

### Problem Set 5

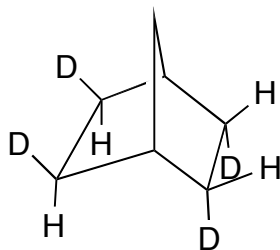
General Instructions: Do not use primary literature.

1. From the mechanism discussed in class for the asymmetric hydrogenation by (dipamp)RhS<sub>2</sub><sup>+</sup>, derive an expression that could be used to predict the ee as a function of [H<sub>2</sub>], and show that it reduces to the values given in class for the limiting cases of very high or very low hydrogen pressure. Calculate the ee if the reaction were carried out with [H<sub>2</sub>] = 0.1 M (which would correspond to a pressure of around 50 atm).

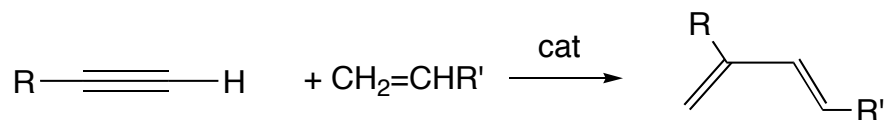
2. The complex [Rh(norbornadiene)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> is a useful pre-catalyst for hydrogenations. A solution containing 1 mol hex-1-yne and 1 mmol of the complex in acetone was exposed to 1 atm of H<sub>2</sub>, and the consumption of H<sub>2</sub> was measured volumetrically while the organic contents of the solution were determined by gc. The following results were obtained:

Time	H <sub>2</sub> consumed	hex-1-yne	hex-1-ene	hexane	norbornene	norbornane
5 min	0.75 mol	0.25 mol	0.75 mol	trace	1 mmol	0
1 h	1.5 mol	0.5 mol	0.5 mol	0	1 mmol	0
10 h	2 mol	1 mol	0	0	0	1 mmol

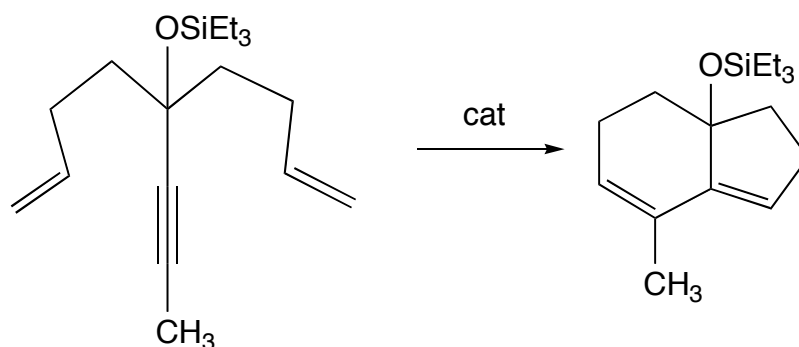
Furthermore, when the reaction was carried out with D<sub>2</sub> instead of H<sub>2</sub>, the norbornane obtained at the end of 10 h was found to consist of a single isotopomer, the di-exo-di-endo-d<sub>4</sub> isomer shown below. Propose a reaction scheme and explain how it can account for all of these observations.



3. Alkylidene complexes have been found to catalyze reactions of olefins with acetylenes to give dienes, as in the following example:

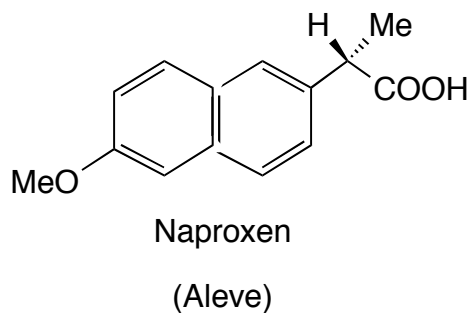


where cat = the Grubbs Ru metathesis catalyst discussed in class. Propose a mechanism for this transformation, as well as the related one shown below:



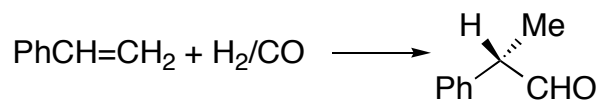
4. There has been a good deal of interest in asymmetric hydroformylation as a route towards chiral products, but so far only very limited success.

a. Show how you might produce enantiomerically pure Naproxen via asymmetric hydroformylation.



b. The best ligand-metal combination for asymmetric hydroformylation of styrene gave ee's as high as 80%, but only at very high hydrogen pressures. Write a mechanism for this process and

comment on the implications of the high-pressure requirement for relative rates of individual steps.



c. Suggest a general reason for the difficulty in achieving good ee's for transformations such as the above.

5. Propose a mechanism for the following reaction:

