

UNIVERSITY OF VICTORIA

EXAMINATIONS DECEMBER 2009

Chemistry 423

Final, 9 am Wednesday 9th December 2009

DURATION: 3 hours

NAME: _____

STUDENT NUMBER: _____

Answer all questions.

There are **180 marks** and **180 minutes** so ration your time accordingly.

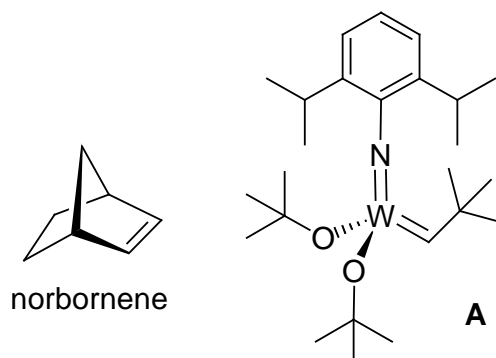
A periodic table is included with this examination.

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																																																																																																																																																																														
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1. The living polymerization of norbornene, catalyzed by **A**, can be halted by the addition of benzaldehyde. The resulting polymer is terminated at one end by $-\text{CH}=\text{CHPh}$ and at the other by $-\text{CH}=\text{CH}^t\text{Bu}$. The byproduct is **B**.



- (a) What type of catalyst is **A**?
- (b) What is a “living polymer”?
- (c) What is the driving force for the polymerization?
- (d) Draw the repeating unit of the polymer.
- (e) Explain the chain termination step.
- (f) Draw the structure of **B**.

[20 marks]

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

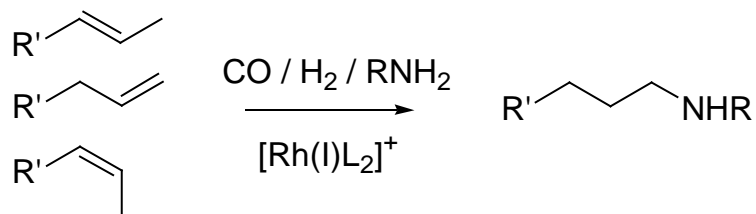
- (a) Pauson-Khand reaction
- (b) Takasago stereoselective isomerization
- (c) Sonogashira reaction
- (d) Monsanto and Cativa processes

[10 marks]

3. Give an account of the uses, strengths, and weaknesses of the various characterization methods commonly used in organometallic chemistry.

[15 marks]

4. The transformation below is called hydroaminomethylation, first reported by Reppe over 60 years ago. There are four stages to this process, all of which occur in the same reaction vessel. Three of these are catalyzed by the same Rh catalyst, $[\text{Rh}(\text{I})\text{L}_2]^+$ (L_2 is a chelating bisphosphine). First, internal alkenes are isomerized to terminal alkenes. Next, the terminal alkene undergoes hydroformylation with a preference for formation of linear instead of branched aldehyde. Third, the aldehyde reacts with a primary amine (without catalysis) to give the imine, which undergoes Rh-catalyzed hydrogenation to the amine in the last step.

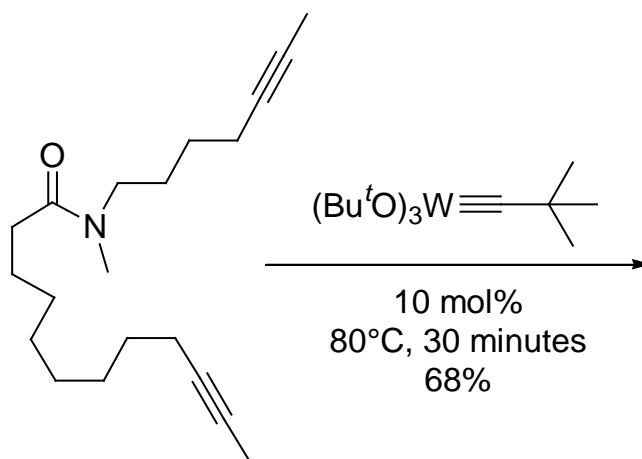


Propose mechanisms for:

- the isomerization of internal to terminal alkenes
- hydroformylation
- hydrogenation of imine to amine.

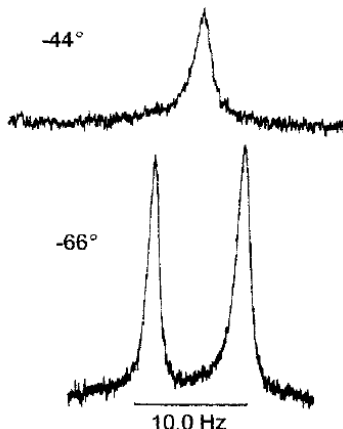
[25 marks]

5. Draw both products of the ring-closing alkyne metathesis reaction below, and show all steps of the mechanism. What is the driving force for the reaction? What are likely byproducts?



[15 marks]

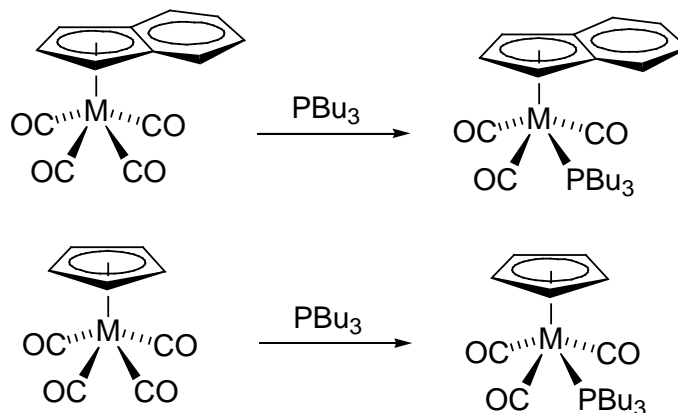
6. At -44°C , the ^1H NMR spectrum of $\text{Fe}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2$ consists of a single peak, but at -66°C it shows two signals:



The IR spectrum is unchanged over this temperature range, and contains peaks in the $2000\text{-}2100\text{ cm}^{-1}$ and $1800\text{-}1900\text{ cm}^{-1}$ regions. Suggest processes that account for these data, and draw all relevant structures.

