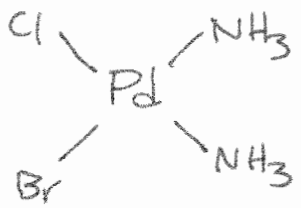
Chemistry 384o
Assignment #2 Answer Key

1a

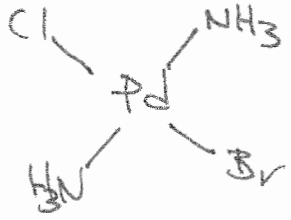
$Pd(NH_3)(NH_3)ClBr \longrightarrow [PdBrCl(NH_3)_2]$

diaminebromochloropalladium (II).

Pd (II), d^8 ∴ square planar.



cis



trans

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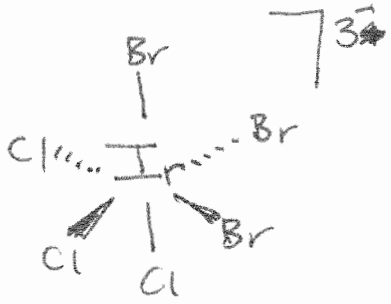
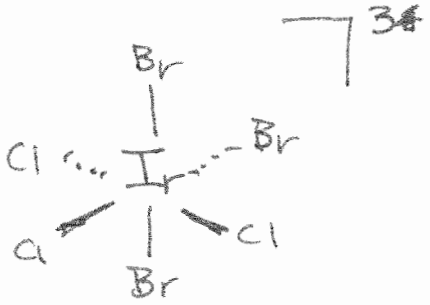
b) $K_3[IrBr_3Cl_3]$

tripotassium tribromotrichloroiridate (III).

Ir (III), d^6, $18e^-$ → octahedral.



fac(ial)



mer(idional).

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c) $[AuCl(PPh_3)]$

chlorotriphenylphosphinegold (I)

Au (I) d^{10}, $14e^-$, 2 coordinate → linear

$Ph_3P - Au - Cl$ No other isomers

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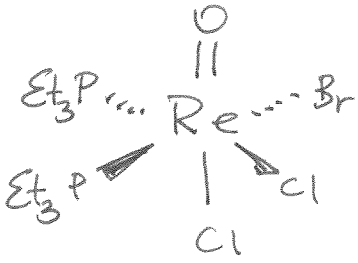
1d

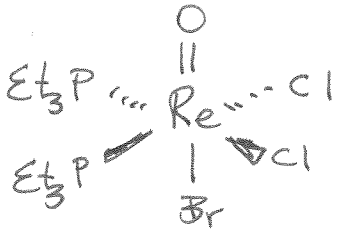
$[ReOBrCl_2(PEt_3)_2]$

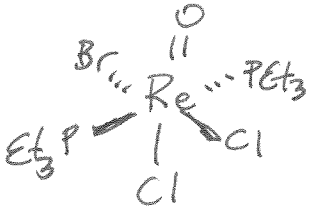
dibromochlorooxobis(triethylphosphine)rhenium(V)

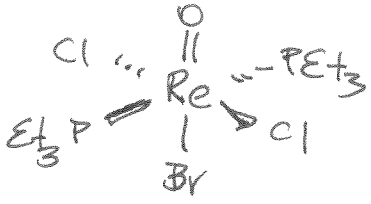
Re(V) d^2, 16 e^-, 6 coordinate ⟶ octahedral.

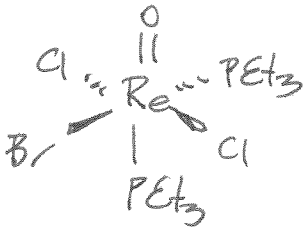
⟶ many cis and trans possibilities

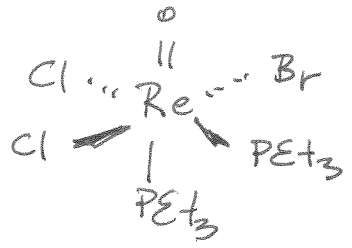










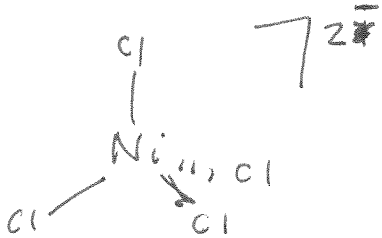


$Li_2[NiCl_4]$

dilithium tetrachloronickelate(II)

