Homogeneous Transition-Metal Catalysis SS 2014

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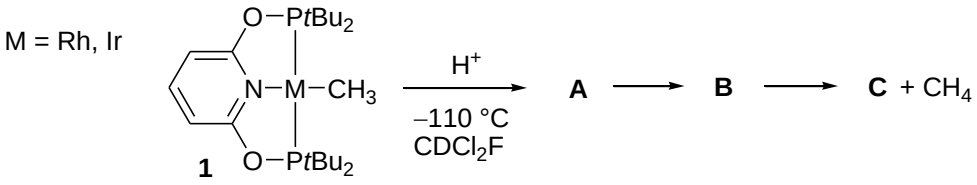
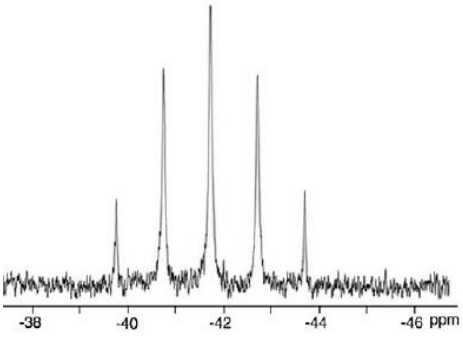
Problem set 2

Question 1

Complex **1** (^{13}C-labeled CH_3) was treated with acid (Brookhart *Science* **2009**, *326*, 553)



The product showed the ^{1}H-coupled ^{13}C-NMR spectrum pictured:



M = Rh: δ −41.7 ppm (quintet, J_{CH} = 124.2 Hz)

M = Ir: δ −20.6 ppm (quintet, J_{CH} = 93 Hz)

CH_4 (for comparison): δ −4 ppm (quintet, J_{CH} = 125 Hz)

Upon warming the initially formed product decomposes into **C** and methane.

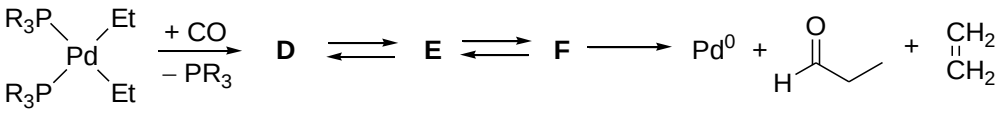
a) Suggest a simple preparation of complex **1**.

b) Suggest plausible structures for **A**, **B**, and **C** (lecture!).

c) Assign the structure of the initially formed product for the Rh and Ir complex with the help of ^{13}C NMR spectral data given.

Question 2

Complete the missing structures. What elementary reaction steps are involved?



Question 3

In the Eastman Acetic Anhydride Process, methyl acetate is carbonylated to acetic anhydride using a rhodium catalyst and lithium iodide as additive. The entire process is very similar to the Monsanto Acetic Acid process. Suggest a plausible mechanism for this reaction. How could you experimentally test your hypothesis?

Literature:

Hydrogenations: Pfaltz *Acc. Chem. Res.* **2007**, *40*, 1402

Dehydrogenation: Brookhard, Goldman *Chem. Rev.* **2011**, *111*, 1761

Corrections.

There was a mistake in the mechanism of the C-H borylation that I put on the board last Friday. Find the corrected mechanism below.

Lit: Marder, Hartwig *Chem. Rev.* **2010**, *110*, 890