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Synthesis and Reactivity of Dihydrogen Diruthenium Complexes.

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Synthesis and Reactivity of Dihydrogen Diruthenium Complexes.

Ryder J. Downey, Dr. Robert Chin, University of Northern Iowa

Introduction

Having two open coordination sites on the diruthenium complex makes for the ability to be able to be more precise when interacting with other compound. The side-on bonding of the bis(dihydrogen) gives it unique characteristics as well as unique capabilities. The Organotransition Metal Chemistry book says that the dihydrogen is bonded by the donation of electrons from the H-H sigma bond as well as the back donation of electron density through the transition metal.³

In the past, many groups have studies on a mononuclear Ruthenium compound similar to the one we are synthesizing (see figure one). Our goal was to find out these characteristics and capabilities of the dihydrogen diruthenium.

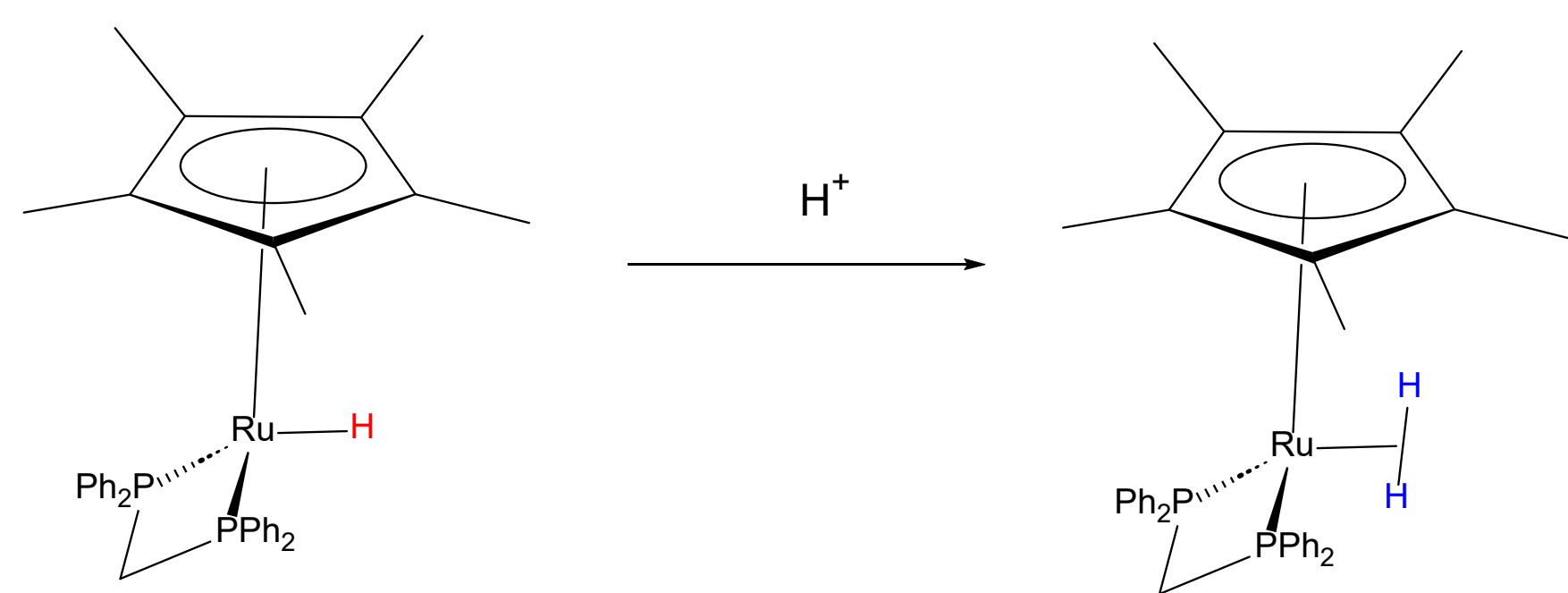


Figure 1. The protonation of a mononuclear complex from hydride to dihydrogen.² Bis(diphenylphosphinomethane) is the chosen chelating ligand as it has been shown to yield the highest dihydrogen complexes.¹



Figure 2. The dihydrogen complex is very reactive to air and moisture. The glovebox (above) is nitrogen filled giving the compounds an inert atmosphere.



Figure 3. The nuclear magnetic resonance (NMR) spectrometer is how we are able to differentiate one compound from another by performing different tests with the spectrometer.

