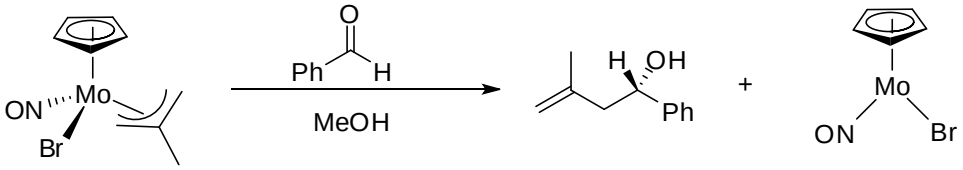
Organometallic Chemistry Name:____Regis Philbin_____
Problem Set #6
Due: Nov. 17, 2011

CHE-334: Complete 3 of 4 questions. CHE-534: Complete all 4 questions.

1. Answer the questions below about the following reaction.



J. W. Faller, et al. *Organometallics*, **1993**, *12 (4)*, 1434–1438.

a) Provide the oxidation state of the metal, the d^n count, the total electron count and the coordination number (CN) for the starting organometallic complex.

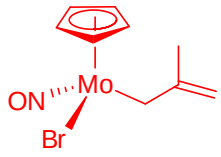
Mo(+2); d^4; 18 total e-'s; CN=7

b) What type of reaction is shown?

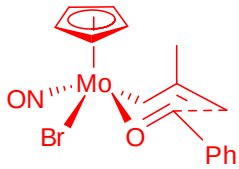
This is an electrophilic abstraction because the benzaldehyde electrophile is removing the allyl ligand from the Mo complex.

c) The reaction is believed to proceed through an η^1-allyl complex and then an ordered, thermodynamically favored transition state. Draw these two intermediate complexes in the space below.

η^1-allyl complex

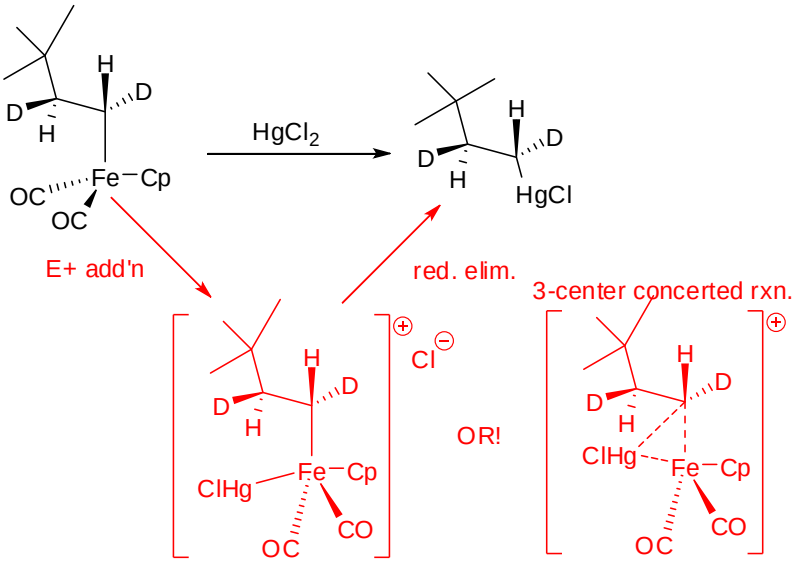


ordered transition state (Zimmerman-Traxler transition state)

