

Assignment 3 (5%) due in by 9.30 am Tuesday 16th March

(a) Determine the enthalpies of formation for WCl , WCl_3 and WCl_6 using a Born-Haber cycle, calculating lattice energies using the Kapuskinskii equation.

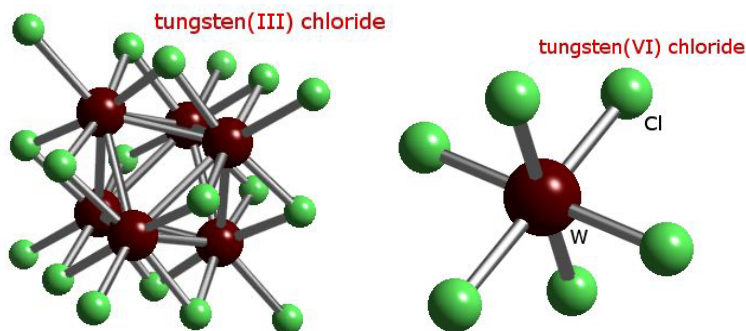
682, 104, -479 kJ mol^{-1} , respectively.

(i) WCl does not exist. What particularly large factor is mitigating against its formation?

High $\Delta H_a(\text{W})$; compare Cs, <10% of the value for W.

(ii) WCl_3 and WCl_6 do exist. Find out their actual structures, and describe them. Do either of these fit the description of a “simple ionic solid”?

WCl_3 has a cluster structure, formula better written $[\text{W}_6\text{Cl}_{12}]\text{Cl}_6$. Retention of some M-M bonding means effectively not all of the ΔH_a need be spent. WCl_6 is a covalent molecule. Neither fit the description of simple ionic solid.



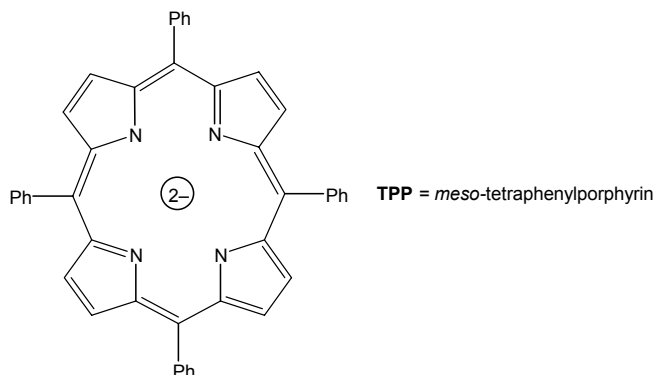
(iii) What do the Born-Haber cycle and Kapuskinskii equation fail to take into account?

M-M bonding, covalent bonding, alternate lattice geometries, etc. Question was intended to illustrate the poor applicability of the approach, especially to high oxidation state compounds.

$IE_n(\text{W})$ 770, 1700, 2300, 3400, 4600, 5900 kJ mol^{-1} ; $\Delta H_a(\text{W})$ 860 kJ mol^{-1} ; $\Delta H_a(\text{Cl}_2)$ 244 kJ mol^{-1} ;
 $EA(\text{Cl})$ 349 kJ mol^{-1} ; r_+ 130 pm, r_{3+} 98 pm, r_{6+} 74 pm, r_- 167 pm. [7 marks]

