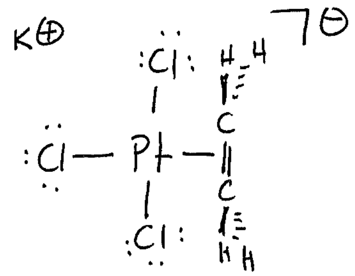
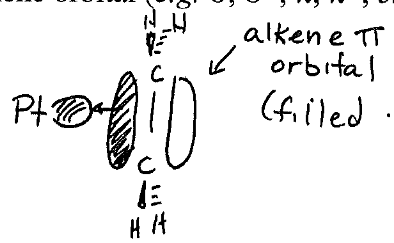
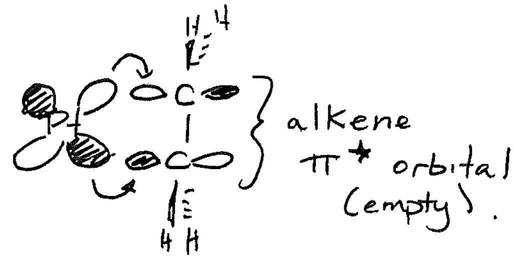
Chemistry 4000/5000
Midterm Examination #1 (October 6, 2021)

1. a) Draw a fully expanded (show every bond and lone pair) Lewis structure for $K^+[Cl_3Pt(H_2C{=}CH_2)]^-$. (5 points)

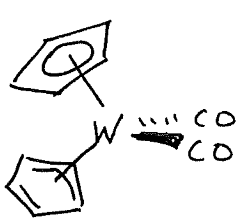


b) Draw all of the bonding interactions between the Pt and $H_2C{=}CH_2$ in question 2a. For each one, name the type of interaction (*e.g.* σ-donation, π-donation, *etc.*) and the type of alkene orbital (*e.g.* σ, σ*, π, π*, *etc.*) involved. (12 points)





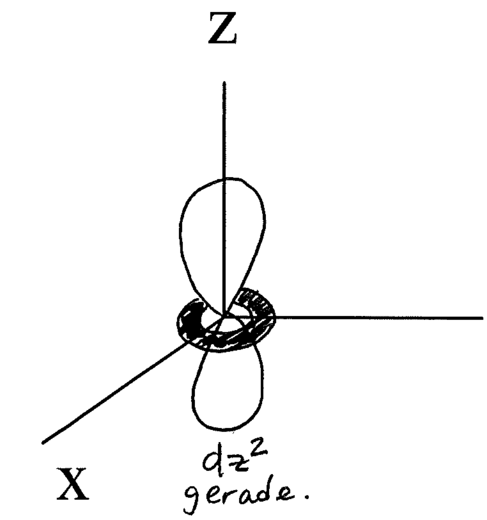
2. State the expected hapticity (hapticity ~ denticity) of each Cp ring in $[Cp_2W(CO)_2]$ and justify your answer. Draw the compound. (12 points)

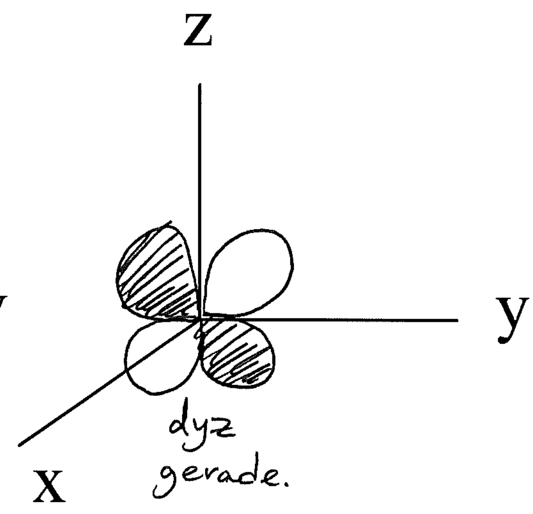


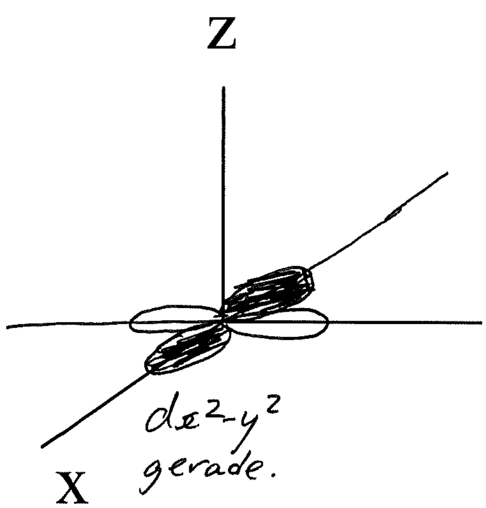
$W(II)\ d^4 \rightarrow 4e^-$
$\eta^5\ Cp^- \rightarrow 6e^-$
$\eta^3\ Cp^- \rightarrow 4e^-$
$2\ CO \rightarrow 4e^-$
$18e^-$

