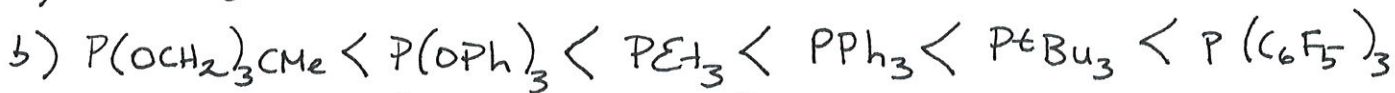
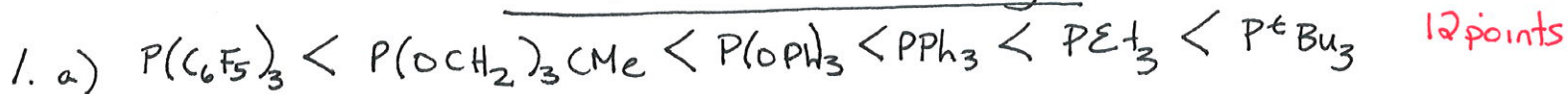
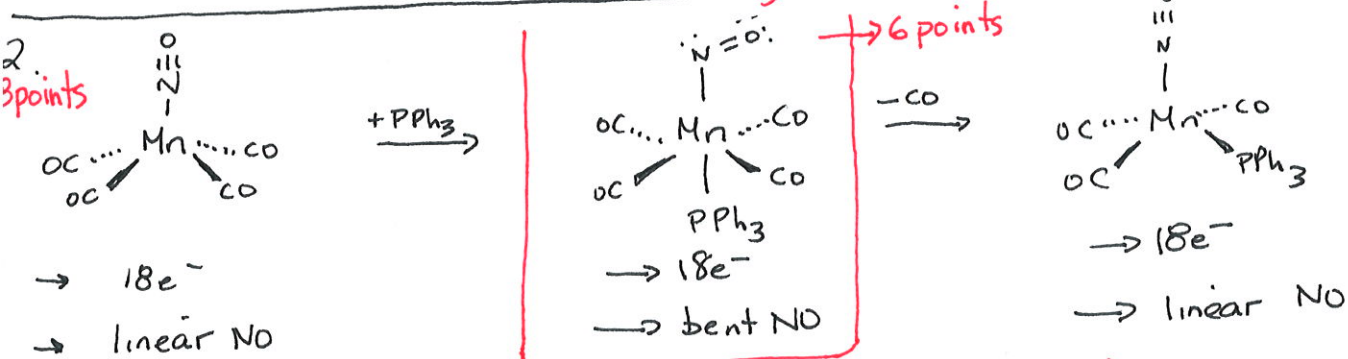


Assignment #1 Answer Key



→ 1 point each (right or wrong)



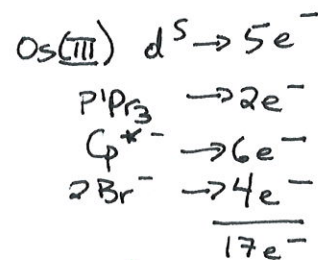
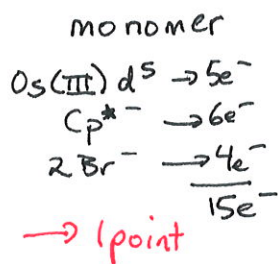
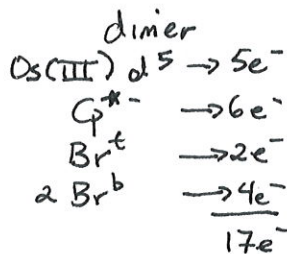
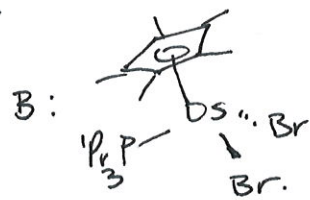
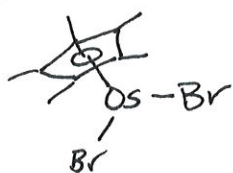
→ $\Delta S^\ddagger \ominus \therefore$ Associative Substitution → 4 points

