CH 611 Advanced Inorganic Chemistry – Synthesis and Analysis

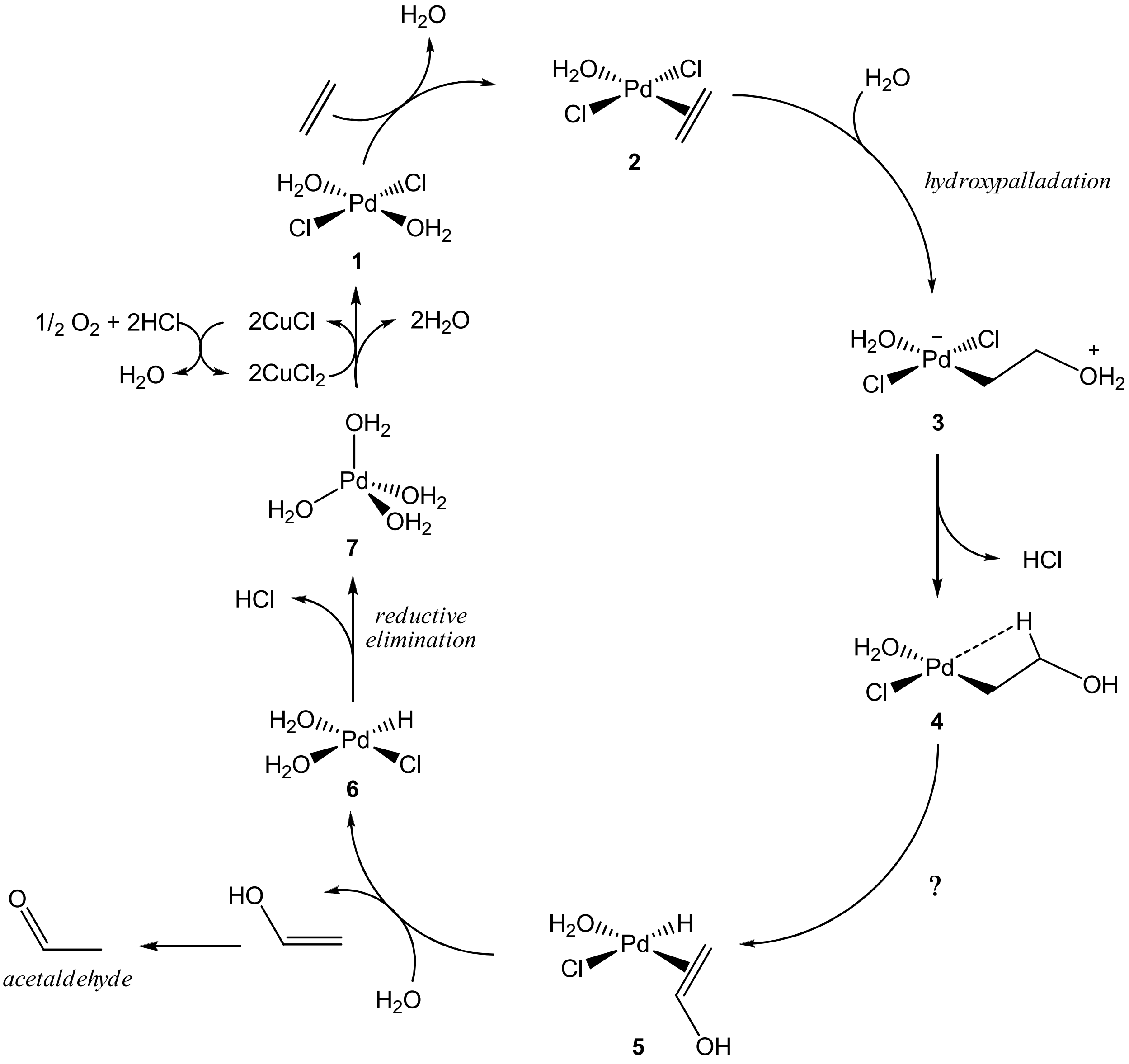
Exam 1 10/14/2009

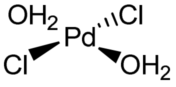
Print Name:__________________________

90 mins to answer all 3 questions. Question 1 carries 30 %. Questions 2 and 3 carry 35 % each.

Question 1

Below is the catalytic cycle describing the *Wacker oxidation* reaction, which is used to produce *ca*. 4 million tons of *acetaldehyde* annually. Using the ionic model, determine the metal oxidation state and total valence electron count of each Pd complex (**1** – **7**). Name the reaction which converts complex 4 to complex 5 (marked ?).