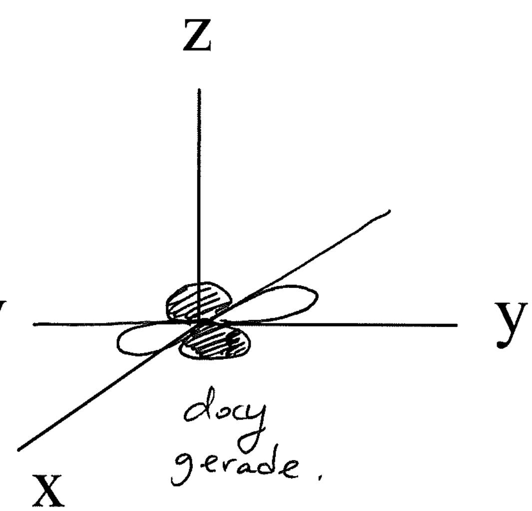
One Cp is η^5 and the other is η^3. As W is in the +2 oxidation state this provides $18e^-$
If both Cp were η^5-bound W would have $20e^-$
↳ as W is a 3rd row metal and ligands include strong π-accepting CO → $18e^-$ rule is expected to be followed.

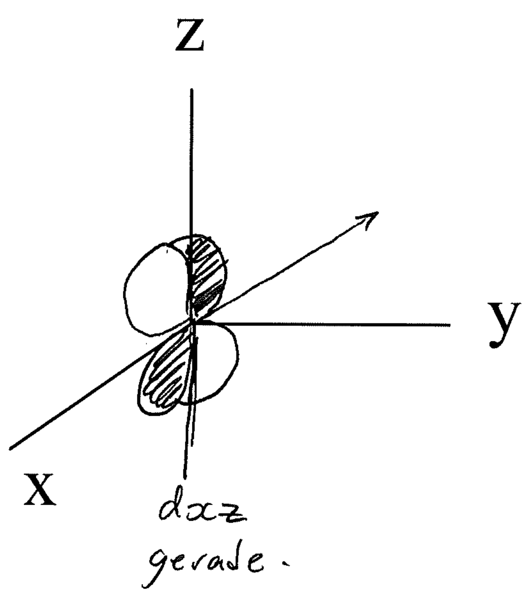
3. Draw and label the d-orbitals. Use the provided axes. Be sure to place signs on the lobes, label each orbital as gerade or ungerade. (15 points).











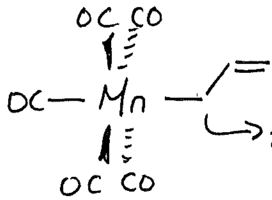
4. Draw the organometallic products of the following reactions - add any explanation you feel is necessary. Identify any by-products. None of the reactants or products **A**-|**C** are present in excess of the amount shown in the equation. However, where formation of a colourless gas or white solid occurs, the number of equivalents of this gas or solid is not specified. (16 points)

a) $[MnBr(CO)_5] + CH_2{=}CH{-}CH_2MgBr \rightarrow$ **A** + white solid

A at 80 ºC → **B** + colourless gas

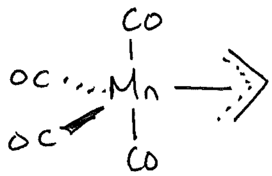
→ both compounds are sterically and electronically saturated

