3 complexes and clearly indicate the hapticity (η) of the ring.

Consider the structure of the cycloheptatrienyl anion.



cycloheptatrienyl anion

$[Co(C_7H_7)(CO)_3]$ $[Co(C_7H_7)(CO)_2]$ $[Co(C_7H_7)(CO)]$

$C7H7^-$: cycloheptatrienyl four possible binding modes η1 η3 η5 η7

1) Co(I) d8 NEV 8+6 + η3 C7H7 =18
2) Co(I) d8 NEV 8+4 + η5 C7H7 =18
3) Co(I)d8 NEV 8+2 + η7 C7H7 =18

5. Draw the product of the following reaction

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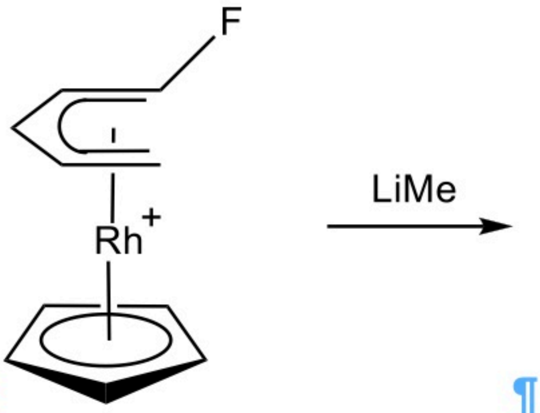

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Open, terminal carbon the one with fluoride more positively charged

6. For each of the following pairs of complexes, which will have the ***lowest*** average CO infrared stretching frequency? Circle your choice and clearly explain your reasoning.

For each of the following pairs of complexes, which will have the ***lowest*** average CO infrared stretching frequency? Circle your choice and clearly explain your reasoning.

a) $[Cp_2Sc(OMe)(CO)]$ or [✓ $[Cp_2Ti(CO)_2]$]

b) [✓ $[IrI_3(CO)_3]$] or $[CoF_3(CO)_3]$

c) $[CpRu(CO)_3]^+$ or [✓ $CpOs(NMe_2)(CO)_2]$]

The *most* electron-rich metal will π-backbond the *most* with the CO ligands and have the *lowest* CO stretching frequency

a)Sc(+3) is a d^0 atom. As such it formally has no *d* electrons to π-backbond to the carbonyl ligands. Ti(+2) on the other hand is a d^2 metal and as such (for titanium which likes the +4 oxidation state) pretty electron rich relative to the Sc complex.

b) The Co atom has three poorly donating electronegative fluoride anions, that are not donating as much electron density to the metal as the iodide anions in the Ir complex. The Co is also more electronegative, and as such, will hold on to it's d electrons more strongly and not want to donate them to the CO ligands.

c) The Ru atom has poorer donating ligands and is more electronegative. All of these make it less electron-rich or willing to share it's electron density via π-backbonding to the CO ligand.