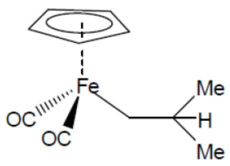
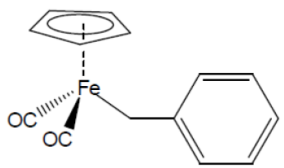
Exercises (I)

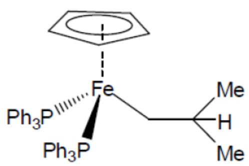
Draw the β-elimination product for A – D



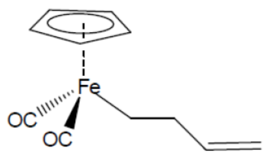
A



B



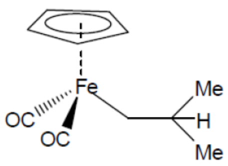
C



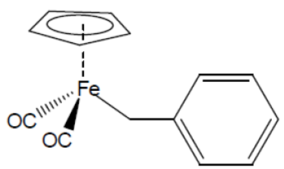
D

Exercises (I)

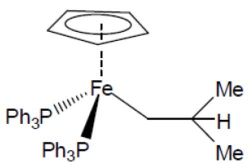
Fe(II)
d6
18 ev



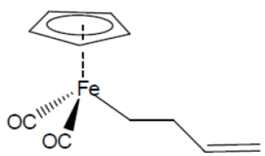
A



B

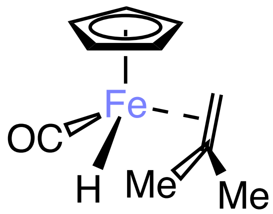


C



D

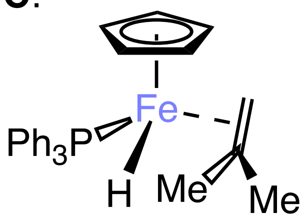
A:



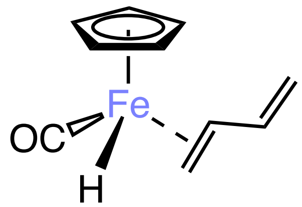
B:

(no beta-proton to eliminate)

C:



D:



Which of the following can undergo oxidative addition?

cis-$[RhI_2(CO)_2]^-$ *cis*-$[Zr(Cp^*)_2(Me)(Cl)]$

($Cp^* = \eta^5\text{-}C_5Me_5$)

Which of the following can undergo oxidative addition?

cis-$[RhI_2(CO)_2]^-$

cis-$[Zr(Cp^*)_2(Me)(Cl)]$

($Cp^* = \eta^5$-C_5Me_5)

Rh(I) d8 16 EV can undergo OA

Zr(IV) d0 16 EV cannot undergo OA

can undergo OA

cannot undergo OA

Which of the following will be **more** reactive towards oxidative addition?

$[Rh(PPh_3)_3Cl]$ *trans*-$[Rh(PPh_3)_2(PF_3)Cl]$

Which of the following will be **more** reactive towards oxidative addition?

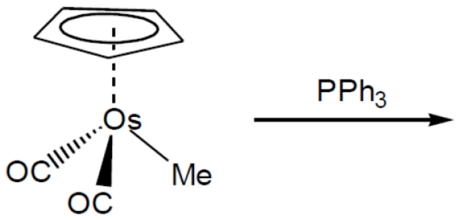
$[Rh(PPh_3)_3Cl]$ *trans*-$[Rh(PPh_3)_2(PF_3)Cl]$

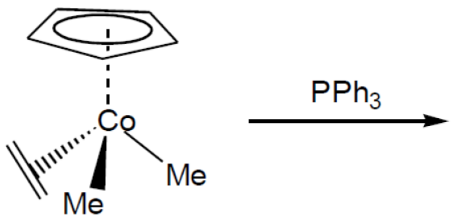
Rh(I) +(16EV)

Rh(I) +16 (EV)

PF3 less donating than PPh3 (F electronegative)
The metal center is less electron-rich