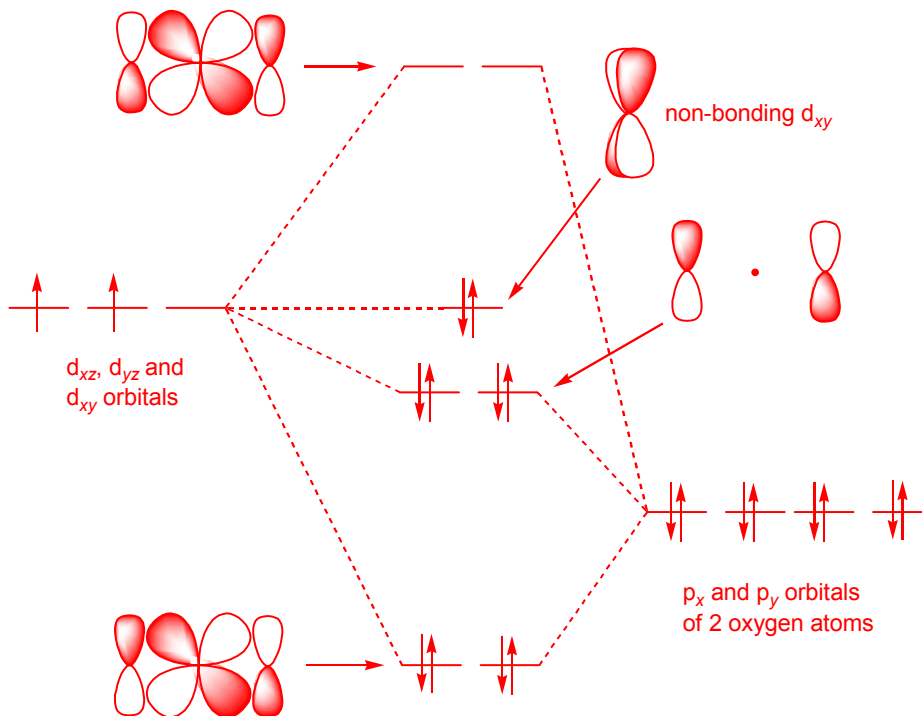
(b) Rationalize the following Mo-Mo bond distances [6 marks]:

$[\text{Mo}_2(\text{O}_2\text{CMe})_4]$	209 pm
$[\text{Mo}_2(\text{SO}_4)_4]^{4-}$	211 pm
$[\text{Mo}_2\text{Cl}_8]^{4-}$	214 pm
$[\text{Mo}_2(\text{SO}_4)_4]^{3-}$	217 pm
$[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$	223 pm
$[\text{Mo}_2(\text{TPP})_2]$	224 pm



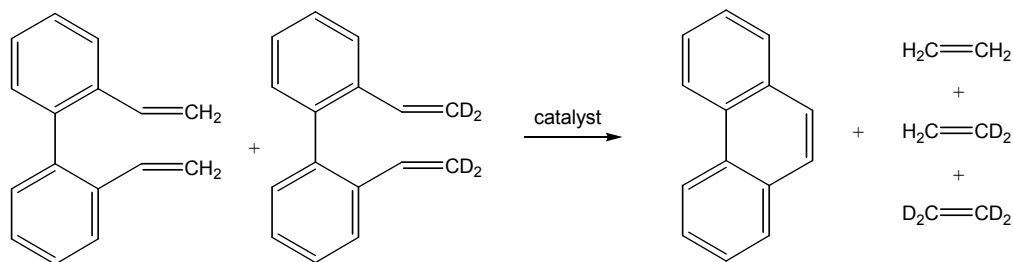
Bond orders 4, 4, 4, 3.5, 3, 4 respectively. MeCO₂ “bite” better matched to Mo-Mo bond than SO₄; some Cl-Cl repulsion in chloride case. TPP ligand extremely bulky, large L-L repulsion lengthens bond.

(c) The complex [OsO₂(OH)₄]²⁻ has a linear O=Os=O group. Construct a simplified MO diagram for the π-bonding in this complex assuming that O=Os=O lies along the z-axis and only the d_{xy}, d_{xz} and d_{yz} orbitals of the metal are involved. Do you expect the complex to be paramagnetic? [4 marks]



O hybridized sp² each of bonding, non-bonding and antibonding MOs, as the picture is repeated in xz and yz planes. Compound is diamagnetic; all electrons are paired.

(d) RCM of a 1:1 mixture of reactants shown below produced phenanthrene and a 1:2:1 mixture of C₂H₄:C₂H₂D₂:C₂D₄. Account for the products formed. [3 marks]



This classic experiment was designed to illustrate the stepwise nature of the reaction (if the metal centre coordinated both alkenes simultaneously, you would end up with a 1:1 mixture of C₂H₄ and C₂D₄. Essentially, after the first round of metathesis you end up with a 1:1 mixture of M=CH₂ and M=CD₂ which effectively go on to catalyze all subsequent RCM. As a result, you generate a statistical mixture of ethylenes.

