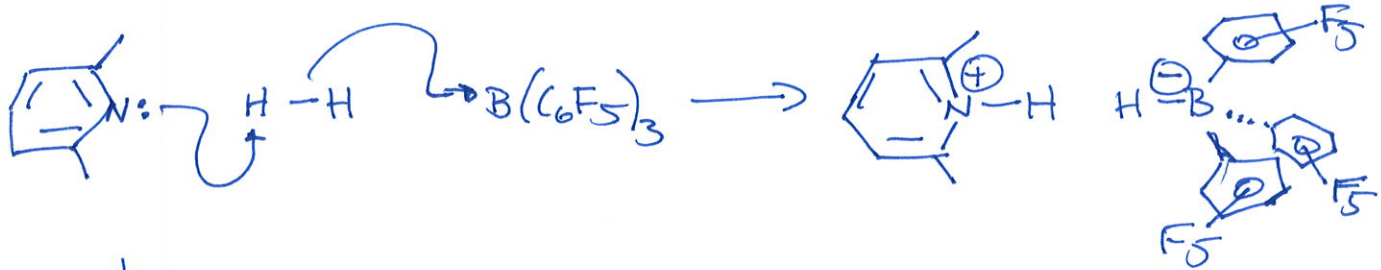
# Chemistry 3840
## Assignment #1 Answer Key

1a) When $PMe_3$ and $BH_3$ are combined they form a strong Lewis acid-base adduct: $:PMe_3 + BH_3 \longrightarrow H_3B{:}PMe_3$

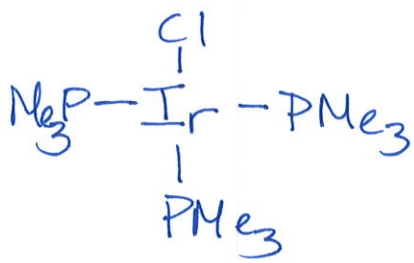
As a consequence this adduct is inert to $H_2$ (the necessary $e^-$ for reaction are already involved in bonding between B and P.).

When $B(C_6F_5)_3$ and  are combined they do not form a Lewis-base adduct because they are too sterically encumbered. However, they act cooperatively to activate $H_2$ with the Lewis acidic borane ending up as $H\overset{\ominus}{B}(C_6F_5)_3$ and the Lewis basic lutedine becoming protonated (  ). The $H_2$ has been cleaved heterolytically to give $H{:}^{\ominus}$ and $H^{\oplus}$. A simplified version of the mechanism can be envisioned as:



b) See above.

2i)



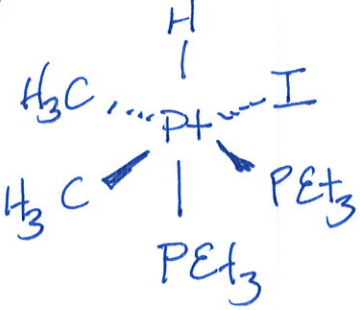
$Ir(I)$ $d^8$ $\longrightarrow$ $8e^-$

$Cl^-$ $\longrightarrow$ $2e^-$

$3PMe_3 \rightarrow 3\times 2e^- \longrightarrow 6e^-$

$16e^-$

ii)