1e

Ni(II) d^8, 16 e^-, 4 coordinate. ⟶ could be square planar or tetrahedral for Ni(II) but Cl^- is a weak field ligand so likely tetrahedral



No isomers

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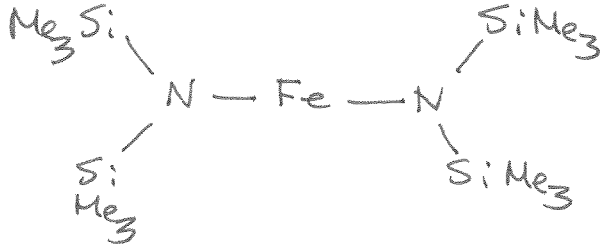
1f

. $[Fe(N(SiMe_3)_2)_2]$

bis(bis(trimethylsilylamide))iron (II)

Fe(II) d^6, $10e^-$, 2 coordinate } linear.

→ Very bulky ligands



No isomers

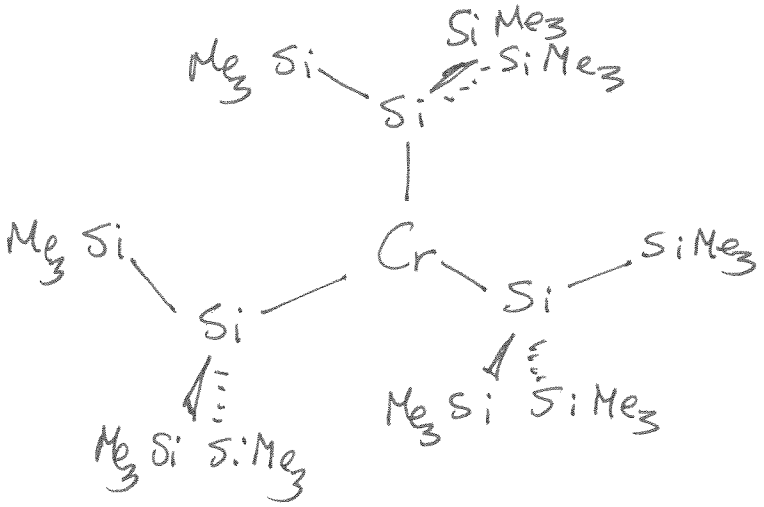
1g

$[Cr(Si(SiMe_3)_3)_3]$

tris(tris(trimethylsilyl)silyl)chromium (III)

Cr(III), d^3, $9e^-$, 3 coordinate. } trigonal planar.

→ very bulky ligans



No isomers.

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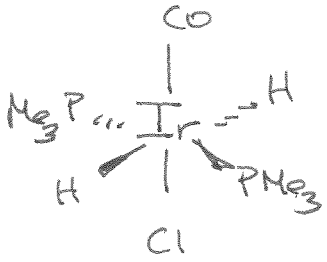
1h

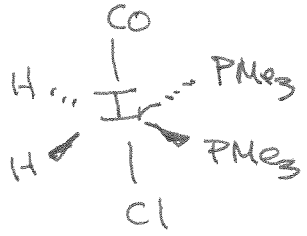
$[Ir(CO)(Cl)(H)_2(PMe_3)_2] \longrightarrow [IrClH_2(CO)(PMe_3)_2]$

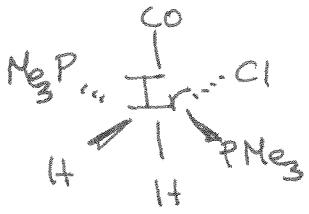
carbonylchlorodihydridobis(trimethylphosphine)iridium(III)