Predict the product of the reaction:



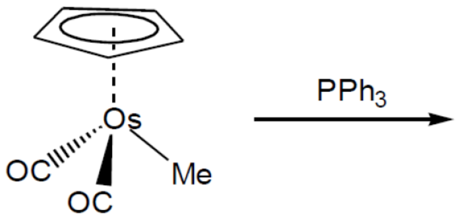


Solution Exercises (IV)

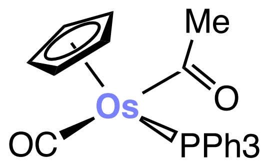
Predict the product of the reacti

Os(II)
d6
EV 18

Os(II)
d6
EV 18

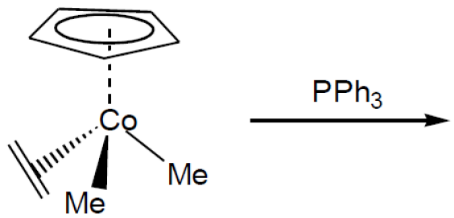


$[CpOs(CO)(PPh_3)(COMe)]$

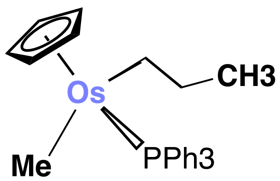


MI + L association

Co(III)
d6
EV 18



$[CpCo(PPh_3)(Me)(CH_2CH_2CH_3)]$



Predict the product from the following reaction:

$Fe(\eta^5\text{-}C5H5)(CO)_2CH_3 + PPh_3$

[Fe(η5-C5H5)(CO)(PPh3)(COCH3)]

Fe(II) d6
EV18

Which of the following is **least** likely to undergo reductive elimination?

cis- $[Rh(CO)_2(I)3(COMe)]^-$

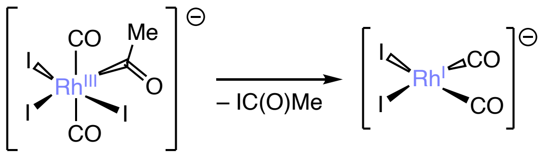
cis-$[Pt(P^iPr_3)_2(H)_2]$

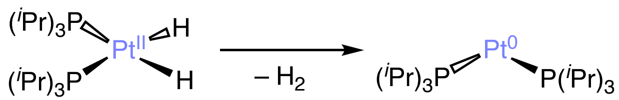
cis-$[Nb(\eta\text{-}C_5H_5)_2(H)(\eta\text{-}C_2H_4)]$

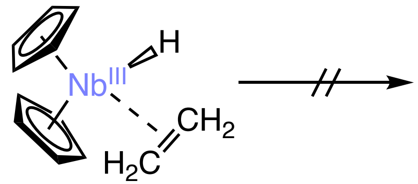
Exercises (VI)

Which of the following is **least** likely to undergo reductive elimination?

cis- [$Rh(CO)_2(I)3(COMe)]^-$ cis-$[Pt(P^iPr_3)_2(H)_2]$ *cis*-$[Nb(\eta\text{-}C_5H_5)_2(H)(\eta\text{-}C_2H_4)]$







18 electrons Rh(III) Eliminates ICOMe

To yield a 16 e- square planare d^8 Rh(I)

Favoured

Pt(II) eliminates H_2
To give Pt(0)
We go from 16 EV to 14 EV
Less favored

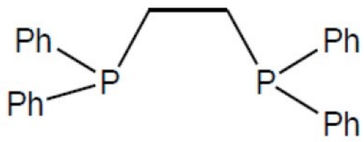
Nothing to eliminate

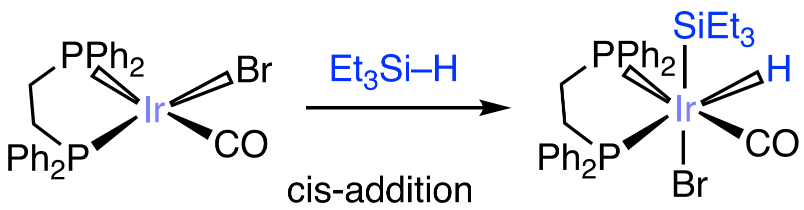
Nb(III) d^2 ER not favored

Exercises (VII)