(e) Interpret the following spectroscopic data:

- (i) The IR spectrum of $[\text{Co}_3(\text{CO})_{10}]^-$ has peaks at 2071, 2006, 1999, 1975, 1865 and 1584 cm^{-1} .

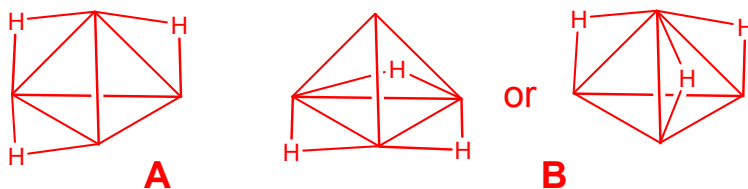
Triangular cluster; has terminal, bridging, face-capping COs (1584 cm^{-1} low for face-capping due to negative charge on cluster). Only symmetric way of arranging is to have two terminal COs per Co, a CO bridging each edge, and one face-capping CO.

- (ii) At 178 K, the ^1H NMR spectrum of $[(\mu\text{-H})_3\text{Ru}_4(\text{CO})_{12}]^-$ exhibits three signals due to two isomers:

- A:** $\delta -15.9$, d, $J = 2.5\text{ Hz}$, relative integral 2
 $\delta -19.1$, t, $J = 2.5\text{ Hz}$, relative integral 1
B: $\delta -17.4$, s, relative integral 3.7

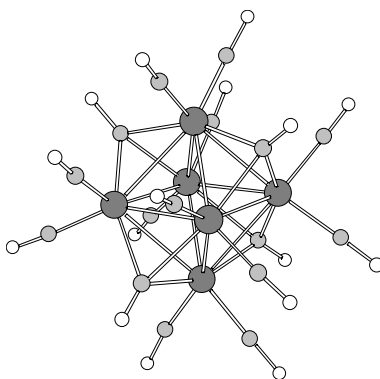
At room T, the cluster exhibits a singlet at $\delta -16.9$.

Electron counting predicts tetrahedral structure. At higher T, structure is fluxional; H migrates across cluster surface.



- (iii) The ^{13}C NMR spectrum of $\text{Rh}_6(\text{CO})_{16}$ shows two signals ($\delta 180$, d, $J = 70\text{ Hz}$ and $\delta 232$, q, $J = 26\text{ Hz}$). However, the ^{13}C NMR spectrum of $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ shows just one signal ($\delta 209$, septet, $J = 14\text{ Hz}$).

Structure as shown below; 2 terminal CO per Rh, 4 tetrahedrally arranged face-capping CO ligands.

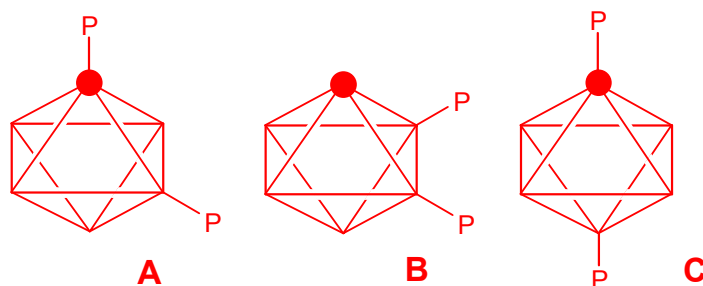


$[\text{Rh}_6(\text{CO})_{15}]^{2-}$ effectively has a similar arrangement of CO ligands but with a “vacant coordination site”. As such, it is highly fluxional; all of the CO ligands are equivalent and they see the 6 Rh as equivalent.

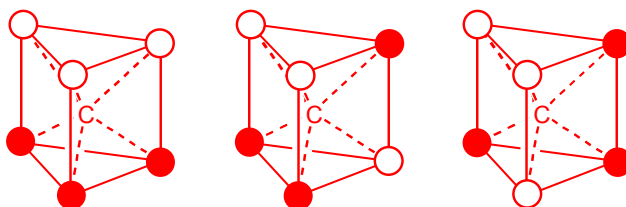
(iv) The solution ^{31}P NMR spectrum of the octahedral cluster $\text{PtRu}_5\text{C}(\text{CO})_{14}(\text{PMe}_2\text{Ph})_2$ shows five signals due to three isomers (note: J_{PtP} appear as satellites):

- A: δ 9.62, $J_{\text{PtP}} = 63$ Hz
 δ -13.45, $J_{\text{PtP}} = 5999$ Hz
 B: δ 4.35, $J_{\text{PtP}} = 63$ Hz
 C: δ -1.11
 δ -11.80, $J_{\text{PtP}} = 6111$ Hz

[11 marks]



(f) How could NMR be used to determine the distribution of the metal atoms in the core of the trigonal prismatic cluster $[\text{Fe}_3\text{Rh}_3(\mu_6\text{-C})(\text{CO})_{17}]^-$? Consider both ^{103}Rh and $^{13}\text{C}_{\text{interstitial}}$ nuclei. [4 marks]



^{103}Rh :	s	s (2Rh), s (1Rh) or d (2Rh), t (1Rh)	d, dd, d or dd, dd, dd
$^{13}\text{C}_{\text{interstitial}}$	q	dt	ddd

(assignments are slightly different depending on whether you include diagonal as well as through-bond $J_{\text{Rh-Rh}}$ couplings).

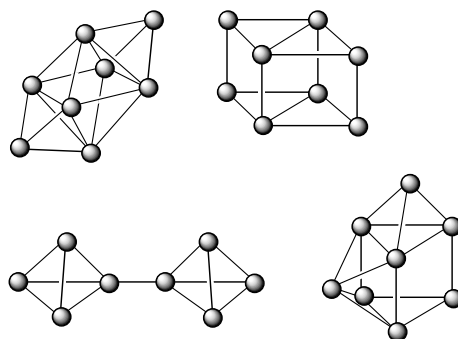
(g) Do the following molecules conform to the Effective Atomic Number rule: $\text{Co}_2(\text{CO})_8$ (dimer), $\text{FeRu}_2(\text{CO})_{12}$ (triangle), $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (tetrahedron), $[\text{Os}_5(\text{CO})_{15}]^{2-}$ (trigonal bipyramid), $\text{Os}_6(\text{CO})_{21}$ (raft), $\text{Ru}_5\text{C}(\text{CO})_{15}$ (square-based pyramid), $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ (trigonal prism), $[\text{Co}_6(\text{CO})_{15}]^{2-}$ (octahedron) and $[\text{Os}_8(\text{CO})_{22}]^{2-}$ (bicapped octahedron)? [3 marks]

All yes except the last two. Question intended to illustrate the limitations of the localized bonding approach.

(h) Use PSEPT to predict the structure of the following clusters: $\text{Fe}_5\text{C}(\text{CO})_{15}$, $[\text{Re}_4(\text{CO})_{16}]^{2-}$, $\text{H}_2\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_9(\text{CO})_{25}$. Discuss the possibility of isomers for $\text{Os}_9(\text{CO})_{25}$. [7 marks]

Square-based pyramid (*nido*); butterfly (*arachno*); octahedron (*closo*; though actual structure is capped *nido*); tricapped octahedron. Lots of isomers for $\text{Os}_9(\text{CO})_{25}$; draw representative examples; one mark was for mentioning the possibility of capping caps.

(i) Use the condensation principle to decide which of the following M_8 cluster geometries corresponds to (i) $Rh_8C(CO)_{19}$, (ii) $Rh_8C_2(CO)_{18}$, (iii) $[Re_8C(CO)_{24}]^{2-}$ and (iv) $[Ir_8(CO)_{22}]^{2-}$. [5 marks]



(i) bottom right, (ii) top right, (iii) top left, (iv) bottom left.

[TOTAL: 50 marks]