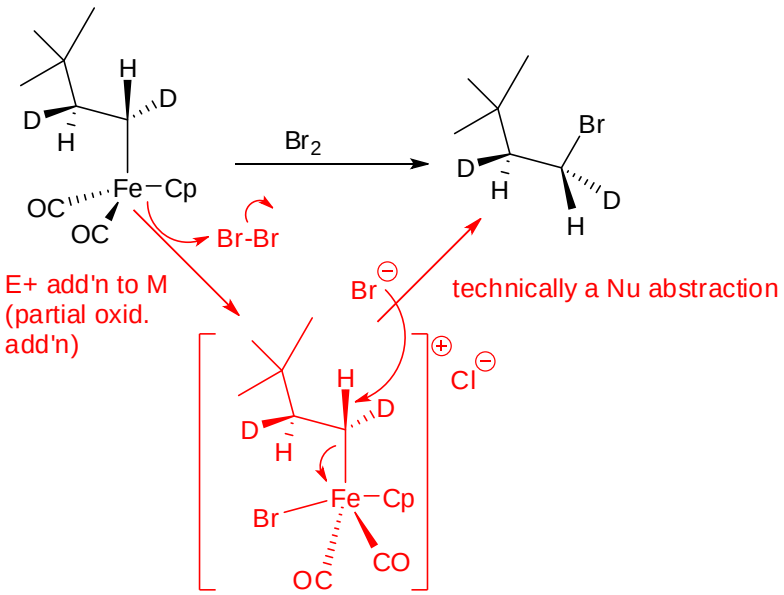


2. Metal complexes with d electrons can undergo electrophilic abstractions by two different pathways. The two paths have been discriminated by stereochemical analyses of products from a chiral alkyl-metal complex. In one pathway, retention is seen, while the second pathway affords inversion of stereochemistry at the chiral carbon bound to the metal. Two reaction examples with stereochemically different outcomes are shown below. Devise a mechanism for each that rationalizes the stereochemical outcome.

a)

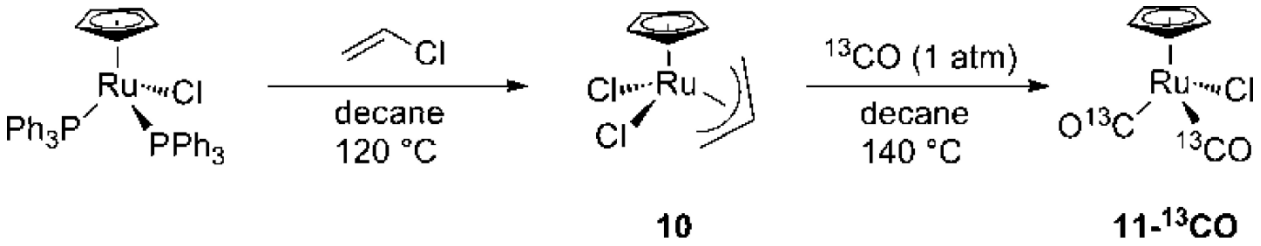


b)



G. M. Whitesides et al. *JACS* **1974**, *96*, 2814 and 2826.

3. The following reaction was recently reported in the journal *Organometallics*. Answer the questions below about the reaction and related course topics.