Draw the products of the following oxidative addition reaction.

$$[(dppe)Ir(CO)Br] + Et_3Si\text{-}H \rightarrow$$

dppe = 

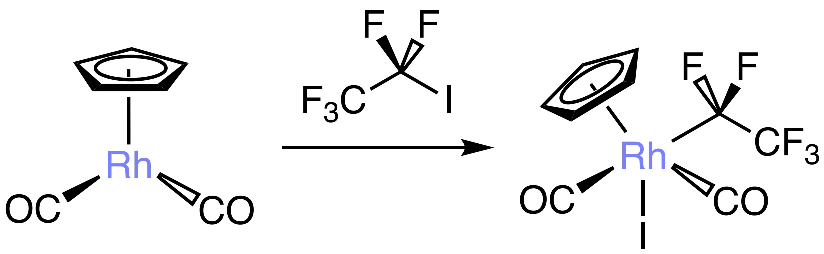


Ir(I)
d8 , EV 16

Ir(III)
d6 , EV 18

Draw the product of the following oxidative addition reaction.

$$[CpRh(CO)_2] \;+\; CF_3CF_2I \rightarrow$$



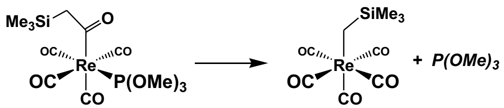
Exercises (IX)

1. Classify the following reactions as oxidative addition, reductive elimination, migratory insertion, elimination, β-hydride elimination, ligand substitution, ligand dissociation, ligand addition, oxidative coupling, hydrogenolysis (i.e., 4-center concerted H_2 activation & transfer), etc. There may be more than one step and that the equations are not necessarily balanced or completely list all possible products. If there is more than one step to label, make sure you list the steps in the correct order ***if*** the order is important. NO discussion or justification is necessary.

a) $[Rh(CH_2CH_2CH_2CH_3)(dmpe)(PMe_3)] \longrightarrow [Rh(H)(dmpe)(PMe_3)] + CH_2{=}CH{-}CH_2CH_3$

b) $[Cp_2Zr(PMe_3)_2] + H_2 \longrightarrow [Cp_2ZrH_2(PMe_3)] + PMe_3$

c)



d) $[Mn(SiMe_3)(dppe)(N{\equiv}CCH_3)_3] + H_2 \longrightarrow [MnH(dppe)(N{\equiv}CCH_3)_3] + SiHMe_3$

e) $[Re({=}CH_2)(Ph)(CO)_4] + PMe_3 \longrightarrow [Re(CH_2Ph)(CO)_4(PMe_3)]$ (CH_2 = neutral carbene)

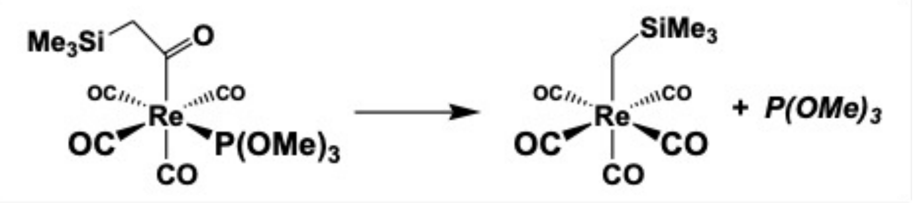
f) $[CpRh(CO)(PMe_3)] + C_6H_6 \xrightarrow[h\nu]{} [CpRh(C_6H_5)(H)(PMe_3)] + CO$

1. Classify the following reactions as oxidative addition, reductive elimination, migratory insertion, elimination, β-hydride elimination, ligand substitution, ligand dissociation, ligand addition, oxidative coupling, hydrogenolysis (i.e., 4-center concerted H_2 activation & transfer), etc. There may be more than one step and that the equations are not necessarily balanced or completely list all possible products. If there is more than one step to label, make sure you list the steps in the correct order ***if*** the order is important. NO discussion or justification is necessary.

