**Diverting Wilkinson's Catalyst: Critical Analysis of a Literature Paper**

Wilkinson’s catalyst is arguably the oldest and best studied homogeneous organometallic catalyst, which might make you think we already know everything about its behavior. However, Perea-Buceta *et al.* recently published an interesting paper (*Angew. Chem. Int. Ed.* **2015**, 14321) showing that certain nitrogen bases will divert Wilkinson’s catalyst into a much more reactive form. Read their paper (attached) and answer the following questions.

1. In Table 1, we see several studies on the effect of added base on hydrogenation of an internal alkyne by Wilkinson’s catalyst. There’s a lot we can learn from this table. Specifically:
   1. Start by drawing Lewis structures for TMP, PhTMP, and TMG, which are not drawn in the paper.
   2. The authors claim that the base plays a Brønsted role (deprotonating Rh–H) rather than a Lewis role (coordinating to Rh). What information in this table (and pKa information given in the text) supports this conclusion?
   3. Every set of conditions gives significantly more *Z* alkene than *E*. Is this a kinetic or thermodynamic phenomenon? If kinetic, then how does the mechanism favor *Z* alkene?
   4. Entry 6 seems to be an outlier, in that it is the only case where added base significantly hurts the reaction. Propose a reason why this might be the case.
2. Examine Table 2, which expands the substrate scope. In general, we see that addition of **12** leads to significantly higher yields of the fully hydrogenated product, but there are some exceptions:
   1. For substrate **2d**, why is a good yield obtained in the absence of base (unlike **2a**–**2c**) but a terrible yield is obtained in the presence of **12**?
   2. Explain why similar yields are obtained for substrate **2e** with and without base but **2f** shows a sharp divergence.
3. Figure 1 details some cool NMR studies showing the reaction of Wilkinson's catalyst with H2 and subsequent reaction with **12**. Carefully analyze these spectra (note that larger and clearer versions are available in the supporting information: <http://onlinelibrary.wiley.com/store/10.1002/anie.201506216/asset/supinfo/anie_201506216_sm_miscellaneous_information.pdf?v=1&s=6b549d9feb2306496016a4fc1f611fa10086cfe4>), showing how they are consistent with the assignments by answering the following questions:
   1. 1H and 31P NMR spectra of complex **14** are presented in Figure 1a and 1b. Why do we see three peaks for Rh–H and three peaks for Rh–P when there are only two hydrides and two distinct phosphine environments?
   2. In Figure 1b, we see that the peak for Ptrans is very broad, whereas the peaks for Pcis are sharp (NOTE: Pcis represents the two phosphines that are *cis* to both hydrides and Ptrans designates the phosphine that is *trans* to the blue hydride in Figure 1). Why is Ptrans so broad? Think about dynamic processes that might result from different coordination environments of the two centers.

**HINTS about organometallic NMR:**

* **31P and 103Rh are highly abundant, I = ½ nuclei just like 1H. When you look at a 31P NMR spectrum it will show you one peak per unique phosphorus center, but these peaks can be split just like 1H by coupling to other I = ½ nuclei.**
* **When a spectrum is reported like 13C{1H}, this means that the observed nucleus (in this case carbon-13) is decoupled from the nucleus in brackets (1H here), so no coupling between those nuclei should be observed.**
* **Late-metal hydrides often show up very upfield, possibly as negative as –40 ppm, depending on the environment.**
* **Nuclei that are in fluxional environments tend to show broader peaks, which are basically averages of the multiple environments.**
* ***J* is used to indicate a coupling constant. *Trans* couplings through metals are generally much stronger than corresponding *cis* couplings.**

1. The authors report that reaction of (PPh3)3Rh(H) with H2 at low temperature leads to the trihydride **17** (see Figure 1e and the paragraphs beginning "We next undertook further spectroscopic studies at low temperature…"), which they apparently attribute to sterics and reduced fluxionality at low temperature: "At such temperature the mixture is in a nearly-zero fluxional regime and thus there is no steric barrier preventing free H2 from approaching and reacting with the rhodium(I) center." I call BS. Provide an alternative explanation for the equilibrium shown below, where the trihydride is favored at low temperature and disfavored at high temperature.

**OPTIONAL: Insert Figure 1e here**

1. The authors describe a series of experiments to show what they believe to be the catalytically active species. Ultimately, they claim that it is closely related to the previously observed (PPh3)3Rh(H) but is not the same species. What evidence do they provide that a different complex is observed in solution and that this new complex is an important species for catalysis (*HINT:* You may need to check out ref. 24).
2. The authors do some computational studies (Figure 3) in an attempt to identify **15.** In Figure 3, they label **15** as a complex with 12·H+ hydrogen-bonded with Rh–H and the Rh–Cl distal to **12·H+**. Based on the energies they compute for the different isomers and your chemical intuition, why is this an unrealistic formulation for **15**? What is the best description for **15**?
3. Taking all of the data into account (including the catalytic assay described in ref. 24 and the SI), do you believe the authors' claim that **15** is really a new and more active catalyst than (PPh3)3Rh(H)? If not, describe further studies that could substantiate this claim.