[10 marks]

7. Consider the reactions below ($\text{M} = \text{Nb, Ta}$).

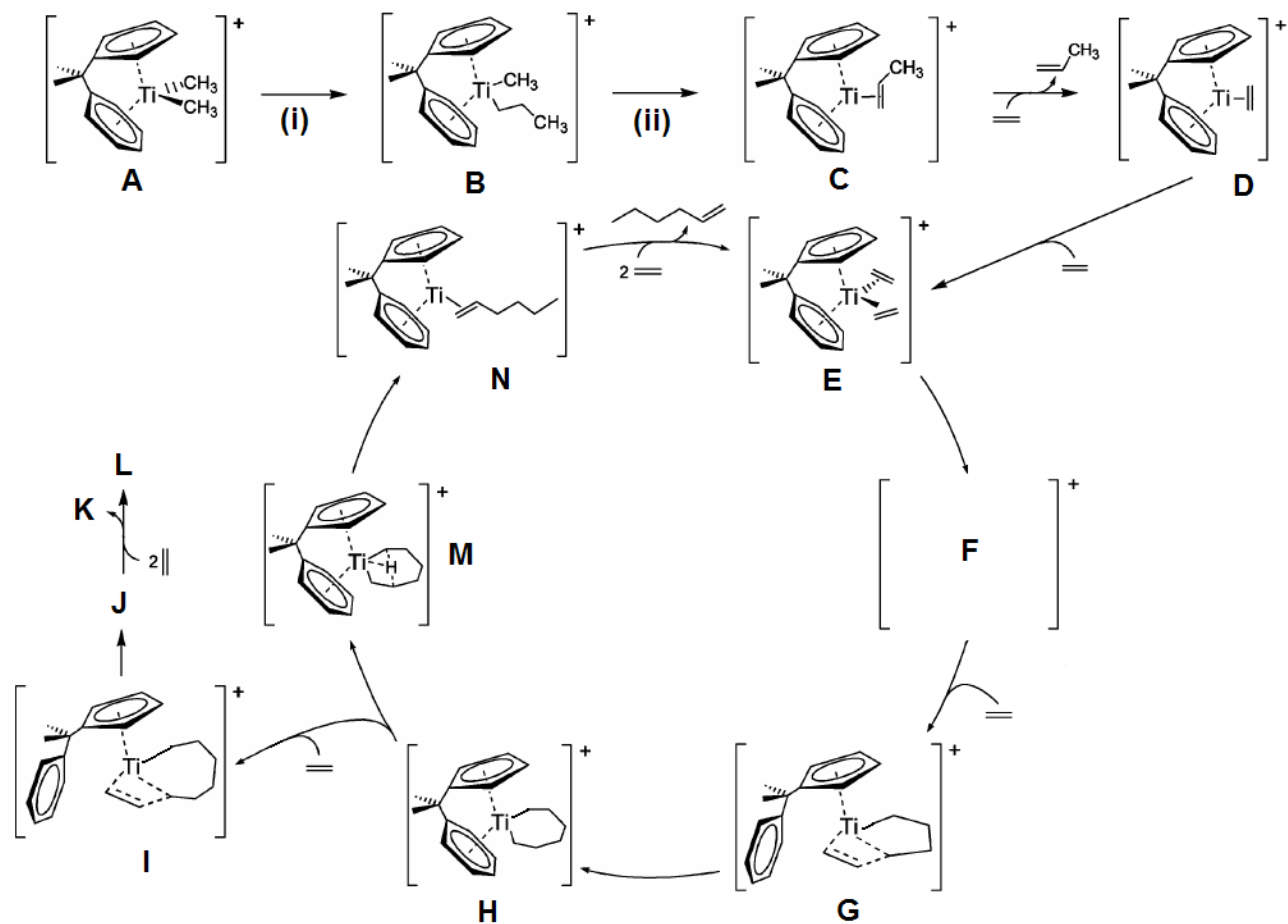


Regardless of the π ligand, the Nb complexes underwent ligand exchange over twice as fast as the comparable Ta complex. The sign of the entropy of activation for ligand exchange was positive or slightly negative for the Nb-Cp and Ta-Cp complexes, but highly negative for either indenyl (Ind) complex. Moreover, rates of ligand exchange were generally faster for the indenyl complexes than for the Cp complexes.

Propose mechanistic pathways for ligand exchange that account for the differences in rate between Cp-M and Ind-M complexes.

[15 marks]

8. Inspect the catalytic cycle below.



- What reagent has been added in step (i)? Describe the reaction.
- What process(es) does step (ii) represent? What is the other product of the reaction?
- Draw the structures of **F**, **J**, **K** and **L**.
- Give the generic terms for species **A**, **E** and **K**.
- Give the oxidation states of Ti in all compounds that contain this element.
- Give the electron counts for **A**, **D** and **E**.
- What is the overall reaction being catalyzed here?
- Which of structures **A-N** represent transition states?

[25 marks]

9. Elaborate upon any **THREE** of the following subjects: (a) the Stille reaction, (b) Schrock alkylidenes and alkylidynes, (c) chiral phosphine ligands, (d) 1973 Nobel Prize in Chemistry, (e) dihydrogen complexes and agostic complexes, (f) self-healing polymers, (g) organometallic compounds in medicine, (h) organolanthanide chemistry.

[45 marks]