A =



↳ η¹ allyl ↳ 2e⁻
Mn(I) d⁶ } 18e⁻
5CO

B =



← η³-allyl ↳ 4e⁻
Mn(I) d⁶ } 18e⁻
4 CO

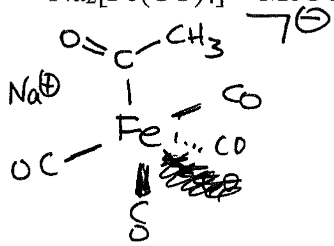
white solid = $MgBr_2$

colourless gas = CO

Graduate Students only (bonus for undergraduate students):

b) $Na_2[Fe(CO)_4] + MeCOCl \rightarrow$ **C** + white solid

C =



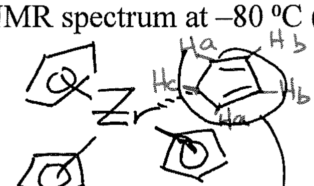
white solid = NaCl

Fe(0) → d8 → 8e⁻
4 CO → 8e⁻
⊖:C(=O)–CH₃ → 2e⁻
18e⁻

5. Given limited ¹H-NMR data, draw the structures for the following two complexes (14 points):

a) $[TiCp_4]$ – 4 signals in the ¹H NMR spectrum at –80 ºC (intesity ratio 10:4:4:2)
b) $[ZrCp_4]$ – 4 signals in the ¹H NMR spectrum at –80 ºC (intesity ratio 15:2:2:1)

Ti(IV) d⁰ 0e⁻
2 η⁵ Cp⁻ 12e⁻
2 η¹ Cp⁻ 4e⁻
16e⁻



Zr(IV) d⁰ 0e⁻
3η⁵Cp⁻ 18e⁻
1 η¹Cp⁻ 2e⁻
20e⁻

→ 5H appear in 3 signals in a 1:2:2 ratio for Hc : Ha : Hb
↳ rotation about Zr–C equilibrates 2 Hb and 2 Ha

Graduate Students only (bonus for undergraduate students):

Also draw the structure for the following complex:

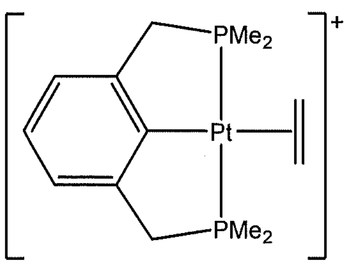
c) $[ThCp_4]$ – a single signal in the ¹H NMR spectrum (–80 to 25 ºC).
d) Give a brief explanation for why the structures of these three complexes are so different. (1 bonus point)

→ Th is much larger than Ti + Zr and can accommodate 4 η⁵Cp⁻ ligands. } all 20 H chemically equivalent due to Cp rotation

→ Zr is in 2nd row so larger than Ti. Hence, it can accommodate 3η⁵Cp⁻ + 1 η¹Cp⁻. Ti has only space for 2η⁵Cp⁻ + 2η¹Cp⁻

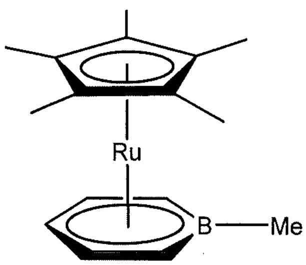
6. Determine the metal oxidation state, the number of d-electrons and the total number of electrons in the following 3 complexes. Briefly explain any choices you make in order to make your assignments. (21 points)

Graduate Students only (bonus for undergraduate students): For any complexes that do not have 18-electrons, give a brief explanation.

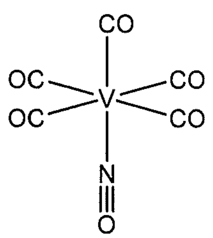


Pt(II) d^8 → $8e^-$
// → $2e^-$
2 PMe_2R → $2\times 2e^- = 4e^-$
(aryl)$:^{\ominus}$ → $2e^-$
$16e^-$

Pt(II) d^8
square planar
↓
$16e^-$ expected



Ru(II) d^6 → $6e^-$
η^5-Cp*⁻ → $6e^-$
(boratabenzene)$^{\ominus}$ B–Me → $6e^-$
$18e^-$



Covalent Bonding Classification → V → $5e^-$
NO^{ℓ} → $3e^-$
5 × CO → $5\times 2e^- = 10e^-$
$18e^-$

Ionic Counting Method: NO^+ ∴ V(−1) d^6

7. The periodic table provided on the last page of this exam paper has 5 missing elements. Add in the symbol and name of the missing elements. (5 points)

Bonus: Ben List + David MacMillan for organocatalysis.

Key:

element name **atomic number** **symbol** atomic weight (mean relative mass)

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	15 P Phosphorus	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	25 Mn Manganese	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	41 Nb. Niobium	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	46 Pd Palladium	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	75 Re Rhenium	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]