$Pt(IV)$ $d^6$ $\longrightarrow$ $6e^-$

$H^-$ $\longrightarrow$ $2e^-$

$I^-$ $\longrightarrow$ $2e^-$

$2\,CH_3^- \rightarrow 2\times 2e^- \longrightarrow 4e^-$

$2\,PEt_3 \rightarrow 2\times 2e^- \longrightarrow 4e^-$

$18e^-$

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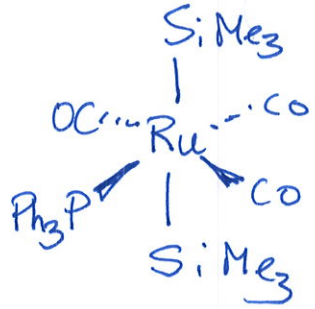
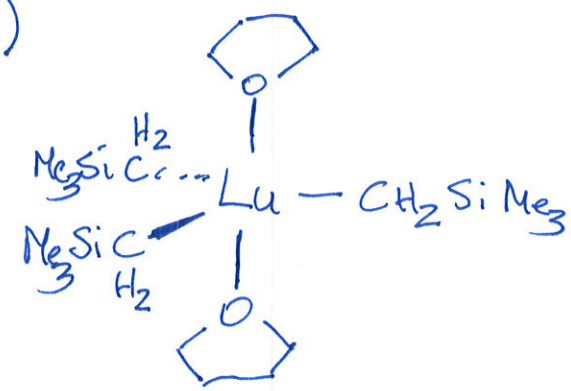
2 iii)



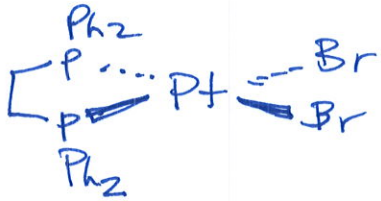
Ru(II) $d^6$ → 6e⁻
$PPh_3$ → 2e⁻
$2 \times SiMe_3^{\ominus}$ → $2 \times 2e^-$ → 4e⁻
3 CO → $3 \times 2e^-$ → 6e⁻
18e⁻

iv)



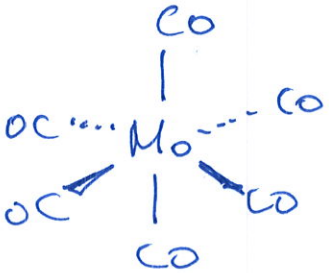
Lu(III) $d^0$ → 0e⁻
2 THF → $2 \times 2e^-$ → 4e⁻
$3\ CH_2SiMe_3^{\ominus}$ → $3 \times 2e^-$ → 6e⁻
10e⁻

v)



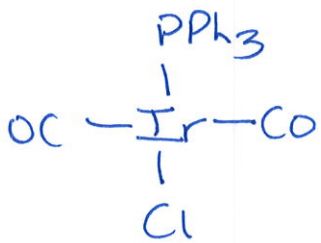
Pt(II) $d^8$ → 8e⁻
$2\ Br^{\ominus}$ → $2 \times 2e^-$ → 4e⁻
$Ph_2P$—$PPh_2$ → 4e⁻
16e⁻

vi)



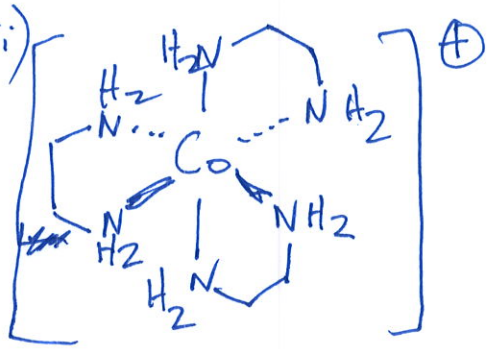
Mo(0) $d^6$ → 6e⁻
6 CO → $6 \times 2e^-$ → 12e⁻
18e⁻

vii)



Ir(I) $d^8$ → 8e⁻
$Cl^{\ominus}$ → 2e⁻
2 CO → $2 \times 2e^-$ → 4e⁻
$PPh_3$ → 2e⁻
16e

viii)



Co(I) $d^8$ → 8e⁻
$3\ H_2N$—$NH_2$ → $3 \times 4e^-$ → 12e⁻
20e⁻

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3.) $[B_{12}H_{12}]^{2-}$

$12\,BH \longrightarrow 24e^-$

$2\ominus \longrightarrow 2e^-$

$26e^-$

$12\,B \hookrightarrow n=12$

$\hookrightarrow \frac{26e^-}{2} = 13$ skeletal $e^-$ pair

$n=12$; $n+1$ skeletal $e^-$ pair

$\therefore$ closo structure.

