The following questions refer to the article "Characterization of the First Examples of Isolable Molecular Hydrogen Complexes, $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = Cy, *i*-Pr). Evidence for a Side-on Bonded H_2 Ligand" by Kubas and co-workers, published in *The Journal of the American Chemical Society* in 1984, volume 106, pages 451–452 (DOI: 10.1021/ja00314a049)

Question 1. *The Journal of the American Chemical Society*, abbreviated *J. Am. Chem. Soc.*, and sometimes just called *JACS* ("Jacks") is a very prestigious journal. Why do you think this article was suitable to be published in this journal?

Question 2. Look at the complexes that are listed in the title of the article. Pick one, and give the geometry, oxidation state, and d-electron count for these complexes. Are the complexes diamagnetic or paramagnetic (and why)? Describe each of the ligands as X or L (or a combination thereof), and described the coordination of *each ligand* in terms of η, κ, and/or μ. Finally, do the complexes fit the 18-electron rule?

Question 3: Given the answer to question 2 above, what is the geometry and electron count of $W(CO)_3(PCy_3)_2$ before H_2 addition?

Question 4. What initial observation allowed the authors to determine that H_2 reacted reversibly with $M(CO)_3(PR_3)_2$? What spectroscopic tools could the authors have used to study $M(CO)_3(PR_3)_2(H_2)$ besides the ones mentioned in the article?

Question 5. The ligands around the metal in complex $M(CO)_3(PCy_3)_2(H_2)$ have *mer-trans* geometry. What does it mean?

Question 6: Determine the point group of $W(CO)_3(P-i-P_3)_2(\eta^2-H_2)$ based on the crystal structure and a computationally found structure shown in the following link:
http://www.people.carleton.edu/~mcass/1-Inorganic-C351/jsmol/Eta2BoundH2WComplex.html

Question 7. The H_2 ligand was structurally characterized on the $W(CO)_3(P-i-Pr_3)(\eta^2-H_2)$ complex. Both X-ray diffraction and neutron diffraction were used. Why is it hard to locate the structures of hydrogen atoms with X-ray diffraction?

Question 8. Sketch the frontier orbitals involved in the interaction of the metal and the H_2 fragment. Consider first the molecular orbitals of free H_2 and then consider the metal orbitals of appropriate symmetry. After you have constructed the potential interactions, what would the H_2 bond length in the bound H_2 be as compared to free H_2? Finally, what does this mean in relation to the concept of a H_2 complex being an "arrested form of oxidative addition"?

Question 9. What is the difference between δ vs τ when reporting NMR chemical shifts.

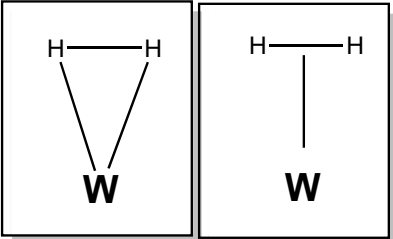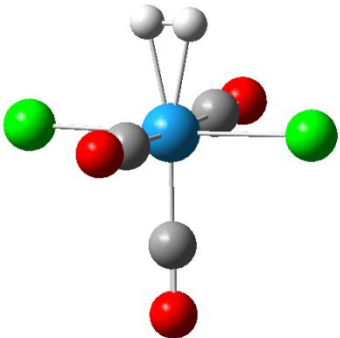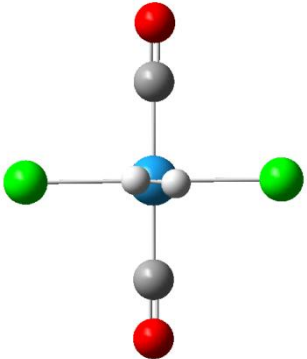**Question 10**. Explain why the signal of the H-D complex is a 1:1:1 triplet.

Question 11. Sketch the *fac* and *mer* isomers of a generic $M(CO)_3(PR_3)_2(H_2)$ species. Assign point groups using the approximations that the P ligands can rotate and are viewed as spherical blobs, and where the H_2 ligand lies approximately parallel to the P-M-P axis. Use group theory to determine how many **C–O stretching vibrations** would be expected to be raman active or IR-active for each species.

Advanced Questions are Below:

Question 1: In the text of the paper when addressing the vibrational spectroscopy the authors state: "Of the six fundamentals expected from η^2-M-H_2 binding, four are observed (Table 1)".

Question 1A. First using a simple calculation, calculate the total number of modes of molecular motions (and split them into the total number of vibrations, translations and rotations) **for the full molecules** (η^2-H_2)$W(CO)_3(PR_3)_2$ where R = isopropyl (**Question 1A**) or cyclohexyl (**Question 1B**).

Question 1C: Now examine only the η^2-M-H_2 fragment. If the fragment were a stand-alone discrete molecule, calculate the number of fundamental vibrations one would expect in the infrared spectrum. Give a symmetry label and a description to each fundamental vibrational mode. Note here you have a choice of symmetry point group, you can choose the symmetry of the molecule as observed in Figure 1 where the P ligands are rigid and cannot rotate around the P-W bonds, or where the P ligands can rotate and/or as noted in the full first sentence on page 452 where "the H_2 ligand axis is approximately parallel to the trans phosphorous-phosphorus direction". We encourage you to use the approximations that the P ligands can rotate and are viewed as spherical blobs, and where the H_2 ligand lies approximately parallel to the P-W-P axes as shown below.

Two views of the **Fragment**: **Left**: shown as a 3 membered ring **Right:** with H_2 side bound to W	**Simplified Full Molecule** **Side View** (the Green blobs represent the P ligands)	**Simplified Full Molecule** **Top View** (viewed from above along the H_2-P-W-P axis)

Question 1D: Does your analysis give you the same number of fundamental vibrations associated with the η^2-M-H$_2$ fragment as that reported in the paper? Suggest why you should get the same answer or why you wouldn't necessarily expect to get the same answer. Explain your reasoning in which ever case you chose to argue.

Advanced Question 2. In Table 1, the authors present assigned experimental IR data for four the six fundamental vibrations associated primarily with the W(η^2-H$_2$) fragment for the three isotopomers: W(η^2-H$_2$), W(η^2-HD), W(η^2-D$_2$). Focusing only the vibration listed in the first row labeled as vHH, use the harmonic oscillator model to predict the expected shift in frequency for the peaks seen for W(η^2-HD)(CO)$_3$(PCy$_3$)$_2$ and W(η^2-D$_2$)(CO)$_3$(PCy$_3$)$_2$ relative to that of W(η^2-H$_2$)(CO)$_3$(PCy$_3$)$_2$. Make the assumption that the H-H, H-D and D-D springs will have essentially the same force constant. How does this data support the proposal that these molecules have side-bound H$_2$ ligands rather than two adjacent hydride ligands?

Advanced Question 3: How is it possible to differentiate spectroscopically or chemically between a complex with a η^2 bound H$_2$ molecule like W(CO)$_3$(P-i-P$_3$)$_2$(η^2-H$_2$) and a dihydride complex like W(CO)$_3$(P-i-P$_3$)$_2$H$_2$?

Advanced Question 4: What is the splitting pattern expected in a ^{31}P NMR of a phosphine in a tungsten compound?