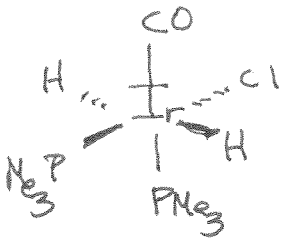
Ir(III), d^6, 6 coordinate, 18e$^-$ → octahedral

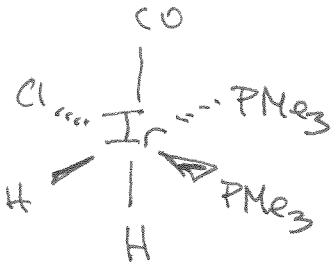
↳ numerous cis and trans isomers

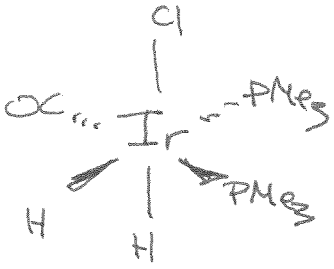












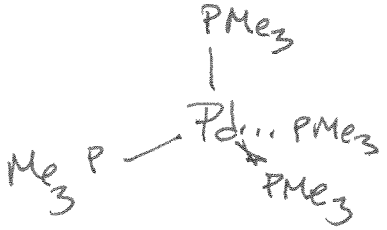
2a

tetra(trimethylphosphine)palladium(II)

↓

tetrakis(trimethylphosphine)palladium(0); $[Pd(PMe_3)_4]$

Pd(0) → d^{10}, 4 coordinate, 18e$^-$ ∴ tetrahedral



No isomers.

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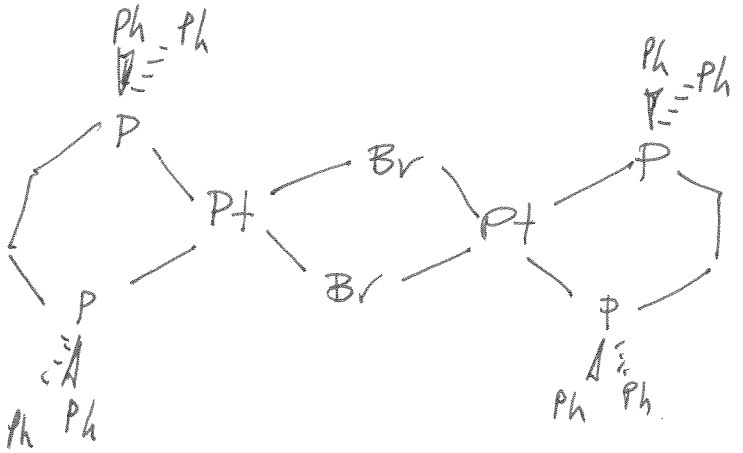
2b

di-μ-bromobis[bis(diphenylphosphino)ethaneplatinum(II)]dicyanide

$[Pt(\mu_2\text{-}Br)(diphos)]_2[CN]_2$ or $[Pt(\mu_2\text{-}Br)(PPh_2CH_2CH_2PPh_2)]_2[CN]_2$



Pt(II) d^8, 16e⁻
↳ square planar

→ No isomers

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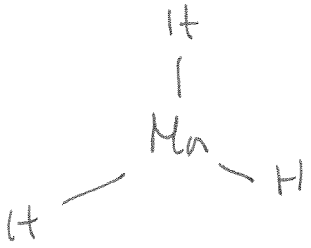
trihydridomanganese(III) $[MnH_3]$

2c Mn(III), d^4, tricoordinate, 10e⁻ → trigonal planar.



→ No isomers.

