UNIVERSITY OF VICTORIA

EXAMINATIONS DECEMBER 2012

Chemistry 423 and 523
Instructor: Scott McIndoe

Final, 2 pm Monday 10th December 2012

DURATION: 3 hours

NAME: _____

STUDENT NUMBER:_____

Answer all questions.
There are **180 marks** and **180 minutes** so ration your time accordingly.
8 pages including cover page and periodic table.
To be answered in booklets.
If you do not know an abbreviation used in this examination PLEASE ASK.

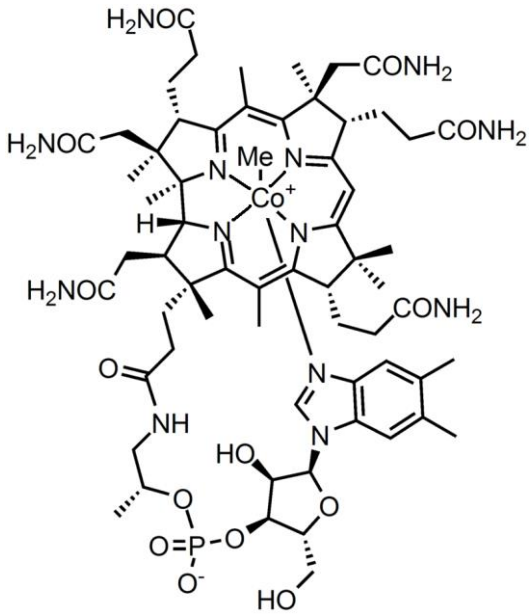
1 IA	2 IIA		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 **H** 1.0079																		2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122		Atomic number **Symbol** Atomic weight										5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305												13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078		21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62		39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 118.71	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-70 †	71 **Lu** 174.97	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** [209]	85 **At** [210]	86 **Rn** [222]
87 **Fr** [223]	88 **Ra** [226]	89-102 ‡	103 **Lr** [262]	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [269]	109 **Mt** [268]	110 **Ds** [281]	111 **Rg** [272]							

†lanthanides	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04
‡actinides	89 **Ac** [227]	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** [237]	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [251]	98 **Cf** [251]	99 **Es** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]

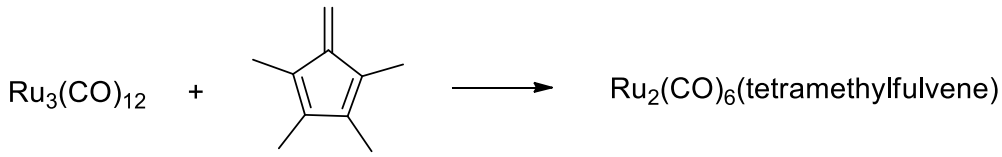
1. The structure of the organometallic complex methylcobalamin (an active form of vitamin B12) is shown to the right.

(a) Identify each of the ligands as X-type or L-type and give the electron count and oxidation state of the Co.
(b) Speculate as to why metal-alkyl bonds are rare in biological systems, and why most examples have Me as the alkyl group.
(c) Methylcobalamin is responsible for the production of highly toxic methyl mercury, $[MeHg]^+$, from biological transformation of mercury. What sort of reaction is this?

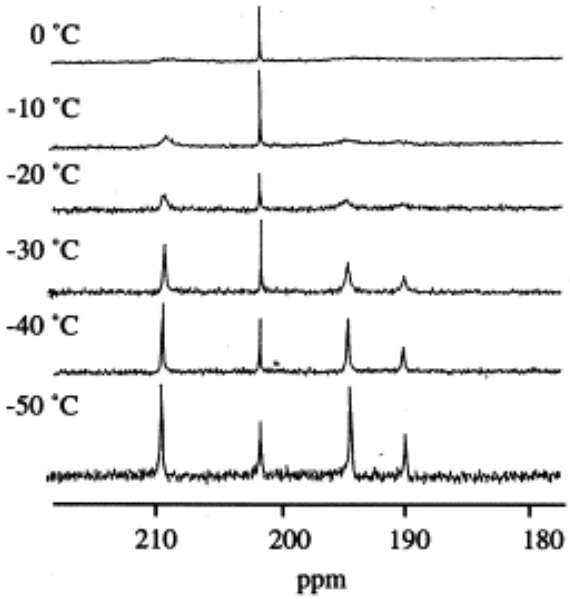
[10 marks]



2. Tetramethylfulvene reacts with $Ru_3(CO)_{12}$ to form a dinuclear complex:



(a) Draw plausible structures for the product, including different possible binding modes for the tetramethylfulvene ligand.
(b) What characterization methods might you use to determine which mode is most appropriate?
(c) The complex displays fluxional behavior (see part of the ^{13}C NMR spectrum below). Define fluxionality, and speculate on what sort of process might be going on to result in these data.