Synthesis of Bis(Dihydrogen)

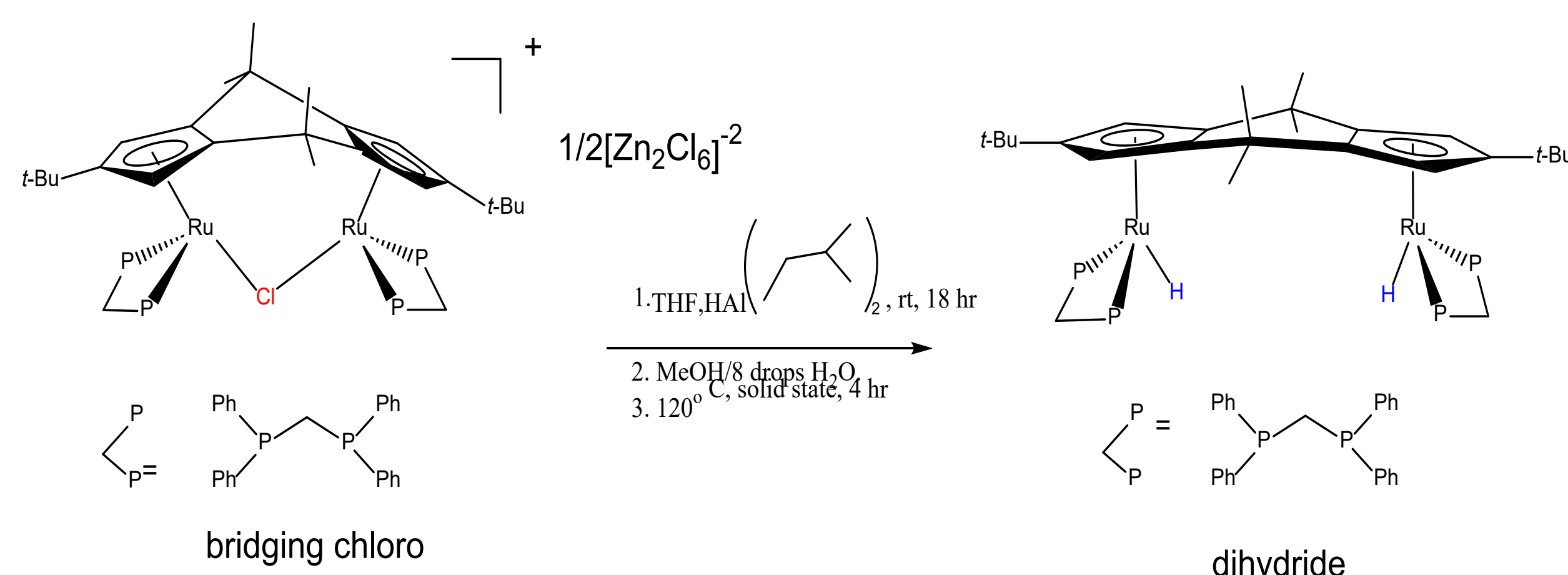


Figure 4. Both ¹H and ³¹P NMR spectra were taken after every step in purpose of finding the most efficient way of making the dihydride product.

Results of Bis(Dihydrogen) Complex

After step 2 from **figure 4** in the making of the dihydride, we saw our product as well as other peaks in the hydride region.