$1,2\text{-}C_2B_{10}H_{12}$

$2C + 10B$

$\Rightarrow n=12$

$10\,BH \longrightarrow 20e^-$

$2\,CH \longrightarrow 4e^-$

$2\,Ce^- \longrightarrow 2e^-$

$26e^-$

$\frac{26e^-}{2} = 13$ skeletal $e^-$ pair.

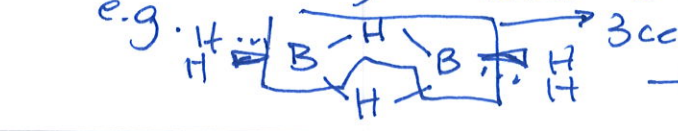
$n=12$; $n+1$ skeletal $e^-$ pair

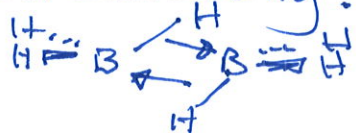
$\therefore$ closo structure

Both $[B_{12}H_{12}]^{2-}$ and $1,2\text{-}C_2B_{10}H_{12}$ have 12 vertex atoms ($n=12$) and both follow Wade's rules indicating a closo structure. Thus, I expect both species to have the same cage structure.

4.) A 2-centered–$2e^-$ bond is what one typically sees in organic chemistry wherein $2e^-$ are shared between 2 atoms. ($H_3C-CH_3$). A Lewis acid~~e~~base adduct adheres to this description as well, even though both electrons donated from one atom to the other ($H_3N: \rightarrow BH_3$)

A 3-centre–$2e^-$ bond is a scenario wherein $2e^-$ are shared between 3 atoms, and as a consequence are often referred to as electron deficient. Such bonding is common for boranes, as well as in coordination chemistry.

e.g.  3 centre 2e bond



→ Sometimes depicted as

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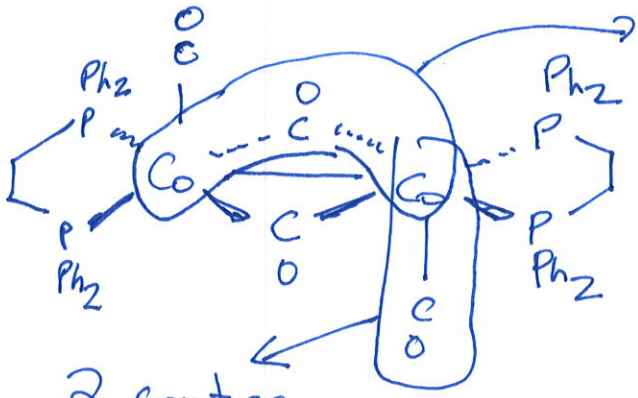
4.) e.g.

