NTNU
Institutt for kjemi

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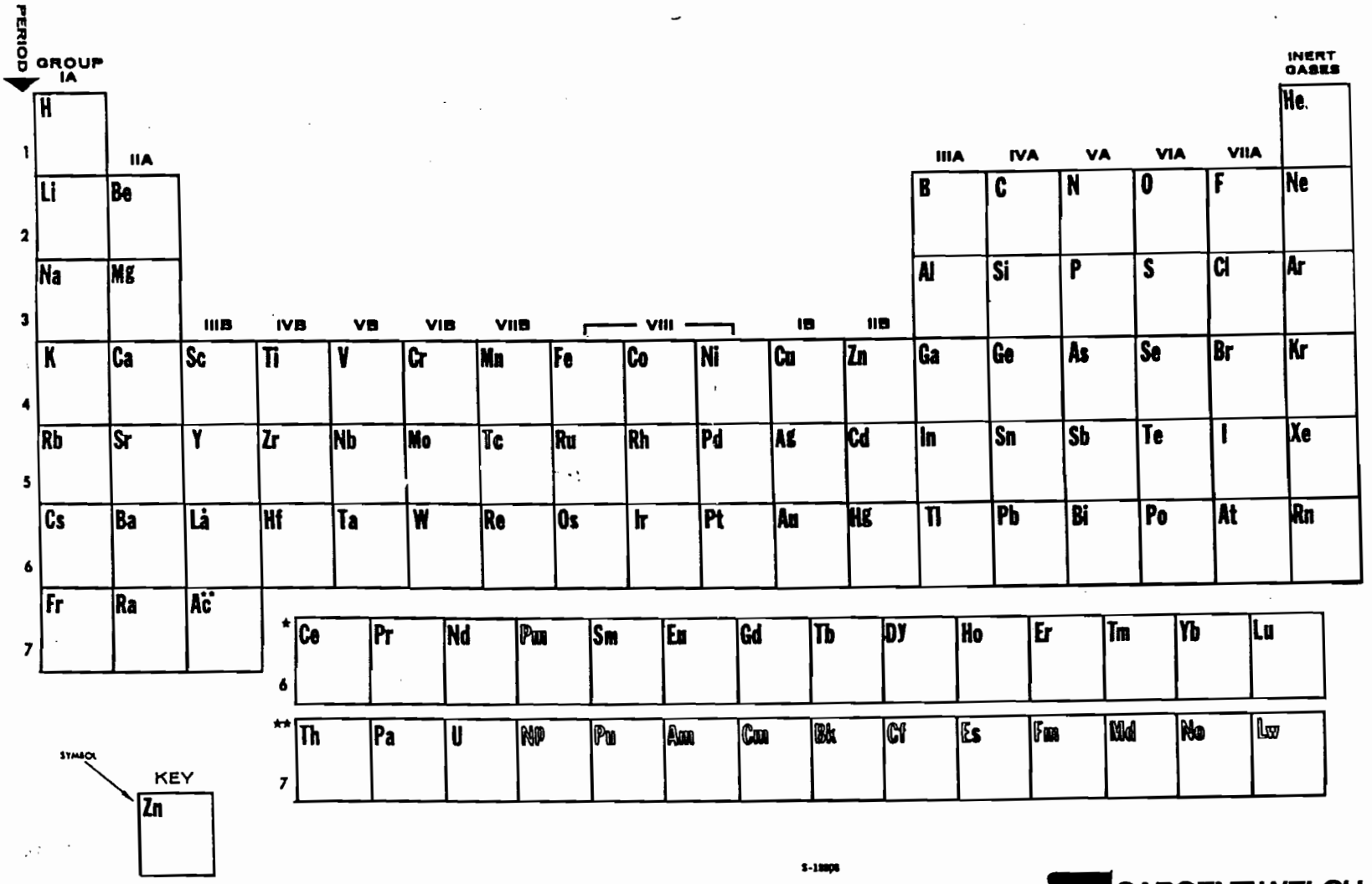
Exam in KJ8105
Organometallic compounds in organic synthesis

Friday 9. December 2005
kl. 0900 – 1300

Permitted tools: D – No printed or written text is permitted.
Molecular models are permitted.

TABLE OF PERIODIC PROPERTIES OF THE ELEMENTS



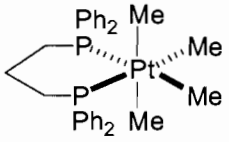
S-18805

SARGENT-WELCH
SARGENT-WELCH SCIENTIFIC COMPANY

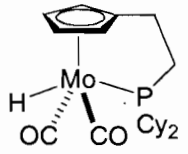
Problem I (*25 points*)

For each of the following compounds, give: (i) Number of electrons in the valence shell of the metal.
(ii) Oxidation state of the metal.