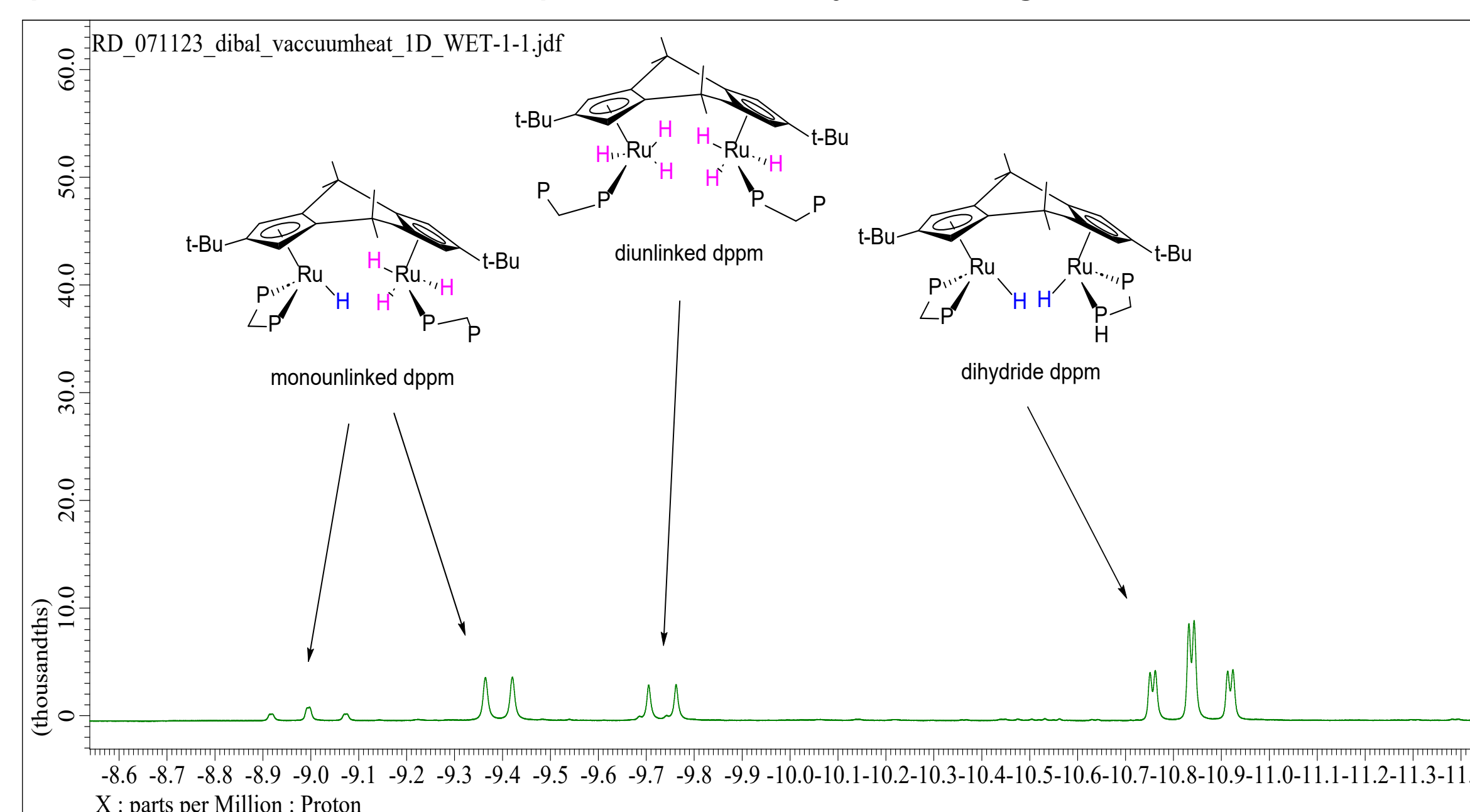


Figure 5. ¹H NMR spectrum of the reaction mixture after step 2 shown in figure 4.

How we found it to be the mono- and di- unlinked structures

- Multiple ³¹P resonance structures
- Two doublets in free dppm range in ³¹P
- Doublets and triplets explaining H coupling.

To clean up ¹H NMR in **Figure 5**, dynamic vacuum at 120 C causes the loss of H₂ gas. Without a hydrogen environment, the dangling phosphine groups have the ability to go back to a bidentate ligand.

