

Based on materials created by Fabiola Barrios-Landos, Yeshiva University, barriosl@yu.edu; Marion Cass, Carleton College, mccass@carleton.edu; and Kyle Grice, DePaul University, kgrice1@depaul.edu in 2016, and by Adam Johnson, Harvey Mudd College (adam_johnson@hmc.edu) in 2016. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike International License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

The following questions are designed to be a deep dive into the first molecular dihydrogen complex, reported in the article “Characterization of the First Examples of Isolable Molecular Hydrogen Complexes, $M(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ ($M = \text{Mo}, \text{W}$; $R = \text{Cy}, i\text{-Pr}$). Evidence for a Side-on Bonded H_2 Ligand” by Kubas and co-workers, *J. Am. Chem. Soc.*, **1984**, *106*, 451-452 (DOI: 10.1021/ja00314a049).

This article shows that molecular hydrogen can be a neutral L-type ligand bound in a side-on fashion. The complexes were structurally characterized, which had not been performed before. These H_2 complexes are relevant to catalytic hydrogenation reactions (among others).

Structure and bonding

Question 1. Look at the complex shown here (Figure 1 from the Kubas paper). Describe it using CBC notation (geometry, VN, LBN, d^n and VEC).

Question 2: Given the answer to question 1 above, predict the geometry and electron count of the starting material, $\text{W}(\text{CO})_3(\text{PCy}_3)_2$, before the addition of H_2 ?

The authors saw a reversible color change when H_2 was added or removed from $\text{M}(\text{CO})_3(\text{PR}_3)_2$, indicating that the species reacted with H_2 but that the H_2 could be removed to regenerate the starting materials. The authors could have studied the reaction using UV-Vis spectroscopy, ^{31}P NMR spectroscopy, ^{13}C NMR spectroscopy, Raman Spectroscopy, or other techniques. However, ^1H NMR and IR spectroscopy were ideal to study the H_2 ligand itself.

Question 3. The H_2 ligand was structurally characterized on the $\text{W}(\text{CO})_3(\text{P-}i\text{-Pr}_3)(\eta^2\text{-H}_2)$ 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? *Hint: X-rays diffract due to electron density while neutron diffraction relies on nuclear cross-section which varies strongly with different isotopes but is strong for both H and D.*

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Question 4. Sketch the frontier orbitals involved in the interaction of the metal and the H₂ fragment.

Hint: you can use a Dewar-Chatt-Duncanson model to describe the bonding. What would you predict the H₂ bond length in the bound H₂ be as compared to free H₂? The authors describe this dihydrogen complex as being an “arrested form of oxidative addition.” While we haven’t discussed OA yet, what do you think this means?

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IR and NMR spectroscopy

In Newtonian mechanics and in the analysis of molecular vibrations in IR/Raman spectroscopy, the reduced mass, μ , allows the 2-body problem to be solved as a 1-body problem. Reduced mass, μ , is

$$\text{defined as: } \mu = \frac{m_1 m_2}{m_1 + m_2}.$$

Question 5: Calculate the reduced mass for H₂, HD, and D₂. Use 1.008 g/mol for the atomic weight of H and 2.014 for the atomic weight of D.

The vibrational frequency of a molecule, ν , can be derived using simple harmonic motion

considerations: $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where k is the force constant of the “spring.” Using this information, one

can calculate the vibrational frequency of H₂ and D₂ given that $k_{\text{HH}} = 574.9 \text{ N/m}$ and $k_{\text{DD}} = 577.0 \text{ N/m}$ (normally one would calculate the force constant from experimental data). The ν in Hz can be converted to cm^{-1} (wavenumber) using $c = \nu\lambda$. This is a fussy calculation that requires μ to be in kg so the results are provided:

$$\text{H}_2: \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{577.0 \text{ N/m}}{8.37 \cdot 10^{-28} \text{ kg}}} = 1.319 \cdot 10^{14} \text{ s}^{-1}$$

$$(1.319 \cdot 10^{14} \text{ s}^{-1})(s / 2.998 \cdot 10^{10} \text{ cm}) = 4399 \text{ cm}^{-1}$$

$$\text{D}_2: \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{574.9 \text{ N/m}}{1.67 \cdot 10^{-27} \text{ kg}}} = 9.349 \cdot 10^{13} \text{ s}^{-1}$$

$$(9.349 \cdot 10^{13} \text{ s}^{-1})(s / 2.998 \cdot 10^{10} \text{ cm}) = 3117 \text{ cm}^{-1}$$

Question 6a. Table 1 of the Kubas paper presents IR data for three isotopomers: W(η^2 -H₂) (2690 cm^{-1}), W(η^2 -HD) (2360 cm^{-1}), W(η^2 -D₂) (1900 cm^{-1}). Use the harmonic motion model presented above to predict the expected shift in frequency for the peaks seen for W(η^2 -HD)(CO)₃(PCy₃)₂ and W(η^2 -D₂)(CO)₃(PCy₃)₂ relative to that of W(η^2 -H₂)(CO)₃(PCy₃)₂. Make the assumption that the H-H, H-D and D-D springs will have essentially the same force constant (the small difference shown above can be considered “the same”). *Hint: use ratios!*

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Question 6b. How does this data support the proposal that these molecules have η^2 -H₂ ligands rather than two adjacent hydride ligands?

Question 7. Explain why the signal of the H-D complex is a 1:1:1 triplet in the ¹H NMR spectrum.

Question 8: How is it possible to differentiate spectroscopically or chemically between a complex with a η^2 bound H₂ molecule like W(CO)₃(P-*i*-P₃)₂(η^2 -H₂) and a dihydride complex like W(CO)₃(P-*i*-P₃)₂H₂?