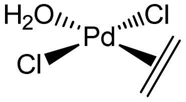




1

Metal oxidation state: +2
Total electron count: 16 electron

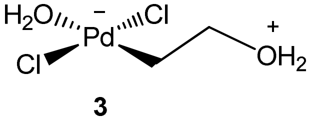
4 points



2

Metal oxidation state: +2
Total electron count: 16 electron

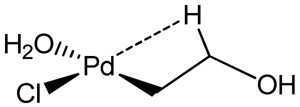
4 points



3

Metal oxidation state: 2+
Total electron count: 16 electron

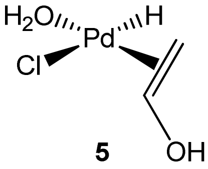
4 points



4

Metal oxidation state: 2+
Total electron count: 14 electron

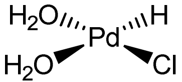
4 points



5

Metal oxidation state: 2+
Total electron count: 16 electron

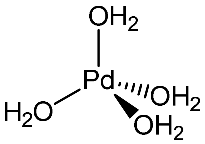
4 points



6

Metal oxidation state: 2+
Total electron count: 16 electron

4 points



7

Metal oxidation state: 0
Total electron count: 18 electron

4 points

Reaction **4** → **5** is a β elimination reaction forming a hydridoalkene complex **5** from an alkyl complex **4.**

2 points

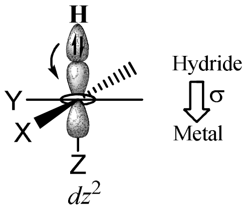
Question 2

a) Using molecular orbitals draw the bonding schemes for the following metal-ligand bonding interactions, inclusive of any π–bonding.

(i) metal hydride

(ligand to metal sigma donation)

This bond can be represented via hydride bonding with the *dz*^{2} or *dx*^{2}-*dy*^{2} orbitals, otherwise it can be represented generically (Hydride σ 2e$^-$ → metal *e*$_g$).



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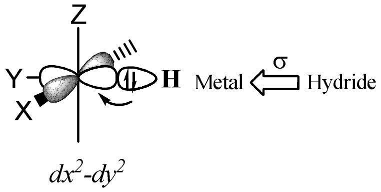

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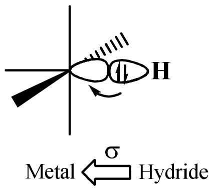
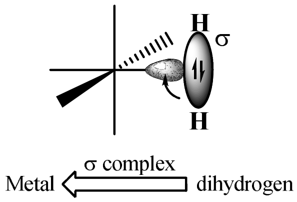


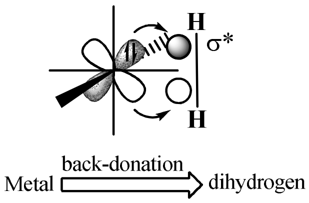
4 points

(ii) metal dihydrogen σ-complex

(ligand to metal σ donation / metal to ligand π back-donation)

This bond can also be represented with a particular geometry as above. A σ–complex is formed by electron donation from the dihydrogen σ-bond with one of the empty *e*$_g$ metal orbitals (*dz*^{2} or *dx*^{2}-*dy*^{2}) and back-bonding occurs from one of the filled *t*$_{2g}$ set of metal orbitals (*dxy*, *dxz* or *dyz*) to the empty dihydrogen anti-bonding σ*-orbital. A generic representation is shown below.

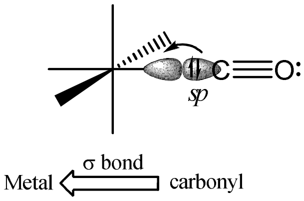


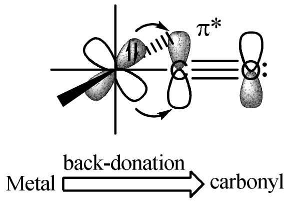


4 + 4 points

(iii) metal carbonyl (ligand to metal σ donation / metal to ligand π back-donation)

This bond can also be represented with a particular geometry as in (i). A σ–bond is formed from the filled CO C*sp* orbital with one of the empty e_g metal orbitals (dz^2 or dx^2-dy^2) and back-bonding occurs from one of the filled t_{2g} set of metal orbitals (*dxy*, *dxz* or *dyz*) to one of the CO anti-bonding π^*-orbitals. A generic representation is shown below.

