

On the Mechanism of Dihydrogen Addition to Tantalocene Complexes

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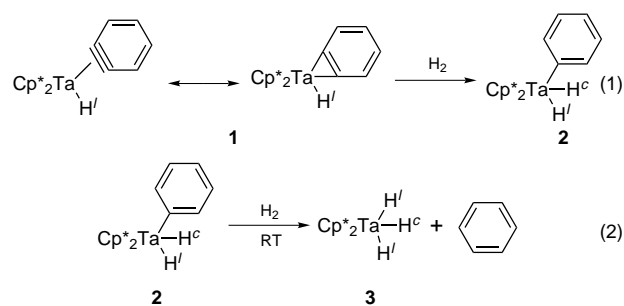
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Parahydrogen induced polarization (PHIP) is a valuable mechanistic tool that can provide definitive evidence for pairwise addition of dihydrogen to unsaturated substrates. PHIP occurs if H₂ enriched in the para spin state adds to a metal complex or an organic substrate in a pairwise manner, such that spin correlation is maintained between the two transferred protons that originated from the same H₂ molecule. If the transfer of the protons occurs fast relative to proton relaxation, non-Boltzmann populations in their spin states can result, leading to enhanced absorption and emission lines in the product NMR spectrum. For the observation of PHIP, dihydrogen addition must lead to a product in which the transferred protons are magnetically distinct and *J* coupled to each other.^{1–8} To date, PHIP in metal complexes has only been observed in the oxidative addition of dihydrogen to late transition metal complexes including those of rhodium,^{2,9–12} iridium,^{2,3,13–15} ruthenium,¹⁶ and platinum.^{17,18} The reaction proceeds in a concerted manner via a 3-centered triangular transition state. Activation of dihydrogen by low valent early

transition metal complexes is presumed to occur by an analogous mechanism, although few systems have been investigated^{19–21} and none have been studied with PHIP. Detailed knowledge of the mechanism of this activation reaction should aid in expanding the catalytic properties of these systems.

Bercaw and co-workers have reported several interesting reactions between hydrogen and bis(pentamethylcyclopentadienyl)tantalum complexes that meet the requirements for PHIP.^{22–25} Specifically, the benzyne hydride complex **1** reacts with H₂ at 0 °C to form a new phenyl dihydride complex **2**, which in turn reacts with H₂ at room temperature to generate benzene and the trihydride complex **3**. The overall transformations are shown as eqs 1 and 2.



Complexes **2** and **3** have bent metallocene structures with three σ -bonded ligands in the central or equatorial “wedge”, resulting in an inequivalence of hydride ligands. For **2** the hydride ligands and the phenyl group lie in the equatorial plane with one hydride ligand in the central position (H^c) and the other hydride ligand (H^l) and the phenyl group in the lateral positions. In the ¹H NMR spectrum, the hydride ligands of **2** are observed at 2.5 and 0.95 ppm (²J_{HH} = 12 Hz, benzene-*d*₆).²⁴ In the case of **3**, the tantalum metal and the three hydride ligands lie in a common plane with the hydride resonances appearing as an AB₂ pattern in the ¹H NMR spectrum. The two lateral hydride ligands are chemically equivalent and appear as a doublet at –0.91 ppm, while the H^c is a triplet and resonates at 1.11 ppm (²J_{HH} = 13 Hz, benzene-*d*₆).²⁶ The formation of **2** and **3** is thought to proceed via Ta(III) species, which are generated respectively by benzyne insertion into the metal–hydride bond and reductive elimination of benzene. Dynamic NMR experiments provide evidence for the existence of a Ta(III) intermediate in eq 1.^{23,24} An alternative mechanism for the H₂ addition reactions is via a four-centered transition state corresponding to σ -bond metathesis. The present study was undertaken since PHIP can provide unambiguous evidence for exclusion of one or the other of these mechanisms.