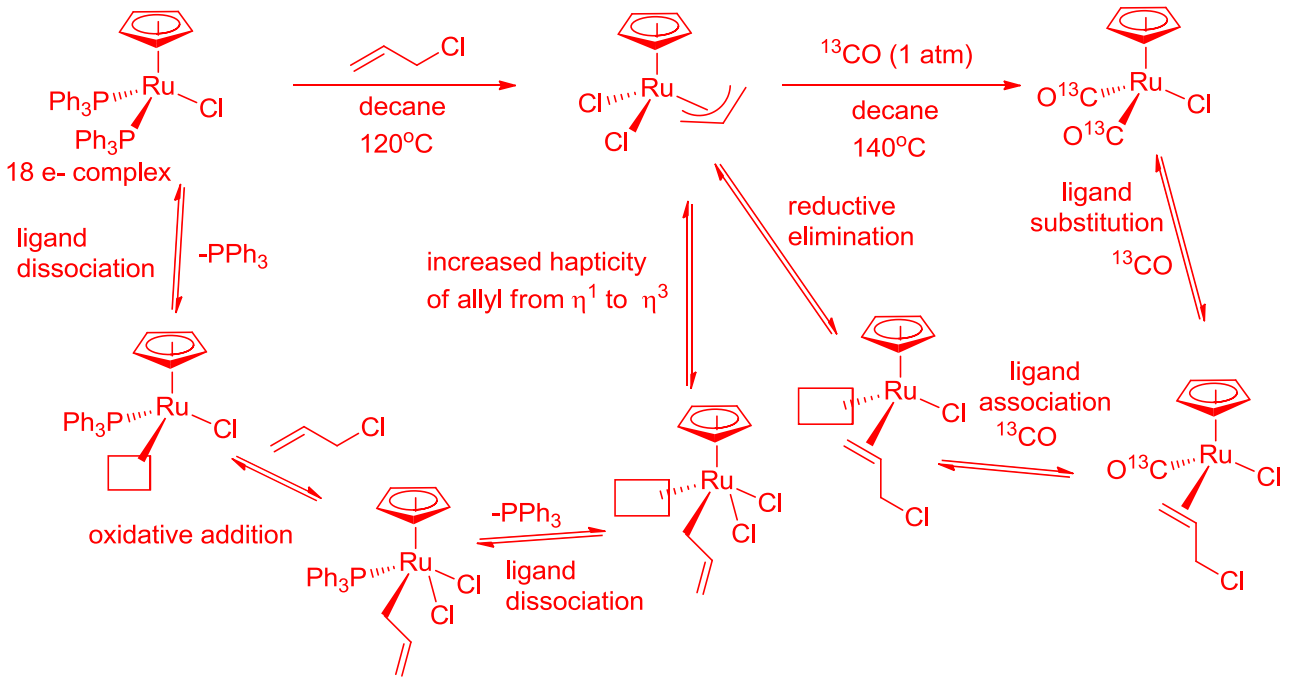
10 **11-^{13}CO**

Daniel Serra, Marie C. Correia, and Lisa McElwee-White Organometallics, **2011**, *30 (21)*, 5568–5577.

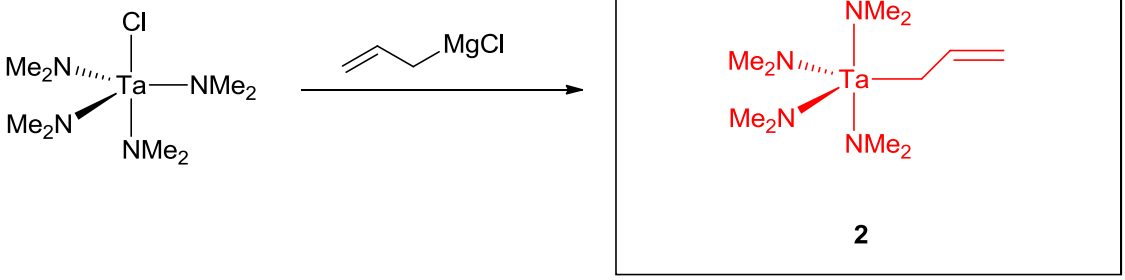
a) True to form, the authors, reviewers and journal disrespected the organic molecules! What a travesty! Find the mistaken organic structure.

The three carbon allyl group (CH_2=CH-CH_2^+) on the Ru complex cannot be derived from the two carbon vinyl chloride (CH_2=CH-Cl) shown. The organic reagent over the arrow should be allyl chloride, CH_2=CH-CH_2-Cl!

b) The small steps leading from the starting material to complex **10** and then on to **11-^{13}CO** were not shown. Fill in the details by proposing a more complete mechanism of this process. Draw all intermediates and identify all mechanistic steps.

