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March 29, 2008
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317-271-5222

Inorganic Chemistry Cume Exam Crib

March 29, 2008

A. This part of the exam deals with the assignment of formal oxidation states and electron counts for compounds of the transition metals.

(a) (20 points). Give the formal oxidation state and d^n configuration for the transition metal atom in each of the following ten neutral mononuclear compounds or ionic species.

1+1	(i) $VO(acac)_2$ (acac = acetylacetonate anion)	V(IV) d^1
1+1	(ii) $ZrCl(acac)_3$	Zr(IV) d^0
1+1	(iii) $[VCl_2(H_2O)_4]^+$	V(III) d^2
1+1	(iv) $[MnBr_4]^{2-}$	Mn(II) d^5
1+1	(v) $Cr[N(SiMe_3)_2]_3$	Cr(III) d^3
1+1	(vi) $[Fe(CN)_6]^{4-}$	Fe(II) d^6
1+1	(vii) $Fe(CO)_5$	Fe(0) d^8
1+1	(viii) $(\eta^5\text{-}C_5H_5)_2Os$	Os(II) d^6
1+1	(ix) $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$	Ti(IV) d^0
1+1	(x) $[V(CO)_6]^-$	V(-I) d^6

(b) (20 points). For each of the following organometallic compounds and ions, give the electron count for the transition metal atom and conclude whether or not the '18-electron rule' is obeyed. Show all working. **NOTE**: you will need to know the structure of these compounds.

2	(i)	$(\eta^4\text{-}C_4H_4)Fe(CO)_3$	18-e	yes
2	(ii)	$(\eta^5\text{-}C_5H_5)_2V$	15-e	(No)
2	(iii)	$(\eta^6\text{-}C_6H_6)_2Cr$	18-e	yes
2	(iv)	$(\eta^5\text{-}C_5H_5)_2TiCl_2$	16-e	(No)
2	(v)	$(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$	18-e	yes

2 (vi) $[Ti(CO)_6]^{2-}$ 18-e Yes

2 (vii) $V(CO)_6$ 17-e (No)

2 (viii) $[Ru(CO)_6]^{2+}$ 18-e Yes

2 (ix) $Os_3(CO)_{12}$ 18-e Yes

2 (x) $Rh_4(CO)_{12}$ 18-e Yes

B. The chemistry of the Group IV transition metals Ti, Zr and Hf is representative of much of the chemistry of the early transition series elements.

3x4 (a) (12 points). The tetrahalides TiF_4(solid), $TiCl_4$(liquid) and $ZrCl_4$(solid) have different structures. Draw very clearly the structure of each of them.

3,3 (b) (15 points). Give balanced equations to show how $TiCl_4$ is converted to $TiCl_3$ and $TiCl_2$. Draw clearly the structure of the three compounds that are formed upon
3x3 reacting $TiCl_3$ separately with (i) THF, (ii) NMe_3, and (iii) $Li^+[N(SiMe_3)_2]^-$.

3 (c) (10 points). Give a balanced equation to show how $TiCl_4$ is converted into
2 $TiOCl_2$. What is the product of the reaction of $TiOCl_2$ with acetylacetone
3,2 (Hacac)? Draw its structure and compare it with that of its vanadium analog.

(d) (15 points). Starting from $ZrCl_4$, show how the organometallic species
3x3 $[Zr(CO)_6]^{2-}$, $[Zr(CH_3)_6]^{2-}$ and $((\eta^5\text{-}C_5H_5)_2ZrCl_2$ are prepared. In the case of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, use balanced equations to show how it is converted to (i) $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ and (ii) $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$.

(e) (8 points). Which infra-red active CO stretching frequency (i.e. ν(CO)), goes with which carbonyl species?

3 { ν(CO): 1998, 2190, 1757 cm^{-1}

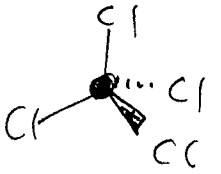
carbonyl species: $[Hf(CO)_6]^{2-}$, $W(CO)_6$, $[Os(CO)_6]^{2+}$

5 Explain your reasoning very clearly.

B.