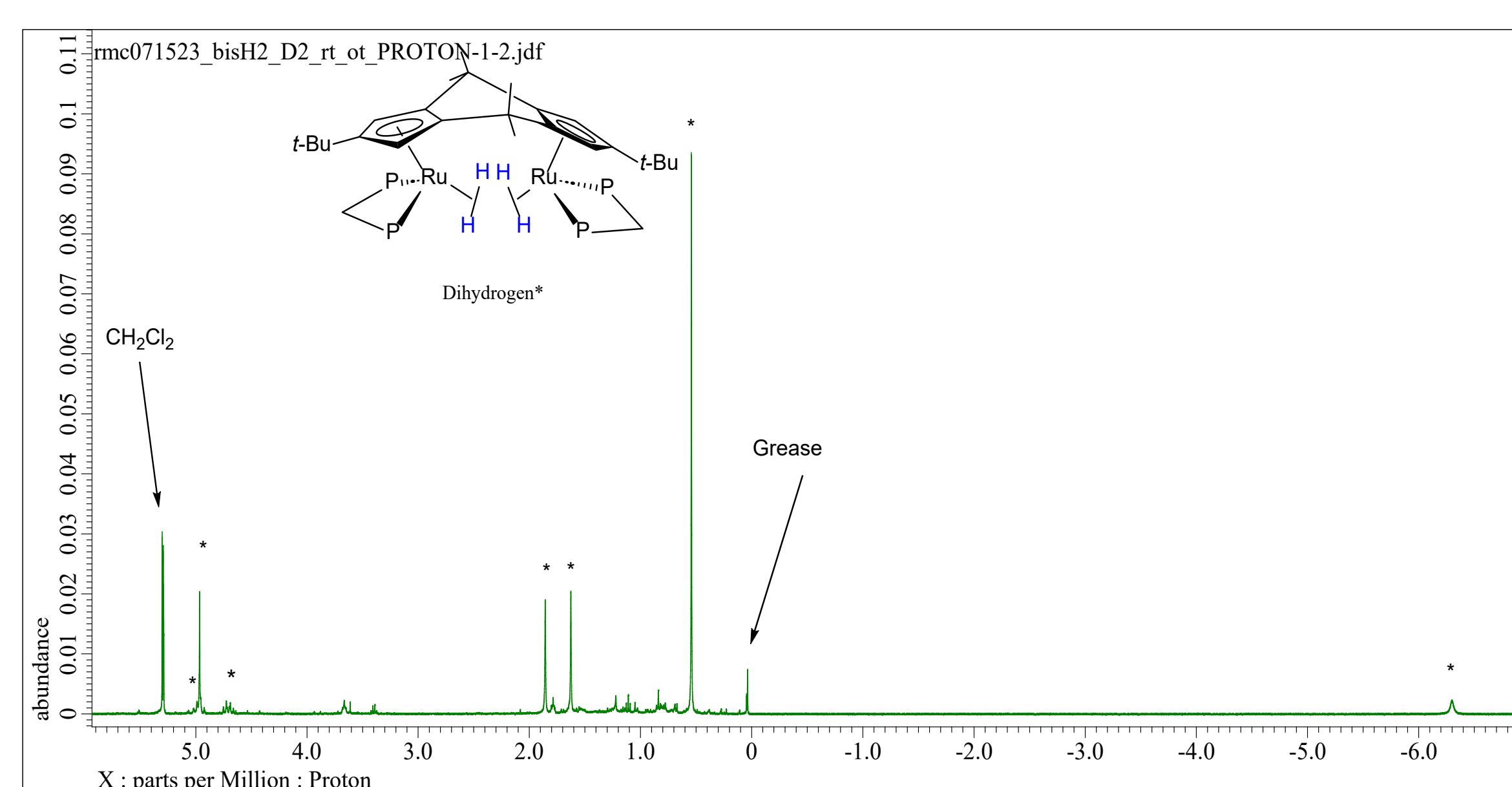
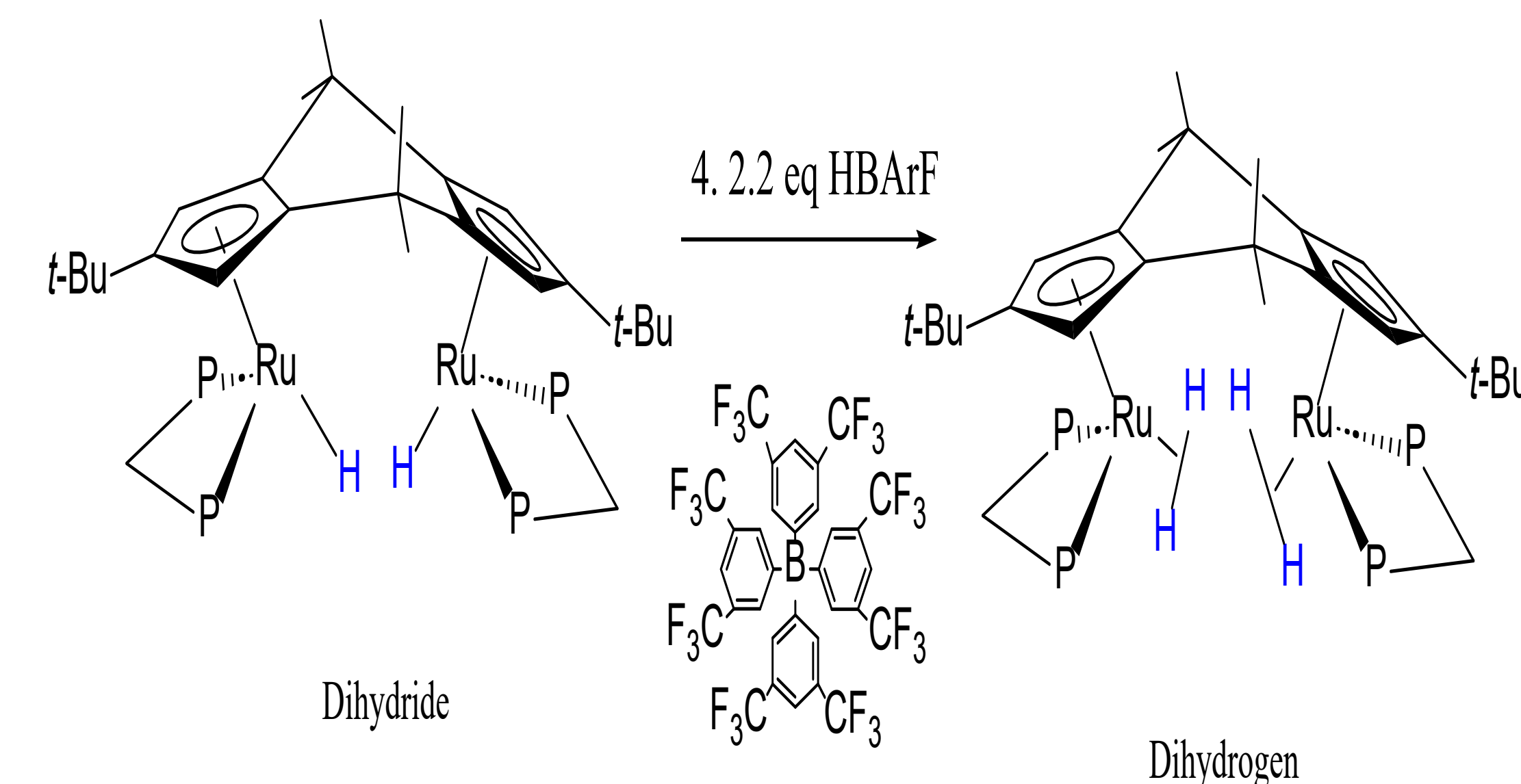


Figure 6. Clean dihydrogen complex.

The peak in the hydride region integrates as 4, telling us that there are 4 equivalent hydrogens. The measured J_{HD} was 15.9 Hz and according to Dutta, the dihydrogen type that we have is an elongated dihydrogen and measures at 1.15 Å for the H-H distance.¹

To find out what structure the hydrogens come in, it was necessary to take a T1 NMR test. T1 test measures the recovery time of spinning nuclei after being flipped 180 degrees.

Note: Classical hydrides have a T1 time in the range of 200 ms to 2 s. Nonclassical hydrides have a T1 time of less than 100 ms

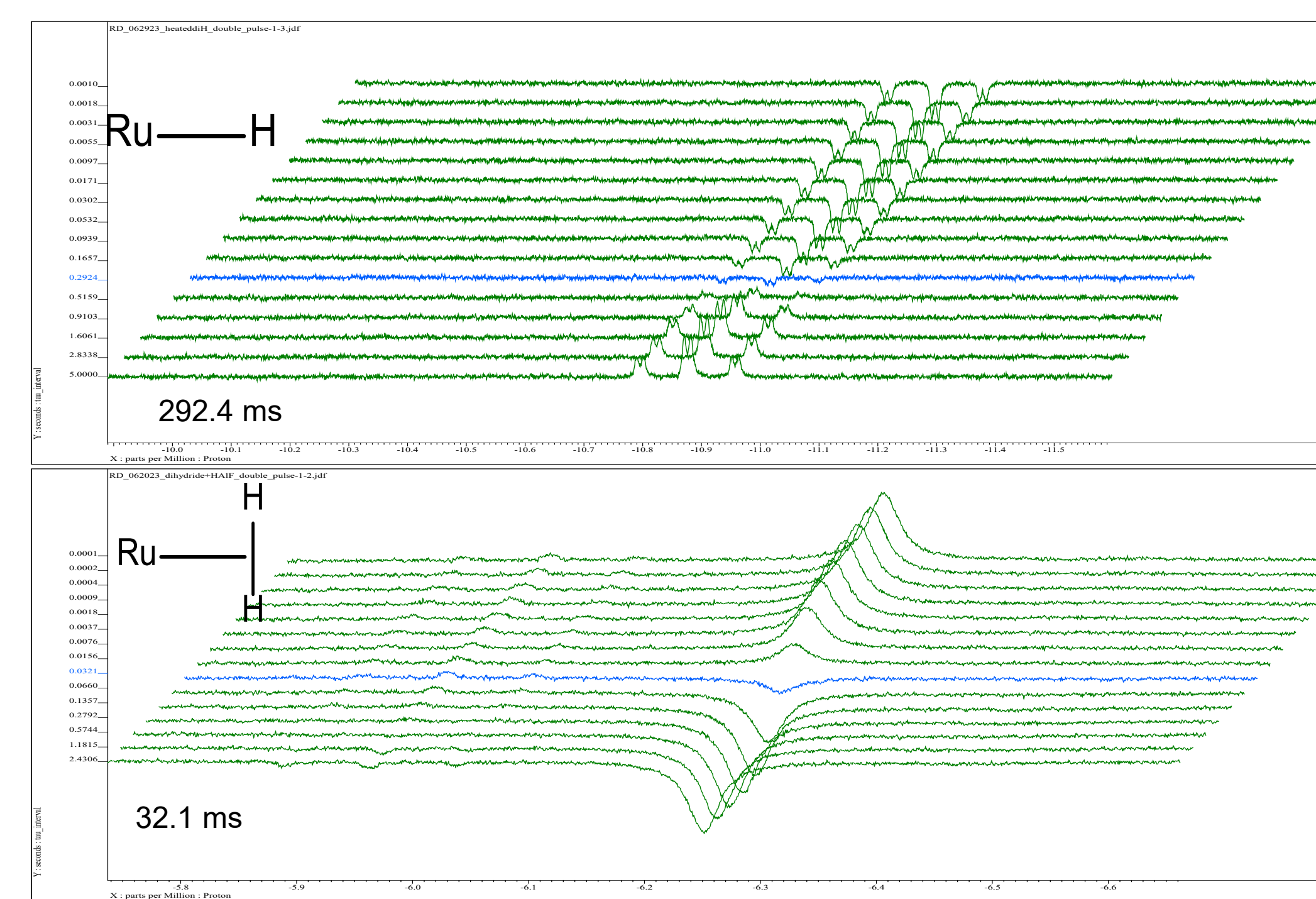


Figure 7. T1 data of classical dihydride complex (top) and nonclassical dihydrogen complex (bottom).

Reactivity of Dihydrogen Ligands

Since making a clean bis(dihydrogen) complex, we have conducted tests to find out more about the reactivity and lability of the product.

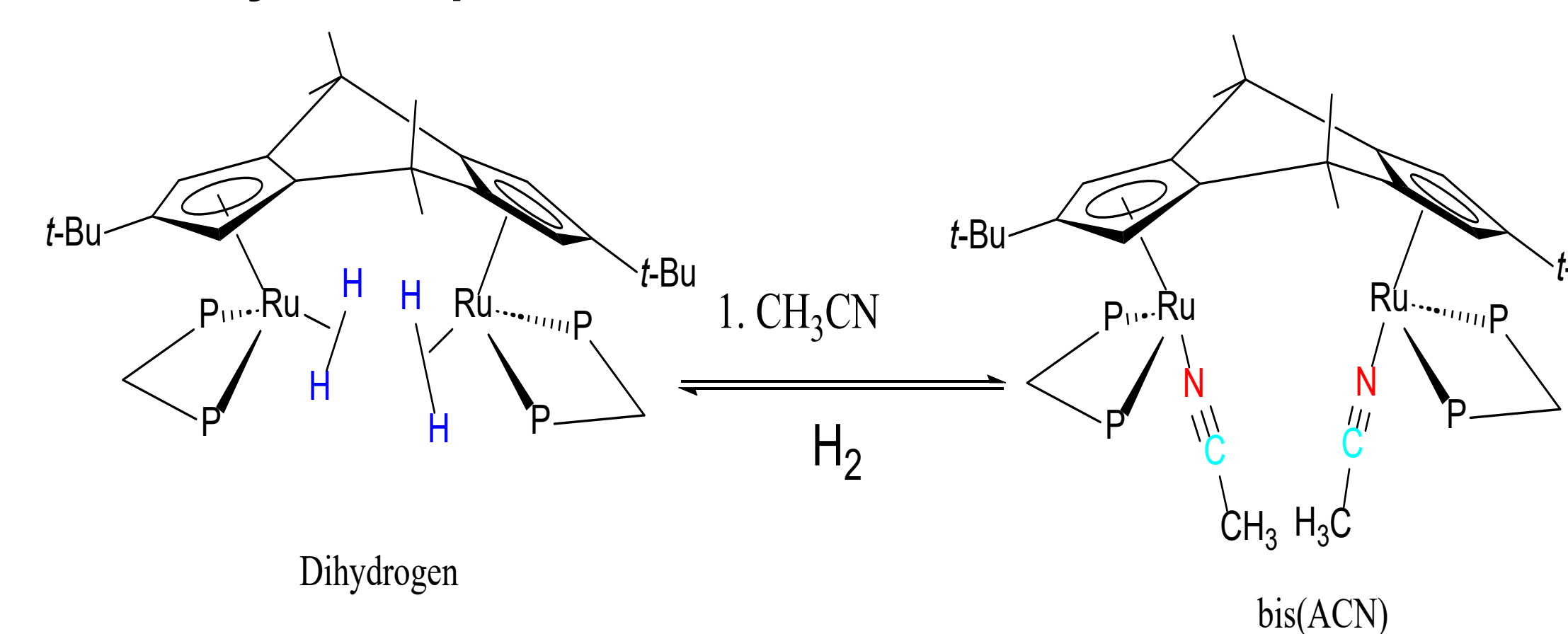


Figure 8. Under hydrogen conditions, the bis(dihydrogen) complex is in equilibrium with bis(ACN)

Recently, we have discovered that another complex containing a dihydrogen ligand that is not the bis(dihydrogen) complex. This complex is a trihydride and it is much more effective with simple hydrogenation. The trihydride complex has one elongated dihydrogen as well as a hydride.