(1)

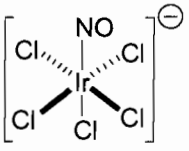


(2)



Cy = cyclohexyl

(3)



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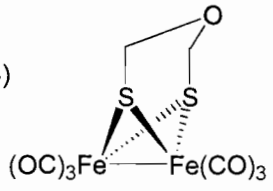

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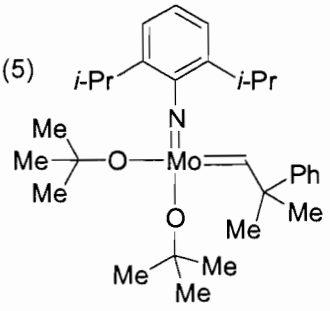

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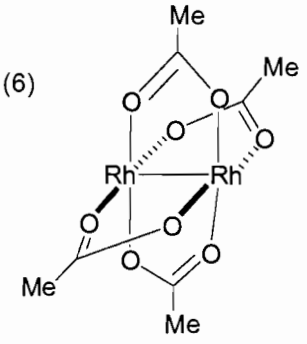
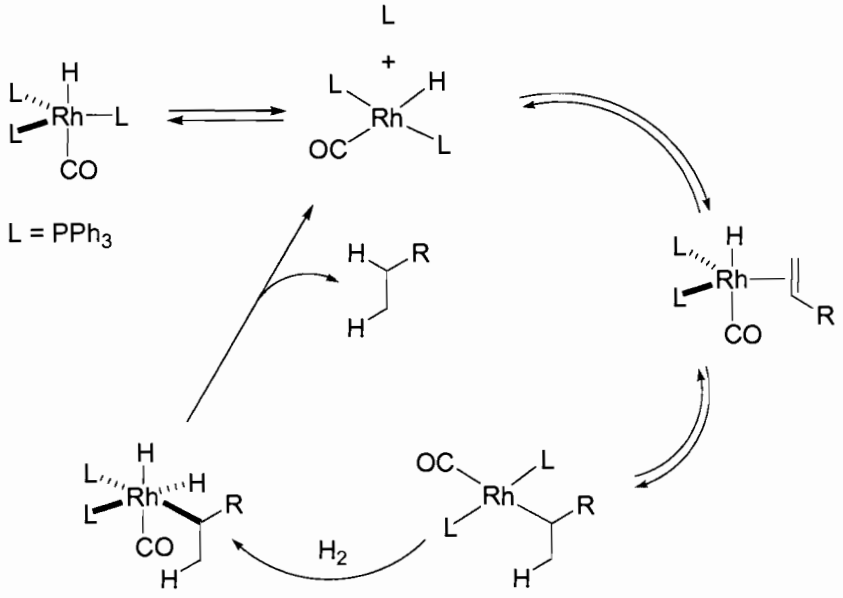
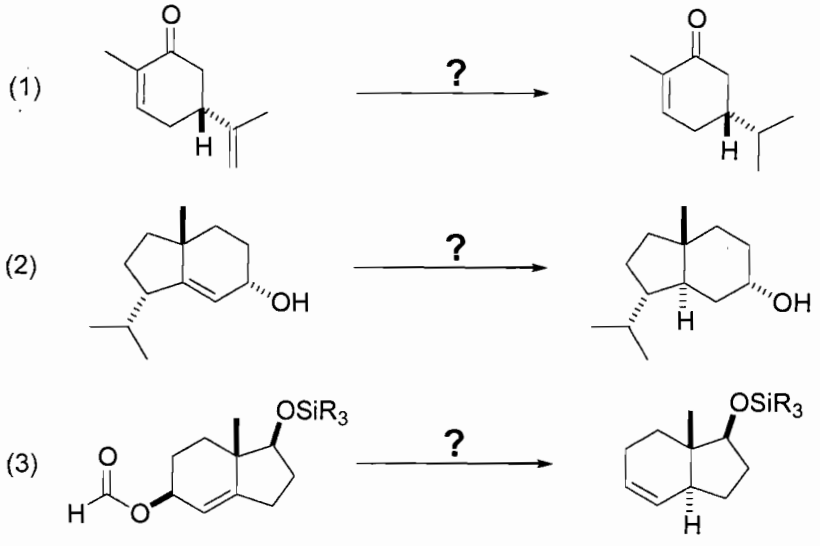


Problem II (*25 points*)

(a) A catalytic cycle for the reduction of olefins with a monohydride catalyst is shown below. Name the elementary steps involved in the cycle. What is the major limitation in using this catalyst for catalytic hydrogenation of olefins?



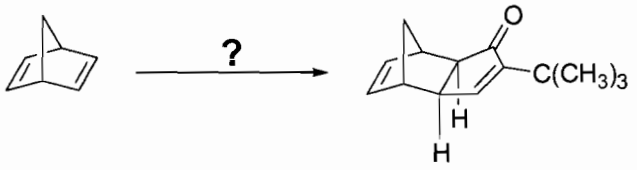
(b) Give appropriate catalysts/reagents for the following reductions:



Problem III (*25 points)*

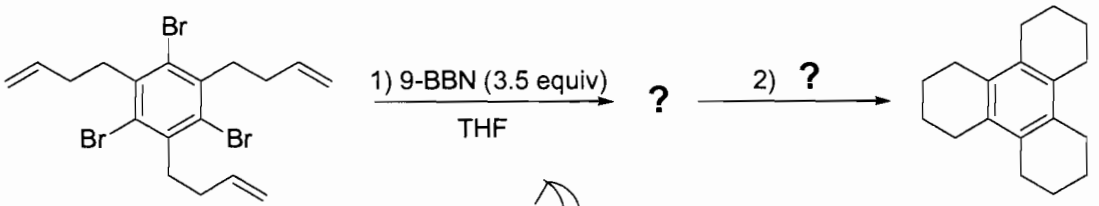
Show the reagents and products missing in the following transformations:

(1)



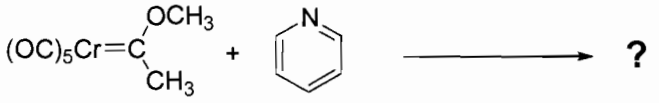
Org. Lett. **2005**, *7*, 3033

(2)



J. Organomet. Chem. **2005**, *690*, 5389

(3)



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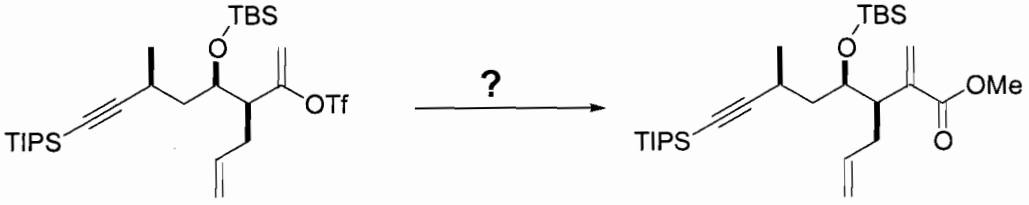
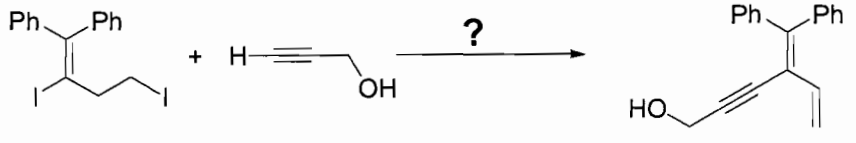


TBS = $Si(Me)_2tBu$
TIPS = $SiPh_3$

Org. Lett. **2005**, *7*, 4621

(5)

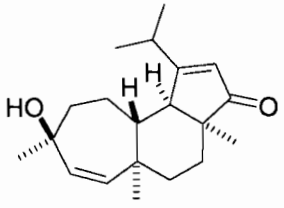


J. Org. Chem. **2005**, *70*, 8635

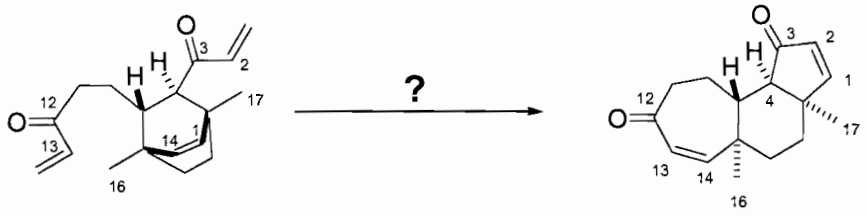
Problem IV (*25 points*)

(a) Matthew W. B. Pfeiffer and Andrew J. Phillips have recently described a total synthesis of (+)-cyanthiwigin U. This compound belongs to a class of diterpenes for which biological activity ranging from cytotoxicity to inhibition of *Mycobacterium tuberculosis* has been reported.

An important step in the synthesis is shown below. Show how this reaction may be performed, including the necessary reagents. Write out a plausible mechanism for the reaction.

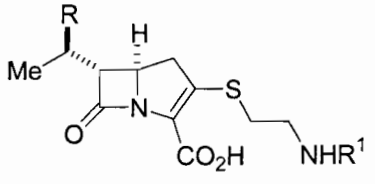


cyanthiwigin U



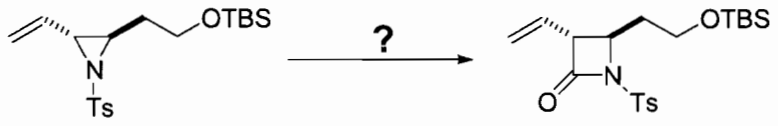
Pfeiffer, M. W. B.; Phillips, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 5334

(b) Since their discovery in the mid-seventies the carbapenems, e.g. (+)-thienamycin (**1**) and (+)-PS-5 (**2**), have attracted great attention, due mainly to their unique activities as broad spectrum antibiotics but also to their challenging structural features.



1 R = OH, R^1 = H
2 R = H, R^1 = Ac

David Tanner and Peter Somfai have published a total synthesis of **2** where the key step is shown below. Give the reagents and the mechanism for the transformation. The mechanism should explain the stereochemical outcome of the reaction.



Ts = *p*-MePhSO$_2$
TBS = Si(Me)$_2$*t*Bu

Tanner, D.; Somfai, P. *Bioorganic & Medicinal Chemistry Letters*, **1993**, *3*, 2415

Good luck!!

ORG