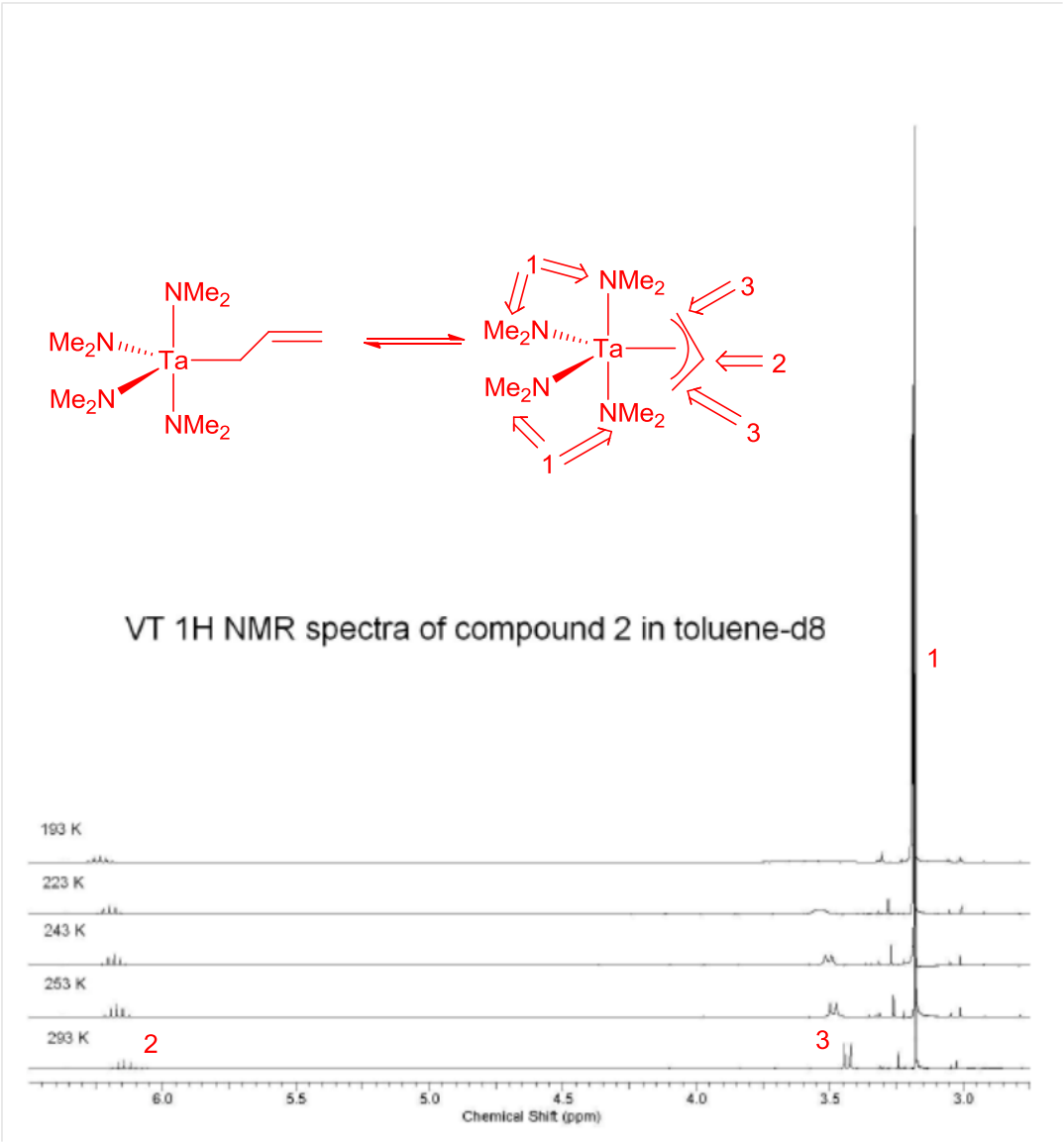


4. The reaction below was recently reported in the journal *Organometallics*.
Michael B. Hall, Michael G. Richmond et al. Organometallics, 2011, 30 (21), pp 5832–5843.
a) Provide the product, **2**, of the reaction in the box below.



2

b) The ^{1}H NMR spectrum and variable temperature study are shown below. Assign all three ^{1}H signals to the structure **2** as seen in the room temperature spectrum: ^{1}H NMR (C_7D_8, 298 K): δ 3.18 (s, 24H), 3.41 (d, 4H, ^{3}J = 11.3 Hz), 6.14 (quintet, 1H, ^{3}J = 11.3 Hz). (Note: other signals were due to impurities or residual protonated solvent.)



c) Based on your analysis and assignment of the NMR, what is happening in the complex 2?

Complex **2** is undergoing fluxional behavior that causes the η^1-allyl group to change to η^3-allyl and back to η^1-allyl. This causes the two CH_2 signals in the allyl group to become equivalent and have only one signal in the NMR.

d) The ^{13}C NMR of compound **2** has the following signals: ^{13}C NMR (C_6D_6): δ 47.26, 88.37, 138.37. Assign these as well.