→ 2nd order rate law: 1st order in $[Mn(CO)_4(NO)]$ and $[PPh_3]$

↳ \therefore Associative Substitution → 2 points

→ 6 points Data implies associative substitution. Sterically this would generate a reasonable octahedral geometry. However, if NO remains linear the intermediate would be $20e^-$. Thus, NO ligand expected to isomerize from $3e^-$ linear to $1e^-$ bent in intermediate back to $3e^-$ linear in final product upon loss of CO.

3. a) 4 points



→ A exists as a dimer because as a monomer it would be sterically and electronically unsaturated ($15e^-$).

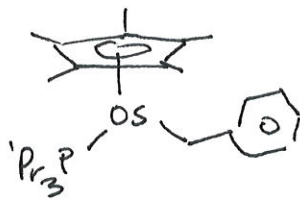
→ B exists as a monomer that is a $17e^-$ complex that is sterically saturated.

↳ 1 point

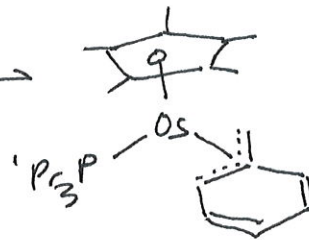
→ 2 points

3b) The equilibrium mixture of D and E is synthetically useful because
 6 points → E is $18e^-$, sterically saturated and thermally stable. → 2 points
 → D is $16e^-$, sterically unsaturated. → 2 points

↳ access to D provides a far more reactive metal centre that one would expect to undergo ready oxidative addition



→ $16e^-$
 → sterically unsaturated
 → more reactive.



→ $18e^-$
 → thermally stable
 → sterically saturated.

∴ an excellent balance between stability and reactivity.

→ 2 points



σ donation
 ↳ 3 points



2 points

π backdonation → 3 points

d) P^iPr_2Me is a weaker e^- donor than P^iPr_3 . Thus $Cp^*(P^iPr_2Me)(CO)OsCH_2Ph$ will have a metal centre that is less e^- rich than $Cp^*(P^iPr_3)(CO)OsCH_2Ph$, and accordingly, less effective @ backdonating (Os to CO). With less e^- density in a MO that is antibonding with respect to $C \equiv O$. Thus the ν_{CO} in $Cp^*(P^iPr_2Me)(CO)OsCH_2Ph$ will be greater than the ν_{CO} of $Cp^*(P^iPr_3)(CO)OsCH_2Ph$.
 ↳ 1 point
 ↳ 1 point
 ↳ 1 point
 → 3 points.

e) A: 20 points

→ symmetric, so identical for each Os centre.

| | | |
|---------------|---|--------------|
| $Os(III) d^5$ | → | $5e^-$ |
| Cp^* | → | $6e^-$ |
| $2 Br^-$ | → | $4e^-$ |
| Br^t | → | $2e^-$ |
| | | <u>17e^-</u> |

1 point
 2 points
 1 point

B:

| | | |
|---------------|---|--------------|
| $Os(III) d^5$ | → | $5e^-$ |
| Cp^* | → | $6e^-$ |
| $2 Br^-$ | → | $4e^-$ |
| P^iPr_3 | → | $2e^-$ |
| | | <u>17e^-</u> |

1 point
 2 points

G:

| | | |
|---------------|---|--------------|
| $Os(IV) d^4$ | → | $4e^-$ |
| Cp^* | → | $6e^-$ |
| H^- | → | $2e^-$ |
| $tripSiH_2^-$ | → | $2e^-$ |
| P^iPr_3 | → | $2e^-$ |
| CH_2Ph^- | → | $2e^-$ |
| | | <u>18e^-</u> |

1 point
 1 point
 2 points