a) $[Rh(CH_2CH_2CH_2CH_3)(dmpe)(PMe_3)] \longrightarrow [Rh(H)(dmpe)(PMe_3)] + CH_2{=}CH\text{-}CH_2CH_3$

b) $[Cp_2Zr(PMe_3)_2] + H_2 \longrightarrow [Cp_2ZrH_2(PMe_3)] + PMe_3$

c)



d) $[Mn(SiMe_3)(dppe)(N{\equiv}CCH_3)_3] + H_2 \longrightarrow [MnH(dppe)(N{\equiv}CCH_3)_3] + SiHMe_3$

e) $[Re(=CH_2)(Ph)(CO)_4] + PMe_3 \longrightarrow [Re(CH_2Ph)(CO)_4(PMe_3)]$ (CH_2 = neutral carbene)

f) $[CpRh(CO)(PMe_3)] + C_6H_6 \xrightarrow[h\nu]{} [CpRh(C_6H_5)(H)(PMe_3)] + CO$

a) [Rh($CH_2CH_2CH_2CH_3$)(dmpe)(PMe_3)] ⟶ [Rh(H)(dmpe)(PMe_3)] + CH_2=CH-CH_2CH_3

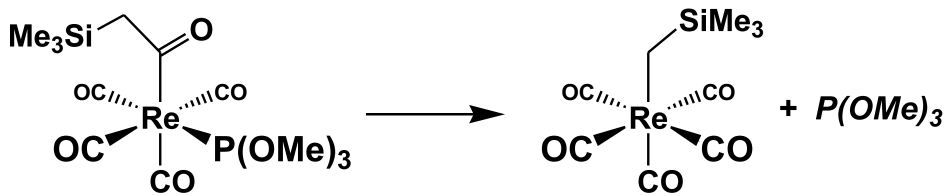
β-hydride elimination

b) $Cp_2Zr(PMe_3)_2$ + H_2 ⟶ [$Cp_2Zr(H)_2(PMe_3)$] +PMe_3

1) ligand dissociation (PMe_3) **2) H_2 oxidative addition**

(The Zr(+2) is an 18e- d^2 center and can do an oxidative addition with H_2, but not until you dissociate one of the PMe_3 ligands to generate an empty orbital on the Zr so the H_2 can coordinate.)

c)



1) $P(OMe)_3$ ligand dissociation

2) carbonyl elimination

Re(I) d6
18ev

d) $Mn(SiMe_3)(dppe)(N{\equiv}CCH_3)_3 + H_2 \longrightarrow MnH(dppe)(N{\equiv}CCH_3)_3 + SiHMe_3$

The Mn is an 18e- d^6 center, so you must dissociate a ligand in order to do the H_2 oxidative addition

1) $N{\equiv}CCH_3$ ligand dissociation **2) H_2 oxidative addition**

3) reductive elimination of $SiHMe_3$ **4) $N{\equiv}CCH_3$ ligand addition**

Re (I) ,18ev

e) $Re(=CH_2)(Ph)(CO)_4 + PMe_3 \longrightarrow Re(CH_2Ph)(CO)_4(PMe_3)$ (CH_2 = neutral carbene)

Re (I) ,18ev

1) migratory insertion (carbene & Ph^- group) **2) PMe_3 ligand addition**

f) $CpRh(CO)(PMe_3) + C_6H_6 \xrightarrow{h\nu} CpRh(C_6H_5)(H)(PMe_3) + CO$

Rh(I)
d8 , 18 ev

1) CO (or PMe_3) ligand dissociation **2) oxidative addition of benzene C-H bond**

(order is important, you must first have a ligand dissociate to make an unsaturated 16e- center that the benzene C-H bond can coordinate to in order to initiate the oxidative addition)