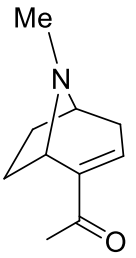
[20 marks]

3. Sketch out a neutral 18-electron structure showing the geometry about the metal center as accurately as you can for the following metals and ligands. Use at least one metal and each type of ligand shown. Try to keep your structure as simple as possible (nothing higher than a bimetallic complex). Ligands are shown without charges; indicate the proper ligand charge and metal oxidation state in your electron counting.

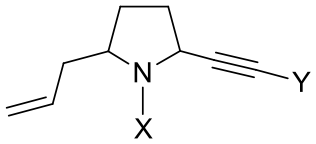
a) W, μ-PR_2, CO, H
b) Hf, Cp, N≡CCH_3, NCH_3
c) Pt, CH, Cl, PMe_3

[15 marks]

4. The molecule (+)-ferruginine is a potent anti-Alzheimer drug, and in February 2004 three different research groups independently published concise routes to its synthesis. All three syntheses used Grubbs' catalyst to transform molecules based on the one shown on the right.



(+)-ferruginine



(a) Draw the structure of Grubbs' catalyst.
(b) Draw a series of catalyzed reactions that lead to the basic framework of (+)-ferruginine. Your reactions should include the structures of intermediates. Note: these reactions are just part of the total synthesis, so the product does NOT have to have all the functional groups in place, just the carbon skeleton of the bicycle.
(c) Name the overall reaction.

[20 marks]

5. Choose **ONE** of the following topics, and give a brief account of the chemistry:

(a) Heck and Sonogashira reactions
(b) Pauson-Khand reaction
(c) Hydrosilylation

[15 marks]

6. Elaborate upon any **TWO** of the following Nobel Prizes for Chemistry:

(a) 2010: "for palladium-catalyzed cross couplings in organic synthesis".
(b) 2005: "for the development of the metathesis method in organic synthesis".
(c) 2001: "for their work on chirally-catalysed hydrogenation reactions".
(d) 1973: "for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds".
(e) 1963: "for their discoveries in the field of the chemistry and technology of high polymers".

[30 marks]

7. Give an account of the strengths, weaknesses, and applications of some of the characterization methods used in organometallic chemistry. You may choose to give a brief summary of many methods or go into more detail on a few.

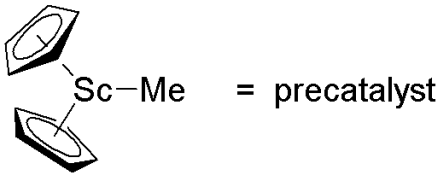
[15 marks]

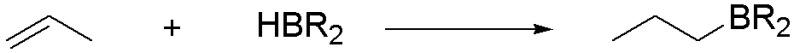
8. Olefin polymerization is responsible for producing over 100 million tons per year of plastic material.

(a) Briefly describe the type of catalysts used in the homogeneous and heterogeneous versions of this reaction.
(b) How are the catalysts activated?
(c) Draw the active catalyst, and indicate how the polymer chain is propagated.
(d) Suggest a possible chain termination step.
(e) Certain single-site catalysts are capable of selectively forming different types of polypropylene. Describe these different types of polymer, and the characteristics of the catalysts that form them.