Reaction of parahydrogen and submilligram samples of **1** leads to PHIP in both of the hydride resonances of **2** in the ¹H NMR spectrum. Equally important, no discernible polarization is observed in any of the phenyl resonances of **2**. This result indicates pairwise addition of H₂ to the Ta center, thus strongly supporting the proposal of a 16-electron Ta(III) intermediate, rather than direct reaction of H₂ with the formally Ta(V) benzyne hydride complex. Optimization of polarized resonances for **2** occurs at 308 K and the spectrum is shown in Figure 1a. Polarization at 308 K decays over a period of 10 min. As the initial polarized peaks of **2** decay, more **2** forms and its polarized

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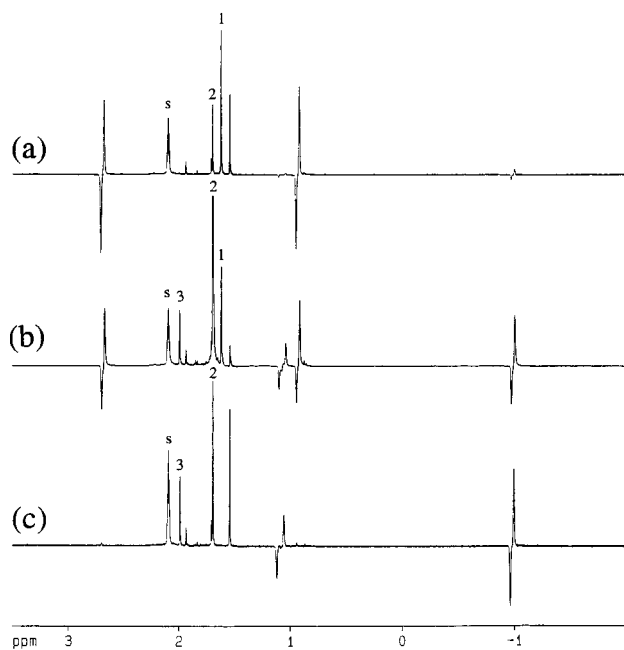


Figure 1. ^1H NMR spectra obtained by using a submilligram sample of $\text{Cp}^*_2\text{Ta}(\text{benzynes})\text{H}$ (**1**) and para-enriched hydrogen in toluene- d_8 . (a) PHIP spectrum of $\text{Cp}^*_2\text{Ta}(\text{phenyl})\text{H}_2$ (**2**) at 308 K. (b) PHIP spectrum of **2** and $\text{Cp}^*_2\text{TaH}_3$ (**3**) at 313 K. (c) PHIP spectrum of **3** at 323 K. Resonances for solvent (s) and Cp^* protons for **1**, **2**, and **3** are labeled.

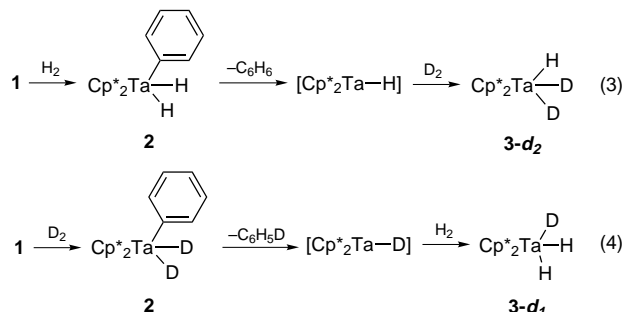
hydride resonances become unsymmetrical, as a result of overlap of the resonances of newly polarized and relaxed phenyl dihydride product. Significantly, up to 333 K hydrogen addition to **2** is not reversible, as shown by the fact that **2** in the presence of parahydrogen does not give polarization of the dihydride resonances.

Further reaction of **2** in the presence of parahydrogen yields the trihydride complex with polarization observed in both hydride resonances of **3**, consistent with pairwise addition of H_2 to the putative $\text{Cp}^*_2\text{Ta}-\text{H}$ fragment. Reaction of parahydrogen with a mixture of **1** and **2** produces polarized hydride resonances in both **2** and **3** (Figure 1b). Once all of **1** has been consumed, the polarization of **2** decays, but as **2** reacts with parahydrogen, polarization for **3** is observed. The largest polarization obtained for **3** occurs at 323 K and is shown in Figure 1c. The hydride resonance at -0.91 ppm is observed as an antiphase doublet with emission and enhanced absorption lines separated by $^2J_{\text{HH}}$ of 13 Hz, while the hydride resonance at 1.11 ppm appears as an antiphase triplet with the central line missing and the outside lines in enhanced absorption and emission separated by $2J$ (26 Hz). The antiphase triplet can be rationalized by using the energy level diagram for an AB_2 spin system, and the notion that parahydrogen adds pairwise to A (central) and B (lateral) positions, giving a non-Boltzmann distribution of spins.^{2,13} Once the trihydride complex is formed, it is stable and is not fluxional on the NMR time scale, even upon warming to 333 K. Placement of **3** under D_2 does not lead to incorporation of deuterium in the hydride positions, and exposure of **3** to parahydrogen up to 333 K does not give enhanced polarized resonances, indicating the absence of hydrogen cycling in this system under these conditions. The inertness of the $\text{Cp}^*_2\text{TaH}_3$ system to hydrogen exchange contrasts with the behavior shown by Cp_2TaH_3 , Cp_2NbH_3 , and $\text{Cp}^*_2\text{-NbH}_3$.¹⁹⁻²¹ The observed polarization enhancements for both **2** and **3** are greater than 100-fold. PHIP is observed for both complexes in toluene- d_8 , benzene- d_6 , and THF- d_8 .