2. For each of the following pairs of metal complexes, circle the one that will ***most readily*** do an **oxidative addition** to the substrate shown. No discussion is necessary.

a) H_2: $Cp_2Nb(NMe)(CH_3)$ - or - $[Rh(CO)_2I_2]^-$

Nb(V)d0 18e

Rh(I)d8 16e

Nb complex is d^0 and can't do an oxidative addition

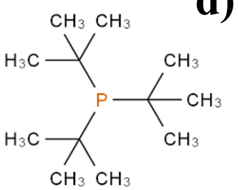
b) Cl_2: $Mo(CO)_3(PMe_3)_3$ - or - $Mo(CO)_3\{P(OMe)_3\}_3$ *this is the most e- rich complex*

c) CH_3I: $IrH(CO)(PMe_3)_2$ - or - $RhCl(CO)_3$ *this is the most e- rich complex*

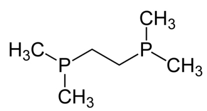
Ir(I)d8 16e

Rh(I)d8 16e

d) CH_3I: $Rh(I)(CO)\{P(\textit{tert}\text{-butyl})_3\}_2$ - or - $[Re(CO)_3(dmpe)]^-$ *the $P(t\text{-butyl})_3$ is too bulky*



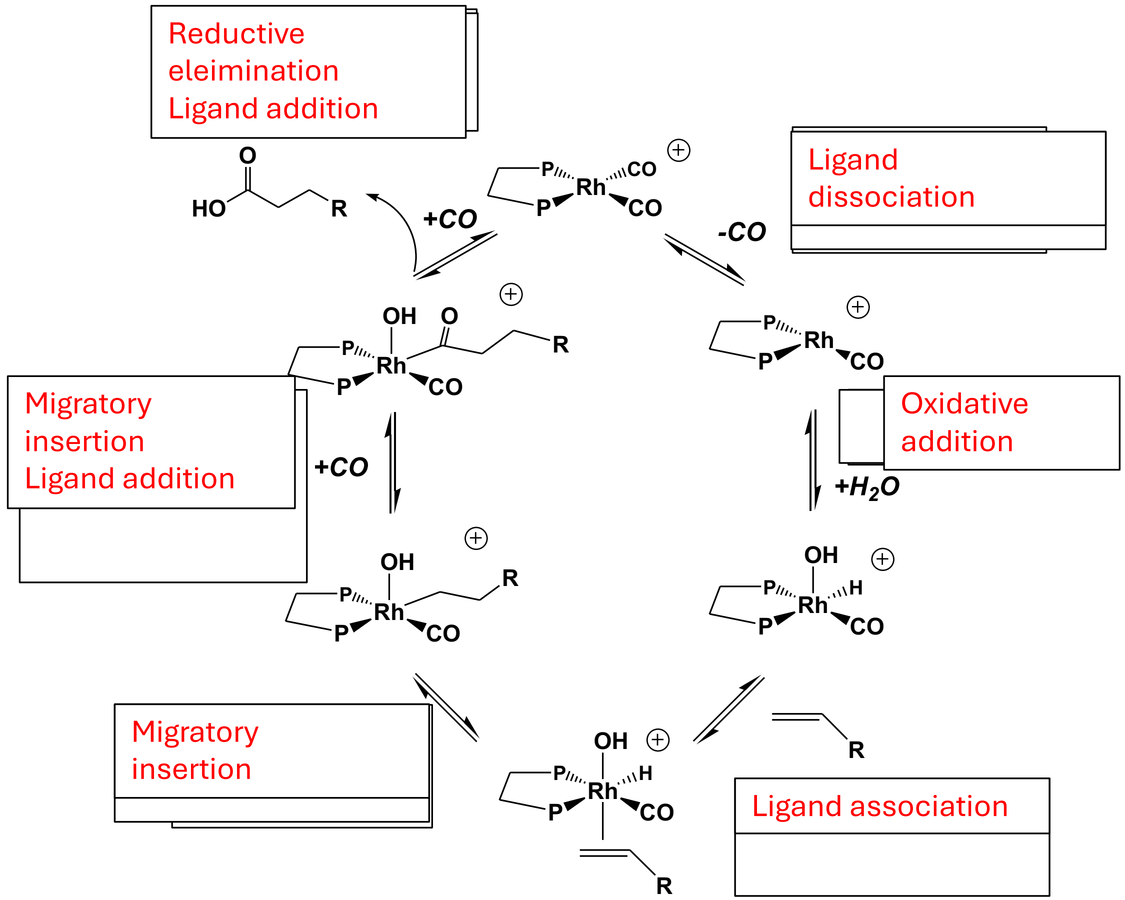
Rh(I)d8 16e



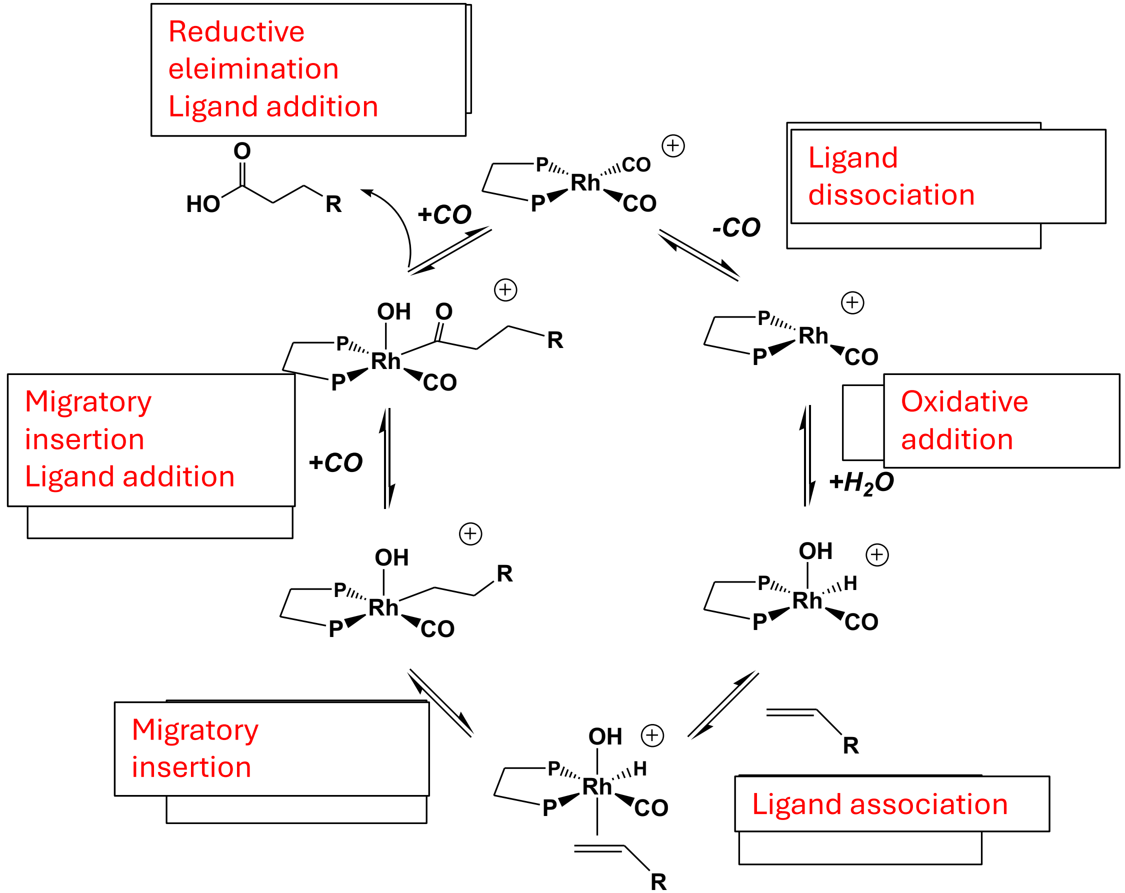
Re(I)d6 16e

Exercises (XI)