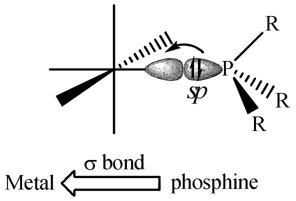


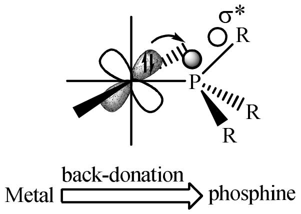


4 + 4 points

(iv) metal phosphine (ligand to metal σ donation / metal to ligand π back-donation)

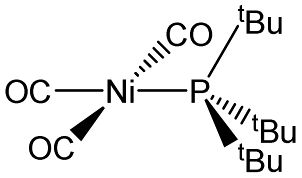
This bond can also be represented with a particular geometry as in (i), however, A generic representation is shown below. A σ–bond is formed from donation of the lone pair on the P atom (*sp* orbital) to one of the empty e_g metal orbitals (dz^2 or dx^2-dy^2) and back-bonding occurs from one of the filled t_{2g} set of metal orbitals (*dxy*, *dxz* or *dyz*) to the P–R anti-bonding σ^*-orbitals.



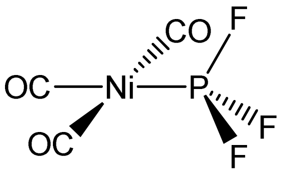


4 + 4 points

b) Using the bonding schemes drawn above for metal carbonyl and metal phosphine complexes explain the difference observed in *v*(CO) by FTIR spectroscopy for the *trans*-CO ligand of the following complexes.

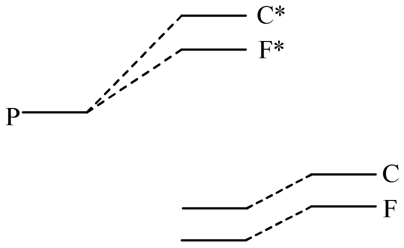


$v(\text{CO})_{\text{trans}} = 2056\ \text{cm}^{-1}$



$v(\text{CO})_{\text{trans}} = 2111\ \text{cm}^{-1}$

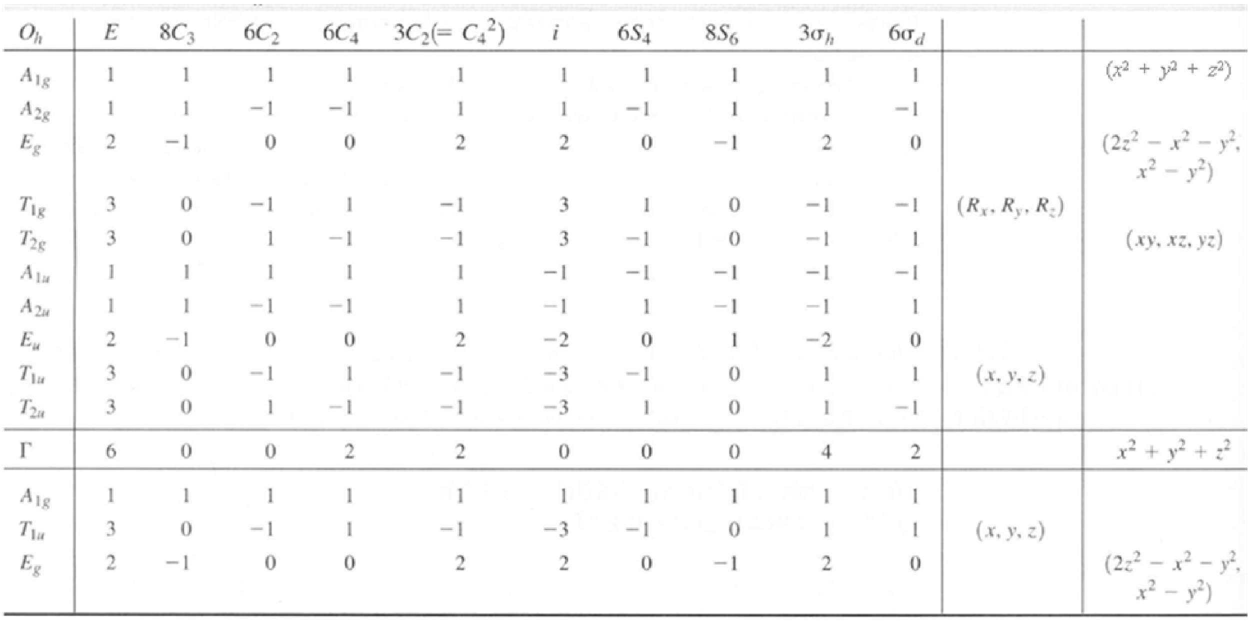
The PF_3 ligand has a lower energy σ* ligand orbital than the $P(^tBu)_3$ ligand due to the greater electronegativity of F *vs.* C. Therefore the PF_3 ligand is a better π-acceptor than the $P(^tBu)_3$ ligand. As a result of this energy difference (shown in MO diagram below) the PF_3 ligand has a greater back-donation from the Ni metal than the $P(^tBu)_3$ ligand and thus decreases the back-donation to the *trans* CO ligand relative to the analogous $P(^tBu)_3$ complex. This decreased back-donation to the *trans* CO ligand in the PF_3 complex results in a stronger C≡O bond and a higher energy stretching frequency in the IR spectrum.