The results from our parahydrogen studies for the formation of **3** provide unambiguous evidence for hydrogen addition to a tantalum hydride intermediate such that the new hydride ligands add to both the central and lateral positions of the trihydride product. In contrast, if H_2 addition proceeded solely to the lateral

positions, with the original hydride ligand remaining in the central position, then PHIP could not be observed since the added hydride ligands would be magnetically equivalent; in effect, the polarization for the added hydride ligands would exactly cancel.

The stereochemistry of H_2 addition was established independently by using complementary labeling experiments. Reaction of **1** with H_2 (or D_2) at 258 K to form **2** (or **2-d**) followed by removal of the initial gas and reaction with D_2 (or H_2) affords **3-d** (or **3-d**), as shown in eqs 3 and 4.



The hydride resonance for **3-d** is observed in the ^1H NMR spectrum (toluene- d_8) as a broad peak at -1.05 ppm, with a peak width at half-height of about 7 Hz. The broadness is the result of unresolved J_{HD} couplings to the deuterides in both central and lateral positions. The hydride resonance of the **3-d** isotopomer is shifted upfield 50 ppb from the H^l resonance of the trihydride complex, which occurs at -1.00 ppm in toluene- d_8 . The lateral hydride resonance for **3-d** is seen in the ^1H NMR spectrum as a doublet at -1.016 ppm ($^2J_{\text{HH}} = 13$ Hz, toluene- d_8), and is shifted upfield 16 ppb.²⁷ The chemical shift and appearance of the Cp^* resonance is not affected by deuterium incorporation in either **3-d** or **3-d**. Under the conditions of eqs 3 and 4, no other isotopomers for **3-d** and **3-d** are detected. No isotopic scrambling is observed in the $\text{Cp}^*_2\text{TaH}_3$ system, in contrast to that seen for the d_1 isotopomers of the isoelectronic cation $[\text{Cp}^*_2\text{WH}_3]^+$.^{28,29} The formation of **3-d** in eq 3 and **3-d** in eq 4, together with the parahydrogen studies, proves unambiguously that the addition of H_2 occurs in a pairwise fashion to one side of the initial hydride ligand in the Ta(III) intermediate. Additionally, photolysis of the trihydride complex under D_2 yields **3-d** after 10 min of irradiation, indicating that photochemically driven reductive elimination of H_2 from **3** takes place. After 80 min of irradiation, more isotopomers are present, as the label is scrambled with the reductive elimination of HD as well as of H_2 and D_2 .

This is the first time that PHIP has been observed with an early transition metal hydride complex. Addition of parahydrogen to $\text{Cp}^*_2\text{Ta}(\text{benzynes})\text{H}$ gives strong polarization in the hydride resonances of $\text{Cp}^*_2\text{Ta}(\text{phenyl})\text{H}_2$, providing evidence for a 16-electron intermediate. Further reaction yields $\text{Cp}^*_2\text{TaH}_3$, and in the presence of parahydrogen, polarization of the hydride resonances is observed. Deuterium labeling experiments complement the PHIP studies and establish unambiguously the stereochemistry of H_2 addition to the monohydride Cp^*_2TaH intermediate. The labeling results also rule against a PHIP-silent σ -bond metathesis mechanism in the formation of $\text{Cp}^*_2\text{TaH}_3$. The experiments reported thus provide definitive evidence of pairwise addition of dihydrogen to two low-valent tantalum complexes and strongly support the notion of concerted H_2 oxidative addition via a triangular transition state.

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