

Cumulative Examination in
Inorganic Chemistry
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- (15 points)
- (18 points). For each of the following molecules and ions, give the formal oxidation state, d^n , and the number of electrons in the valence shell of the metal ion.
 - $[\text{Os}(\text{CN})_5(\text{NH}_3)]^{3-}$
 - $(\text{CO})\text{Cl}_2\text{Re}(\mu_2\text{-dppm})_2\text{ReCl}_2(\text{CO})$. dppm is the bidentate ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2$. There is a triple bond between the Re atoms.
 - cis*- $\text{Pd}(\text{PMe}_3)_2(\text{CH}_3)(\text{OCH}_3)$
 - fac*- $\text{VCl}_3(\text{thf})_3$
 - $\text{Cp}_2\text{W}(\eta^2\text{-C}_2\text{H}_4)(\text{CH}_2\text{CH}_2\text{CH}_3)$
 - CrO_2Cl_2
 - $\text{Cr}(\text{O}_2)\text{Cl}_2$
- (20 points)
 - Based upon Wade's rules, do you expect the cluster compound $\{\text{Mo}(\text{CO})_3\}\text{Pb}_9^{4+}$ to be *closo* or *nido*? Why?
 - Shown below is the structure of $2,3\text{-}\mu\text{-(Cp}_2\text{ClZr)B}_5\text{H}_8$ which appears to be based upon an octahedron with one site unoccupied. Show by electron count that this is a reasonable interpretation of the structure.
- (15 points). When light shines upon the molecular switch $\text{Fe}(\text{phen})_2(\text{NCS})_2$ which has six N atoms in an octahedral array about the Fe(II) center, S increases from 0 to 2 as the number of unpaired electrons goes from 0 to 4. Simultaneously, the Fe-N bond lengths in the molecule grow by about 8%. Explain why this molecule increases in size when the electrons become unpaired.
- (15 points).
 - After much study, Gafney et al. determined that when SnMe_3I interacts with glass to generate a 5-coordinate species in which the three methyl

groups, the iodide and an oxygen atom are all attached to the tin, the structure of this species is as expected. What is the expected structure? Why?

- b. How (mechanism) are the ligands in compounds like PF_5 equilibrated on the nmr timescale?
6. (14 points) In the molecule shown below, the authors indicate that in the NiI_2L_2 ion, where L is a carbene ligand containing the $:\text{CN}_2$ grouping, the CNiI angles are all very close to 90° thus the Ni ion must be a Ni(II) d^8 ion. The result is that the carbene carbon does not increase the formal oxidation state of the metal. What is the difference between carbene ligands that do increase the formal oxidation state of metal ions and those that do not? What are the names of these two types of ligand?