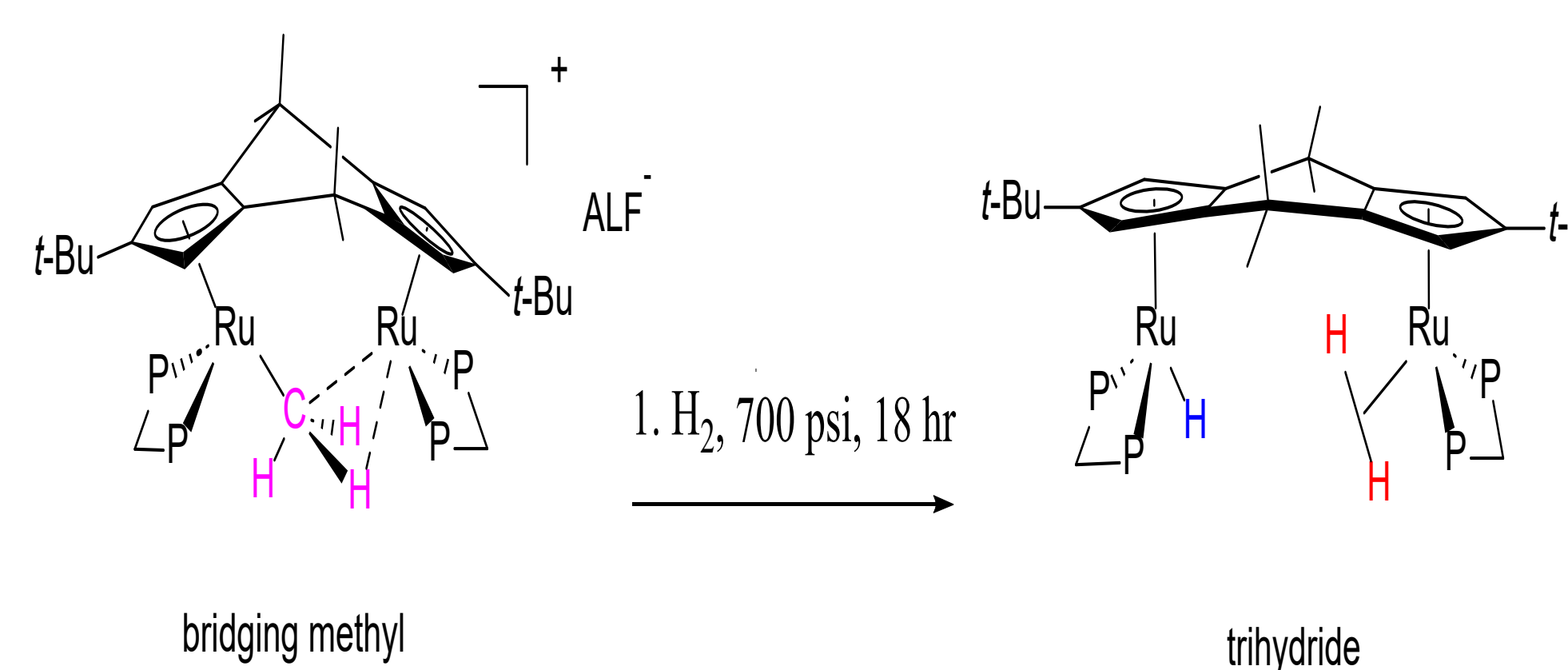
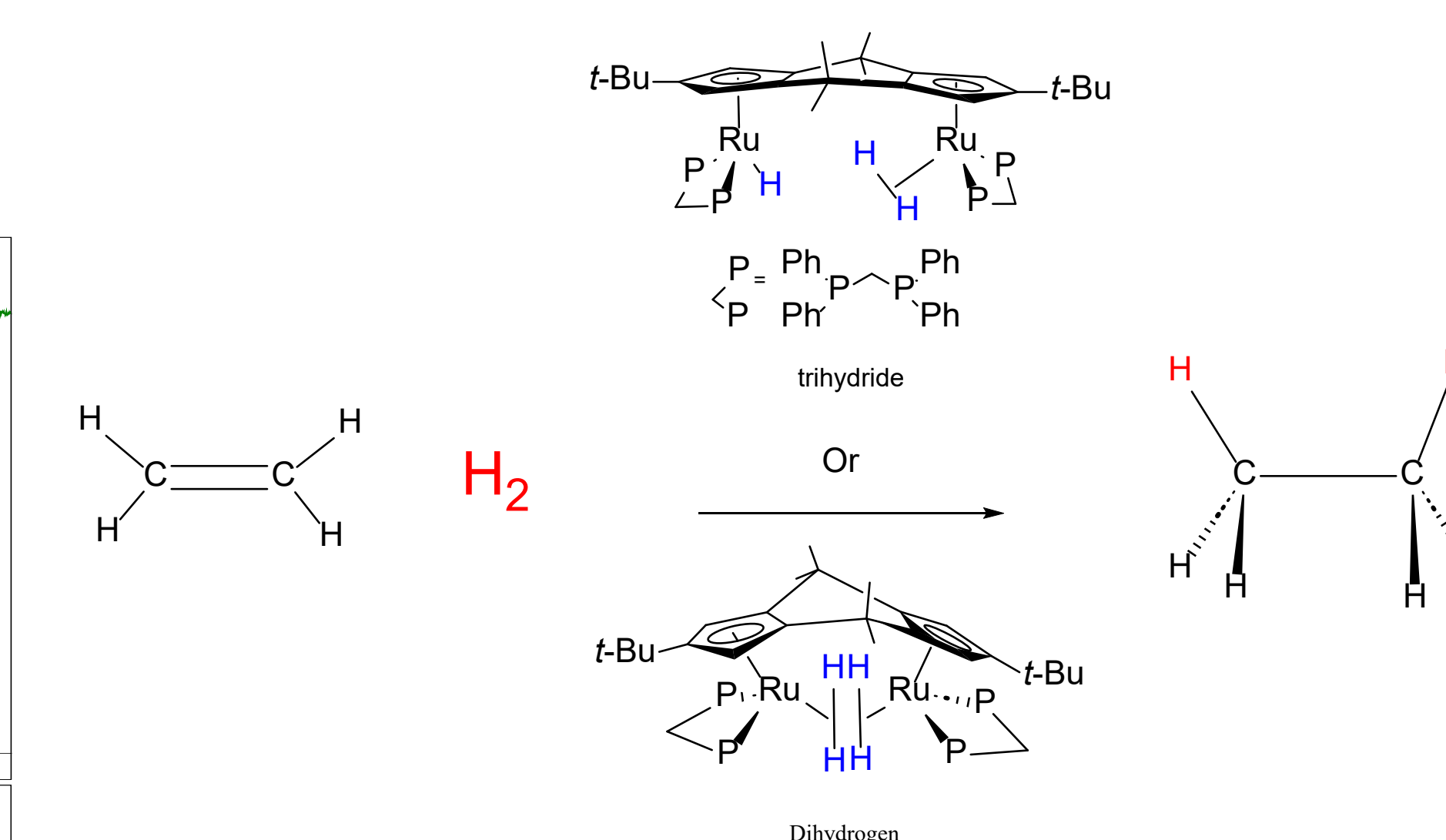


Figure 9. Synthesis of the trihydride complex.