(a)

~~4~~ trans - $[TiF_2F_{4/2}]_\infty$

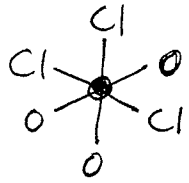
~~4~~ 

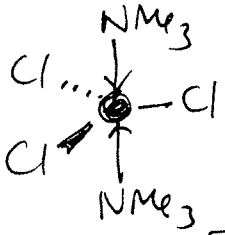
Draw clearly

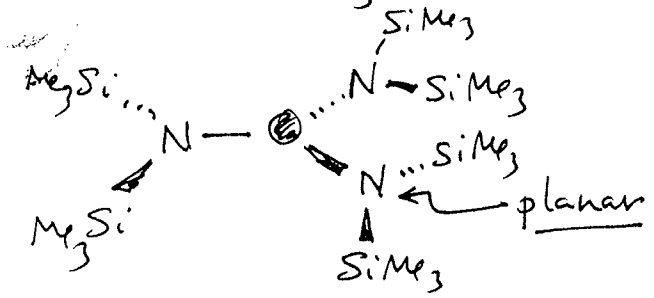
~~4~~ cis - $[ZrCl_2Cl_{4/2}]_\infty$

3 (b) $2TiCl_4 + H_2 \longrightarrow 2TiCl_3 + 2HCl$

3 $2TiCl_3 \longrightarrow TiCl_4 + TiCl_2$

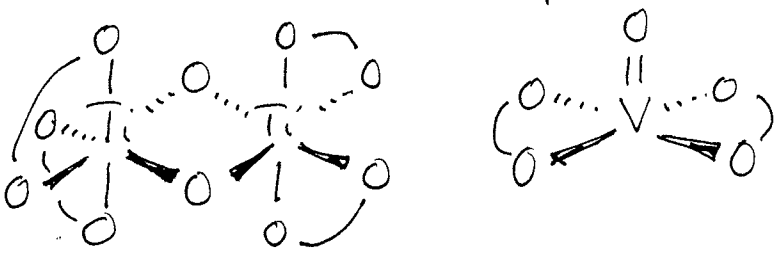
3 (i) mer-  or fac-ismer

3 (ii) 

3 (iii) 

3 (c) $3TiCl_4 + Sb_2O_3 \longrightarrow 3TiOCl_2 + 2SbCl_3$

2 $[TiO(acac)_2]_2$ is the product

3, 2 

3 (d) $ZrCl_4 \xrightarrow[\text{crown ether or cryptand, CO}]{Na^+C_{10}H_8^-,\ THF,\ -70^\circ C} [Zr(CO)_6]^{2-}$

3 $ZrCl_4 + 6\ MeLi \ (xs) \xrightarrow[\text{low T}]{THF \text{ or } dme} [Zr(CH_3)_6]^{2-}$

3 $ZrCl_4 + 2Na^+C_5H_5^- \xrightarrow[-10^\circ C]{THF} (\eta^5\text{-}C_5H_5)_2ZrCl_2$

3 $(\eta^5\text{-}C_5H_5)_2ZrCl_2 + 2\ MeLi \xrightarrow[-10^\circ C]{THF} (\eta^2\text{-}C_5H_5)_2Zr(CH_3)_2$

3 $(\eta^5\text{-}C_5H_5)_2ZrCl_2 + Mg \xrightarrow[\text{low T}]{THF,\ CO} (\eta^5\text{-}C_5H_5)_2Zr(CO)_2 + MgCl_2$

or $(\eta^5\text{-}C_5H_5)_2ZrCl_2 + Mg \xrightarrow[\text{low T}]{THF,\ PMe_3} (\eta^5\text{-}C_5H_5)_2Zr(PMe_3) + MgCl_2$

$(\eta^5\text{-}C_5H_5)_2Zr(PMe_3) \xrightarrow{CO} (\eta^5\text{-}C_5H_5)_2Zr(CO)_2$

(c)

3

$[Hf(CO)_6]^{2-}$	$1757\ cm^{-1}$
$W(CO)_6$	$1998\ cm^{-1}$
$[Os(CO)_6]^{2+}$	$2190\ cm^{-1}$

5

$Hf < W < Os$ $M(d_\pi) \rightarrow CO(\pi^*)$ back bonding decreases; so, CO bond order and $\nu(CO)$ increase.