[20 marks]

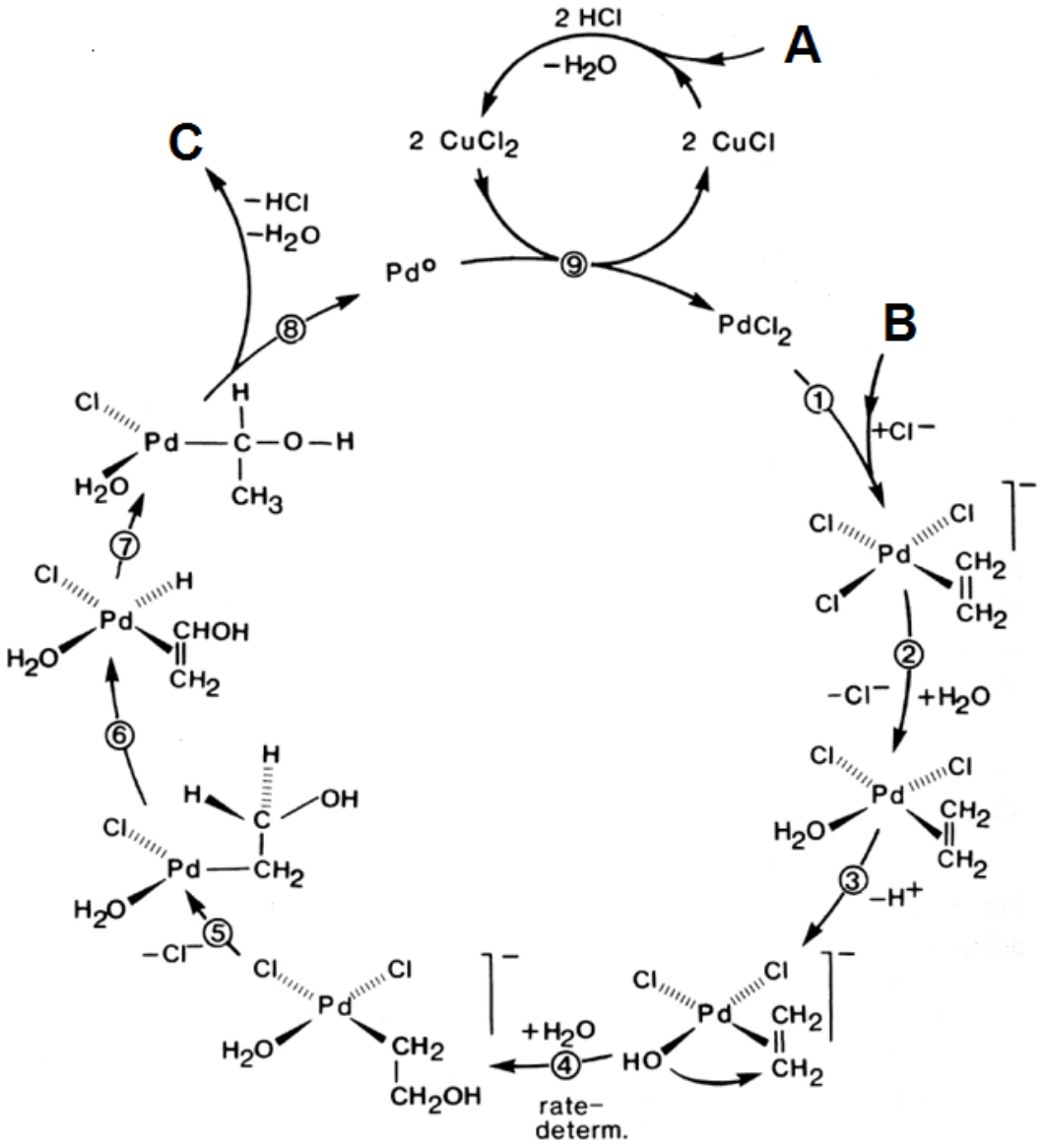
9. Sketch out a reasonable catalytic cycle for the following reaction (hydroboration) and name each reaction step. Make sure the oxidation state of the metal is reasonable. Use the precatalyst complex shown to generate your active catalyst by reaction with HBR_2 (R = alkyl group) to eliminate CH_4 (don't forget to label what this step is called).





[15 marks]

10. Inspect the catalytic cycle below, for the so-called "Wacker process". The reaction is carried out in the presence of air.



(a) Identify **A**, **B** and **C**.
(b) Write down the overall reaction, and describe it.
(c) For each of steps 1-9, name the reaction(s) occurring.
(d) Comment on the changes in Pd oxidation state and electron count during the catalytic cycle.

[20 marks]

END