The Bergman and Arnold groups as UC-Berkeley recently published a fascinating paper (*JACS* **2011**, *133*, 14904–14907) in which high-valent niobium catalysts accomplish the semihydrogenation of alkynes by an unusual mechanism. After reading the attached paper, work with your group to propose answers to the following questions.

1. What is the reported reaction and what is its significance?
2. How is this transformation typically performed? What are typical side products related to this method?
3. What is the most common reactivity of alkynes with low-valent early metals (such as Nb(III))?
4. What experimental result(s) [prior to those in this manuscript] led the investigators to consider the Nb(III) complex presented here as an alkyne hydrogenation catalyst?
5. What is the role of CO in the reported reaction?
6. The authors report a couple of side products observed under low CO loadings. What are they and how do they form?
7. The authors claim that a higher νCO (observed by IR spectroscopy) indicates a high oxidation state? Why does **3a** have a higher effective oxidation state than **1**? How does νCO show this? How would we expect a high effective oxidation state to affect the proclivity of **3a** to oxidatively add H2 (an important step in Scheme 1, Pathway C)?
8. What do experiments under a mixture of H2 and D2 show about the mechanism of hydrogenation?
9. Why do the authors claim that neither mechanism from Scheme 1 is likely to be operative for this system?
10. How is the H–H bond broken in the reaction that is reported? What evidence do the authors provide to support this mechanism? How convincing are their arguments?

Question for further discussion:

\* The authors note that the isocyanide stretch in **3b** is 2167 cm–1, compared with 2125 cm–1 in free *t*-BuCN. How is it possible that the C≡N bond is stronger in **3b** than in free *t*-BuCN? What does this suggest about the niobium center in these alkyne adducts?