While the hydrogenation of ethylene to ethane only occurs in trace amounts with the bis(dihydrogen) complex as a catalyst, the hydrogenation occurs at a much higher rate than when using the trihydride complex

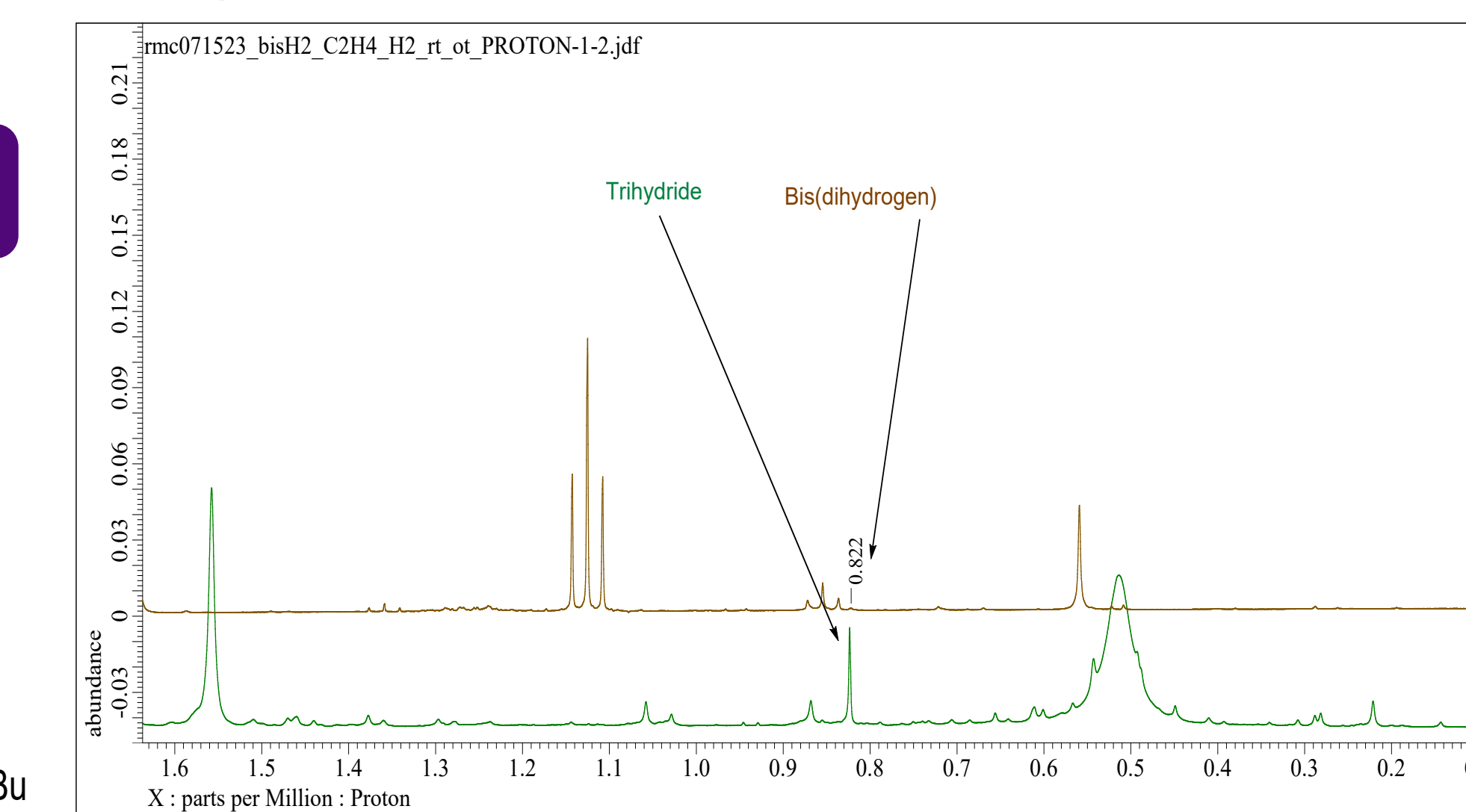


Figure 10. ¹H NMR of the ethane peak in CD₂Cl₂.

Conclusions

This way of making the bis(dihydrogen) complex has shown to be out most effective and efficient process. It promotes lability with acetonitrile as well as simple hydrogenation in small amounts. Another dihydrogen ligand possessing complex, the trihydride, has shown to be very effective at simple hydrogenations. The two different coordination sites seem to show different characteristics than in a mononuclear compound.

Citations & Acknowledgements

I would like to thank Dr. Chin for this opportunity as well as the department of chemistry, biochemistry, and the college of humanities arts and science.

[1]Dutta, S. (2011). Phosphine supported metal-dihydrogen complexes: Elongation of H-H bond to reversible release of H₂. *Comptes Rendus Chimie*, 14, 1029-1053.

[2]Guocheng, J., Lough, A., and Morris, R. (1992). Synthesis and the Kinetic and Thermodynamic Acidity of η²-Dihydrogen and Dihydride Complexes of the Type [Ru(C₅Me₅)H₂L₂]⁺. X-Ray Crystal Structure Determination of the Complex [Ru(C₅Me₅)(η²-H₂)(PPh₂CH₂PPh₂)]BF₄. *Organometallics*, v. 11, 1992, 161-171, 0276-7333.

[3] Hartwig, J., "Organotransition Metal Chemistry. From Bonding to Catalysis," University Science Books, New York, 2010.