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N.B. Isomers are sometimes indicated for formulae. e.g. Δ-$[Co(en)_3]^+$

3a $[PtCl_2(diphos)]$ or $[PtCl_2(PPh_2CH_2CH_2PPh_2)]$

cis-dichlorobis(diphenylphosphino)ethaneplatinum(II)

b) $[Fe(CO)_5]$ pentacarbonyliron(0)

c) $[IrCl(CO)_2(PPh_3)_2]$

trans-dicarbonylchlorotriphenylphosphineiridium(I)

d) $[Co(en)_3]^{\oplus}$ or $[Co(NH_2CH_2CH_2NH_2)_3]^{\oplus}$

Δ-tris-(K²-ethylenediammine)cobalt(I)

---

4 Coordination Isomers: $[Co(NH_3)_6][Cr(CN)_6]$

+

$[Cr(NH_3)_6][Co(CN)_6]$

Linkage Isomers: $[NBu_4][Pt(\underline{S}CN)_3(PEt_3)]$

+

$[NBu_4][Pt(\underline{N}CS)_3(PEt_3)]$

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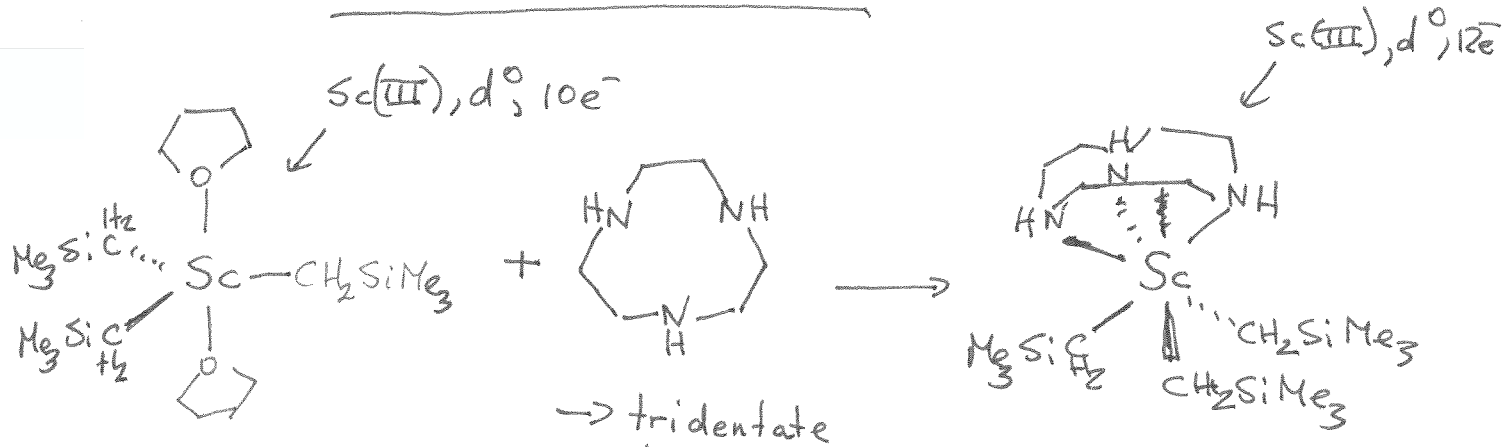

→ 5 coordinate
→ trigonal bipyramidal with large ligands in equatorial sites

→ tridentate ligand.

+ 2

→ 6 coordinate
→ octahedral
→ tacN is a facially capping ligand.

→ THF is a neutral monodentate ligand whereas tacn is a tridentate neutral ligand. Seeing as THF is a stable molecule a straightforward substitution reaction would be expected. The chelate effect would favour the product because tacn will chelate to the metal in a κ^3 fashion.

→ Since the product is more sterically (6 coordinate vs 5) and electronically (12e⁻ vs 10e⁻) saturated, it would be expected to be more stable than starting material!

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b. Since the starting material (1) is 5 coordinate one would expect the substitution reaction to be associative (the first tacn donor would coordinate prior to dissociation of the first THF ligand) one would expect the Sc complex with smaller ligands to react faster (keeping in mind that there should be no substantial electronic difference between th $-CH_2SiMe_3$ and $-CH_2SiMe_2Ph$ ligands.) Hence, one would expect $Sc(CH_2SiMe_3)_3(THF)_2$ to react faster than $Sc(CH_2SiMe_2Ph)_3(THF)_2$

→ N.B. One would come to the opposite conclusion if