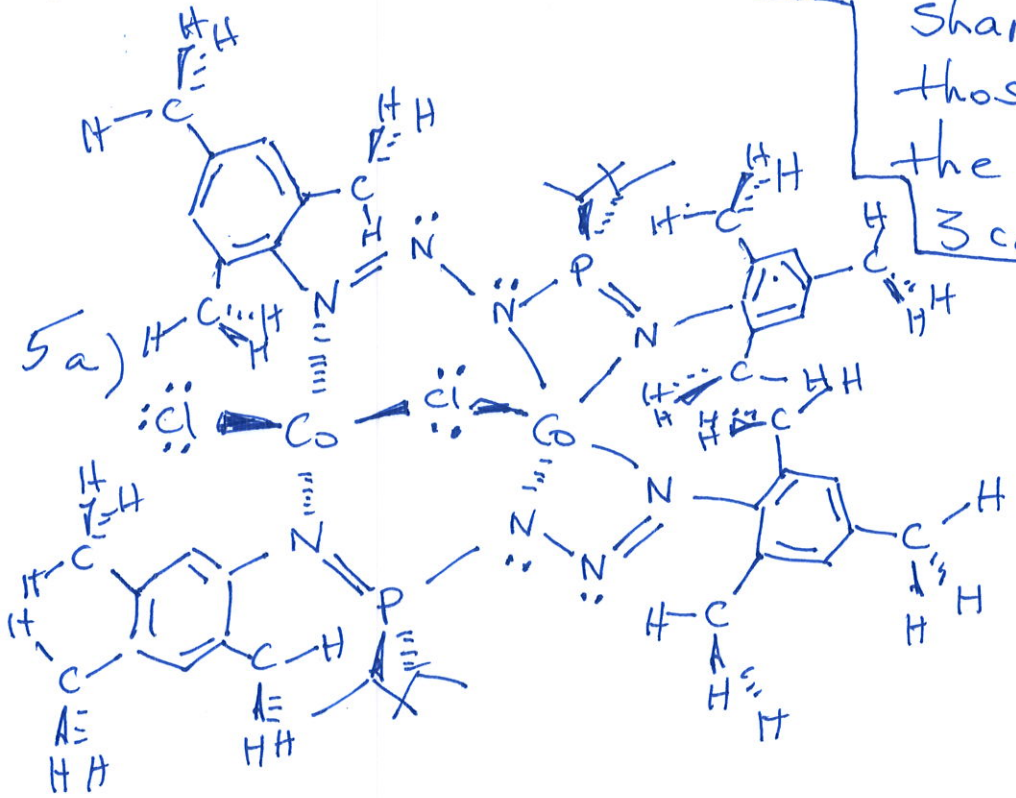


→ 3 centre 2e⁻ bond

→ $:C\equiv O:$ is a 2e⁻ neutral donor. Thus, if it is a terminal ligand to one metal, there is a 2 centre 2e⁻ bond, but if it bridges 2 metals the 2 electrons are shared between those 2 metals and the carbon atom; hence, 3 centre 2e⁻ bonding.

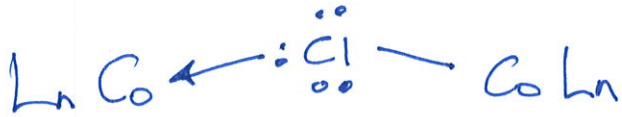
2 centre 2e⁻ bond.

5a)



→ The only ambiguity is whether or not the bridging $Cl^{\ominus}$ should be considered as an anionic donor to the right (or left) cobalt, and as a neutral donor to the left (or right) cobalt. Given that the distance to the right cobalt is significantly shorter (2.332 Å) than the distance to the left cobalt (2.395 Å), it is likely most appropriate to consider the bonding as:

5a)



5b) Assuming the bonding described above:

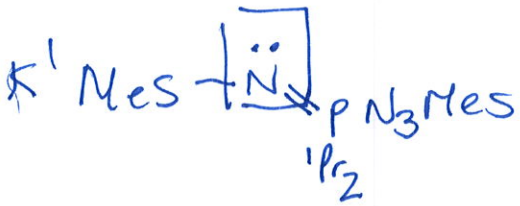
Left cobalt

Co (I) $\longrightarrow$ $d^8$ $\longrightarrow$ 8e⁻

$^t$Cl $\longrightarrow$ 2e⁻

$^b$Cl $\longrightarrow$ 2e⁻

$\longrightarrow$ 2e⁻



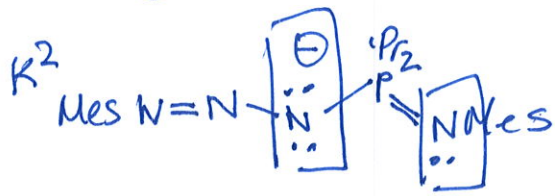
$\longrightarrow$ 2e⁻

16e⁻

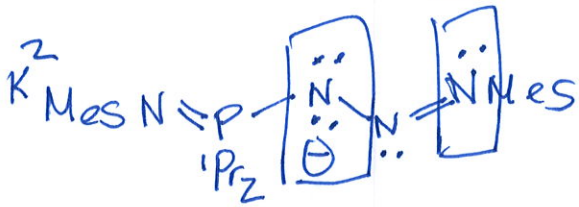
right cobalt

Co (III) $\longrightarrow$ $d^6$ $\longrightarrow$ 6e⁻

$^b$Cl $\longrightarrow$ 2e⁻



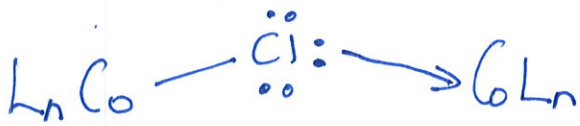
$\longrightarrow$ 4e⁻



$\longrightarrow$ 4e

16e⁻

5b) If the bonding were assumed to be:



