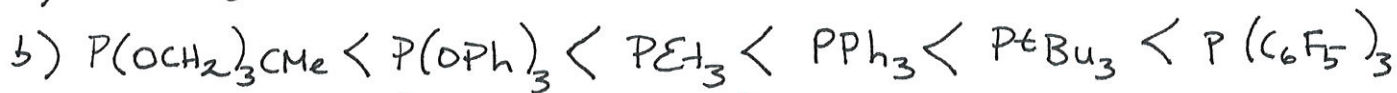
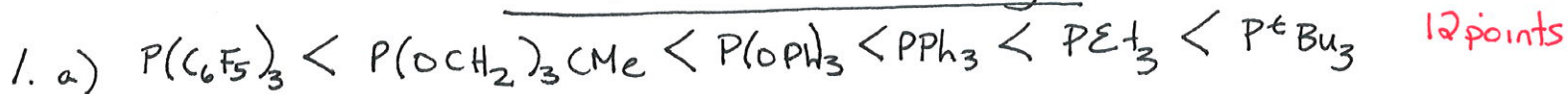
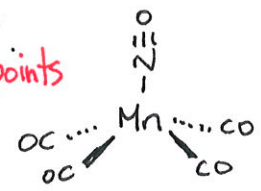


Assignment #1 Answer Key

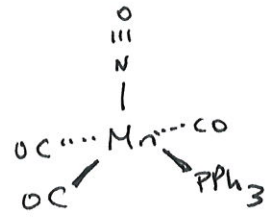
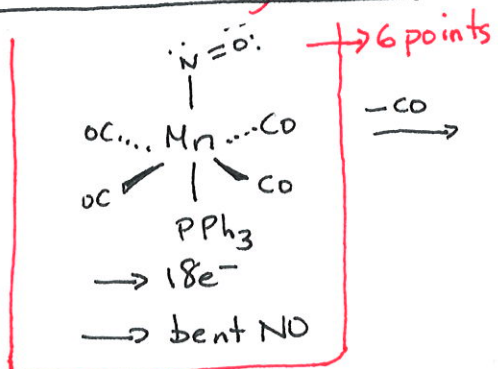
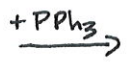


→ 1 point each (right or wrong)

2. 3 points



→ $18e^-$
→ linear NO



→ $18e^-$
→ linear NO

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

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

↳ \therefore Associative Substitution → 2 points

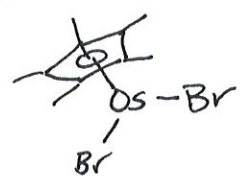
→ 6 points

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.

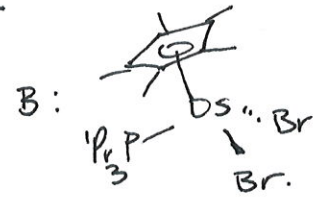
3. a) 4 points



dimer
 $Os(III) d^5 \rightarrow 5e^-$
 $Cp^{*-} \rightarrow 6e^-$
 $Br^t \rightarrow 2e^-$
 $2 Br^b \rightarrow 4e^-$
17e^-



monomer
 $Os(III) d^5 \rightarrow 5e^-$
 $Cp^{*-} \rightarrow 6e^-$
 $2 Br^- \rightarrow 4e^-$
15e^-
→ 1 point



$Os(III) d^5 \rightarrow 5e^-$
 $PPh_3 \rightarrow 2e^-$
 $Cp^{*-} \rightarrow 6e^-$
 $2 Br^- \rightarrow 4e^-$
17e^-

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

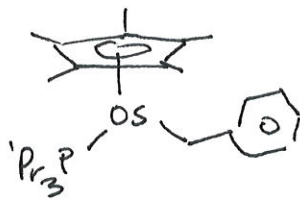
→ B exists as a monomer that is a $17e^-$ complex that is sterically saturated.

↳ 1 point

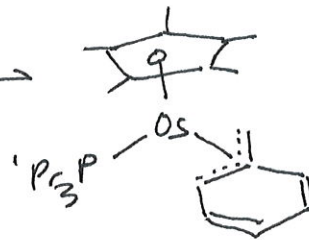
→ 2 points

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.



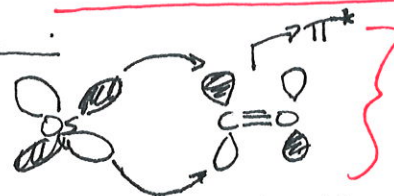
→ $18e^-$
 → thermally stable
 → sterically saturated.

∴ 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	→	$2e^-$
		<hr/>
		$17e^-$

1 point
 2 points
 1 point

B:

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

1 point
 2 points

G:

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

1 point
 1 point
 2 points