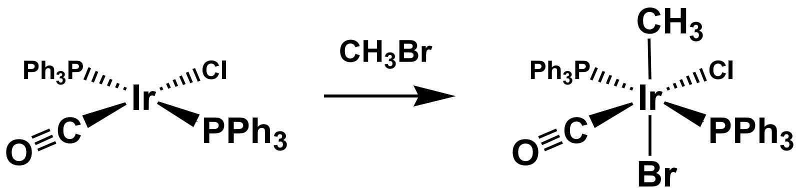
Use the boxes to label the following steps to identify what is going on in the following catalytic cycle



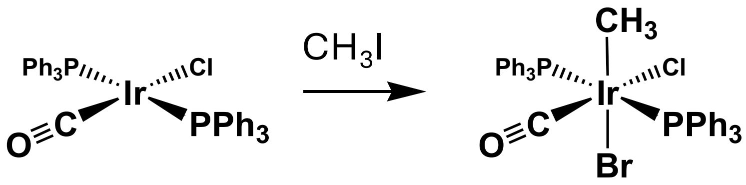
Use the boxes to label the following steps to identify what is going on in the following catalytic cycle



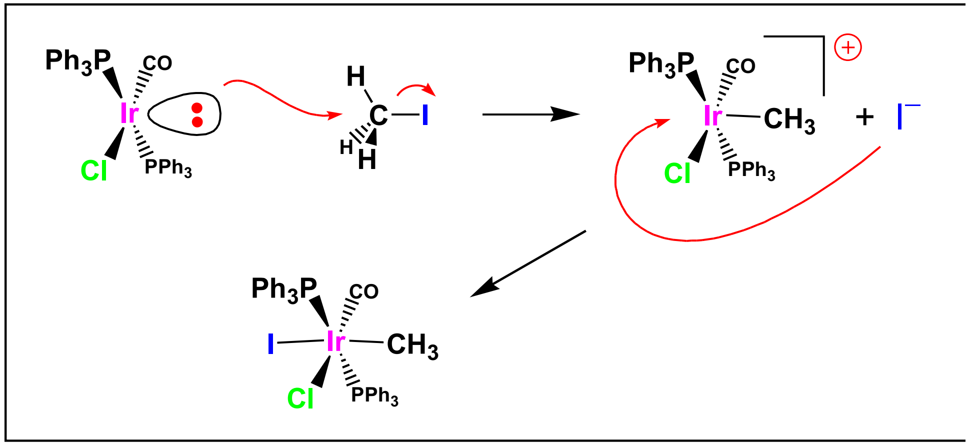
Explain how the methyl and bromide ligands in the following reaction end up in the indicated positions. Use diagrams to clearly illustrate your vivid description of this process.



4. Explain how the methyl and bromide ligands in the following reaction end up in the indicated positions. Use diagrams to clearly illustrate your vivid description of this process.



The 16e- Ir(+1) d^8 metal center is e- rich enough to perform an S_N2 type nucleophillic substitution on the electrophillic carbon of the CH_3I. This is an ***oxidative addition*** type reaction that kicks off an anionic I- ligand and generates the Ir(+3) 16e- cationic fragment. The I- anion can diffuse through the solution to bind to the empty cationic coordination site to make the trans-product.



The reaction of [IrCl(CO)(PPh3)$_2$] with H_2 gives the *cis*-dihydride [Ir(H)2Cl(CO)(PPh3)2].
Explain why this is different from part a) above.

The reaction of [IrCl(CO)(PPh3)$_2$] with H_2 gives the *cis*-dihydride [Ir(H)2Cl(CO)(PPh3)2].
Explain why this is different from part a) above.

In the H_2 case, the less electrophilic and reactive H2 needs to precoordinate to the empty pz orbital on the Ir.
Then the oxidative addition occurs in a more or less concerted fashion to give the cisoidal dihydride.
The main difference is that this is not proceeding by the SN2 type reaction shown above.