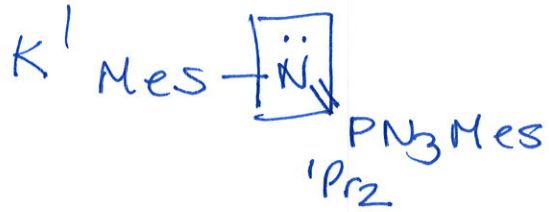
Left Cobalt

Co(II) $d^7$ ⟶ 7e⁻

$^t$Cl$^\ominus$ ⟶ 2e⁻

$^b$Cl$^\ominus$ ⟶ 2e⁻

K$^1$ Mes ⟶ 2e⁻



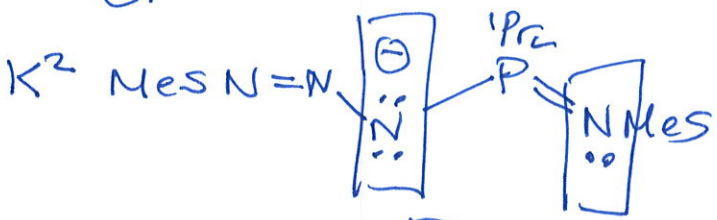
K$^1$ Mes ⟶ 2e⁻

15e⁻

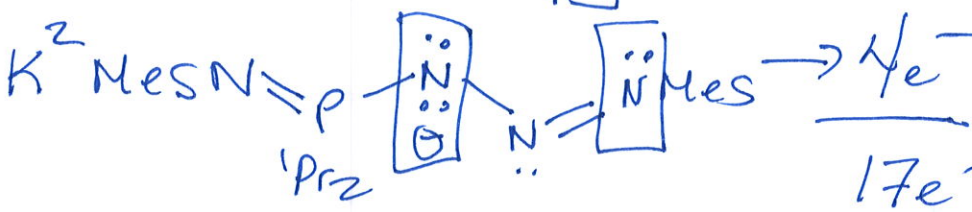
Right Cobalt

Co(II) $d^7$ ⟶ 7e⁻

$^b$Cl$^\ominus$ ⟶ 2e⁻



K$^2$ MesN=N ⟶ 4e⁻



K$^2$ MesN=P ⟶ 4e⁻

17e⁻

More likely

Hence either Co(I) 16e⁻ and Co(III) 16e

or

Co(II) 15e⁻ and Co(II) 17e⁻

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6a) $B_5H_9$ (n=5)

$5\,BH \rightarrow 5 \times 2e^- = 10e^-$

$4H \rightarrow 4 \times 1e^- = 4e^-$

$14e^-$

$\frac{14e^-}{2} = 7$ skeletal $e^-$ pair

↓

n+2 skeletal $e^-$ pair o.o nido structure

→ Since borohydride clusters with the same number of skeletal $e^-$ pair are related by the removal or addition of a BH unit, one can predict that $B_5H_9$ (7 skeletal $e^-$ pairs) would be related to the octahedral, closo $[B_6H_6]^{2-}$ → 7 skeletal $e^-$ pair.

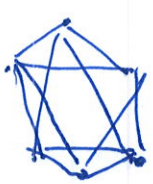
↓

$6\,BH \rightarrow 12e^-$

$2e^- \rightarrow 2e^-$

$14e^-$

→ As $[B_6H_6]^{2-}$ has a closo structure and n=6, one would expect that the nido $B_5H_9$ (n=5) structure would be like an octahedron with one vertex removed ⟹ a square pyramid



$]^{2-}$ removal of BH vertex / addition of 4H

octahedral $[B_6H_6]^{2-}$

square pyramidal $[B_5H_9]$