

A Classic Paper – Worksheet – Due Oct. 3rd η^2 -H₂ Complexes

G. J. Kubas, R. R. Ryan, B.I. Swanson, P. J. Vergamini, and H. J. Wasserman
J. Am. Chem. Soc. **1984**, *106*, 451-452.

1. Describe the difference in a σ -complex and an agostic interaction.
2. Kubas originally sought the coordination unsaturated WL₅ complex for the purpose of synthesizing an SO₂ adduct. Give a drawing of the orbital overlap that should account for the stability of an η^2 -H₂-metal interaction and an analogous SO₂ metal interaction.
3. Discuss the role of steric and electronic effects of phosphine ligands in the isolation of the first η^2 -H₂ complex.
4. Why was a neutron diffraction study required for establishing the structure of the η^2 -H₂ complex? Why are H–H positions (distances) different in the x-ray vs the neutron diffraction studies?
5. What is the significance of the HD complex in terms of NMR spectroscopic data/configuration of the dihydrogen complex?
6. For the $(\eta^2\text{-H}_2)\text{W}(\text{CO})_3\text{P}_2$ complex calculate the predicted $\nu(\text{H-D})$ stretch from the known $\nu(\text{H-H})$ of 2690 cm⁻¹. How close does your computed value match the observed?
7. What is the difference between heterolytic and homolytic H₂ activation by a transition metal complex?
8. What is the acidity of free H₂ when dissolved in an organic solvent and how does the complexation of H₂ to a metal in an η^2 -H₂ fashion change it?
9. Which complex is the more stable, $(\eta^2\text{-H}_2)\text{W}(\text{CO})_3[\text{P}(i\text{Pr})_3]_2$ or $(\eta^2\text{-H}_2)\text{W}(\text{CO})_3(\text{Pc-hex}_3)_2$? What data allow you to come to this conclusion? What does “stable” mean?
10. The complex of formulation $[(\text{R}_3\text{P})_2\text{IrH}_6]^+$ is not a hexahydride. Predict the structure of this “polyhydride”. At temperatures above 200°K only one signal is observed in the ¹H NMR that might result from a metal hydride or metal-H₂ complex. What conclusion might you derive from this information?