9 points

Question 3

Using the given character table construct a molecular orbital correlation diagram for the O_h complex $Cr(CO)_6$ including <u>only the σ-bonding interaction</u> (indicate the oxidation state of the metal, label all metal valence orbitals with their respective Mulliken symbols, label HOMO and LUMO orbitals).



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$(x^2+y^2+z^2)$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,$ $x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		
Γ	6	0	0	2	2	0	0	0	4	2		$x^2+y^2+z^2$
A_{1g}	1	1	1	1	1	1	1	1	1	1		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,$ $x^2-y^2)$

$Cr(CO)_6$

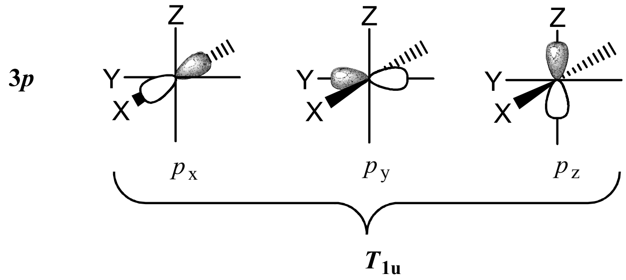
Metal oxidation state = Cr^0 therefore d^6 , i.e. Cr :[Ar] $3d^6$ $4s^0$ $4p^0$

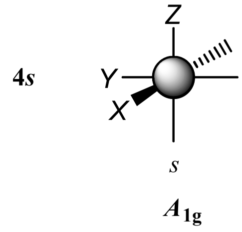
CO is a 2 electron donor, therefore 12 ligand electrons donated in total.

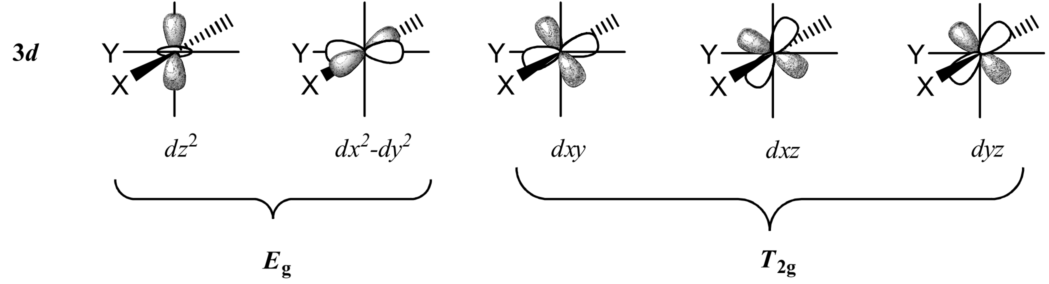
$Cr(CO)_6$ therefore has 18 valence electrons.

3 points

Metal orbitals and corresponding Mulliken symbols in an O_h ligand field:





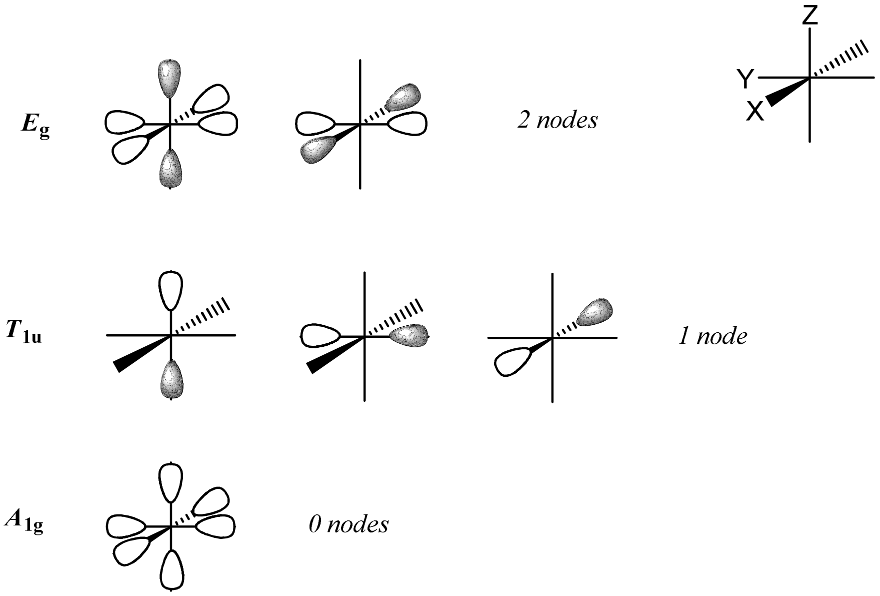


3 + 3 + 3 points

Symmetry adapted linear combination of ligand orbitals (SALCs)

$\Gamma_\sigma = A_{1g} + T_{1u} + E_g$

3 points



7 points

Map ligand SALCs onto metal atomic orbitals using Mulliken symbols

metal ligand (SALCs)

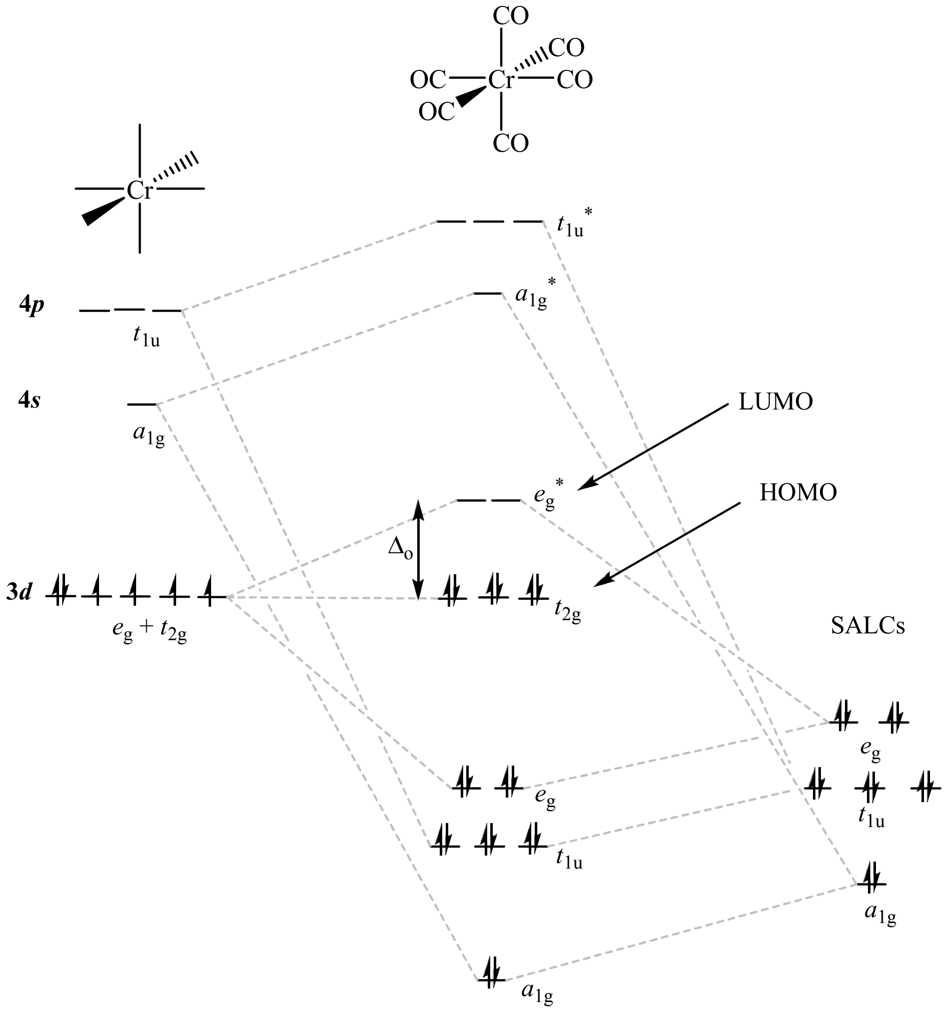
$T_{1u} \xrightarrow{\sigma} T_{1u}$

$A_{1g} \xrightarrow{\sigma} A_{1g}$

$E_g \xrightarrow{\sigma} E_g$

$T_{2g} \longrightarrow$ *non-bonding* (in σ-only consideration)

3 points



Energy level alignment 4 points

Electron filling and LFSE: 3 points

HOMO and LUMO: 3 points