

Mechanistic Studies on the Addition of Dihydrogen to Tantalocene Complexes

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Abstract: The mechanism of dihydrogen addition to $\text{Cp}^*_2\text{Ta}(\text{CH}_2)(\text{H})$ was examined using parahydrogen-induced polarization (PHIP), ^{13}C labeling, and comparison to the related complex $\text{Cp}^*_2\text{Ta}(\text{CH}_2)(\text{CH}_3)$. The reaction of para-enriched hydrogen with $\text{Cp}^*_2\text{Ta}(\text{CH}_2)(\text{H})$ leads to polarized resonances for both $\text{Cp}^*_2\text{Ta}(\text{CH}_3)(\text{H})_2$ and $\text{Cp}^*_2\text{TaH}_3$, even at the earliest reaction times. Use of the labeled compound $\text{Cp}^*_2\text{Ta}(^{13}\text{CH}_2)(\text{H})$ shows that the polarized resonances of $\text{Cp}^*_2\text{Ta}(\text{CH}_3)(\text{H})_2$ correspond to the two hydride ligands. The results thus support a mechanistic pathway of H_2 addition to an unsaturated Ta(III) intermediate, $[\text{Cp}^*_2\text{Ta}(\text{CH}_3)]$, rather than addition directly across the $\text{Ta}=\text{C}$ bond. In a same sample comparison, the rates of initial H_2 addition and subsequent C–H reductive elimination for both $\text{Cp}^*_2\text{Ta}(\text{CH}_2)(\text{H})$ and $\text{Cp}^*_2\text{Ta}(\text{C}_6\text{H}_4)(\text{H})$ were examined. The methylene complex exhibits greater reactivity than the benzyne complex, with the major difference due to the C–H coupling step, in which formation of methane is more facile than that of benzene. The reactivity of the related ethylene hydride complex, $\text{Cp}^*_2\text{Ta}(\text{C}_2\text{H}_4)(\text{H})$, with hydrogen was also examined. The PHIP study of this system leads to unusual and unexpected polarization, which is found to be due to a minor impurity in the sample.

Introduction

In examining the addition of dihydrogen to an unsaturated substrate, parahydrogen-induced polarization (PHIP) is a valuable mechanistic tool. In PHIP, pairwise addition of hydrogen can be definitively established by enhanced resonances in the product of the hydrogen nuclei that were formerly part of the H_2 addend.¹ Homogeneous organometallic hydrogenation catalysts are widely used in organic synthesis, and an understanding of the fundamental mechanism aids in the design of new and improved systems.² The utility of PHIP in determining the mechanism of H_2 addition to a metal center and incorporation of hydrogen nuclei into resulting products has proven successful for many late metal complexes, including those of rhodium,^{3–7} iridium,^{3,8–11} ruthenium,¹² and platinum.^{13,14} For the early

transition metals, many systems are known to undergo H_2 addition,^{15–20} but the use of PHIP to analyze the addition process and dihydrogen activation by these systems remains relatively unexplored.²¹

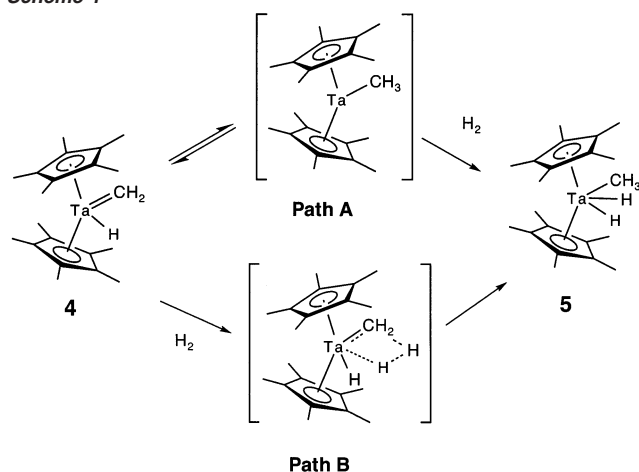
In a previous report, PHIP in early metals complexes was described for the first time in the course of a mechanistic study of hydrogen activation by the tantalum benzyne complex, $\text{Cp}^*_2\text{Ta}(\text{C}_6\text{H}_4)(\text{H})$ (**1**) [$\text{Cp}^* = \text{pentamethylcyclopentadienyl}$],²¹ originally prepared by Bercaw and co-workers.²² The addition of hydrogen to **1** is shown in eq 1, leading to sequential formation of the phenyl dihydride species $\text{Cp}^*_2\text{Ta}(\text{C}_6\text{H}_5)(\text{H})_2$ (**2**) and the trihydride final product $\text{Cp}^*_2\text{TaH}_3$ (**3**). The mechanistic question addressed by PHIP in that study was whether H_2 additions to give **2** and then **3** proceed via four-centered transition states or

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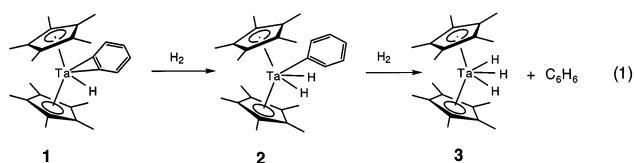
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Scheme 1



by prior formation of coordinatively unsaturated Ta(III) intermediates and concerted H₂ oxidative addition. Previous magnetization transfer studies had shown that **1** and related Cp*₂Ta derivatives were capable of forming 16 e⁻ Ta(III) species,²³ but that result did not answer directly the mechanism of H₂ addition in eq 1. However, on the basis of the PHIP results, it was possible to conclude that eq 1 does indeed occur by formation of Ta(III) intermediates followed by d² → d⁰ oxidative additions, rather than by direct additions across the Ta–C bonds of **1** and **2**.



In the present study, the reaction of dihydrogen with the related complex Cp*₂Ta(CH₂)(H) (**4**)²⁴ is examined through PHIP to gain further insight into H₂ activation by a tantalocene system and to see which path of Scheme 1 is followed. In Path A, addition occurs by α-insertion to form a Ta(III)-methyl species followed by oxidative addition, whereas in Path B, H₂ addition takes place via a four-centered transition state with no change in the Ta oxidation state. Each of these pathways would yield different PHIP results. For Path A, polarization would exist in both hydrides of **5** because they were part of the same parahydrogen molecule in the addition process, while for Path B, polarization would exist in the methyl and central hydride resonances, although the effect may be somewhat diminished because of reduced coupling between these product protons. To address the question more definitively, the reaction of ¹³C-labeled **4** with parahydrogen is examined as well. Additionally, the reaction of H₂ with the related complexes Cp*₂Ta(CH₂)(CH₃) (**6**)²⁴ and Cp*₂Ta(C₂H₄)(H) (**7**)²⁵ is probed through parahydrogen methods to establish the hydrogen activation pathway. Differences in the rates of hydrogenation of the benzyne complex **1** and the methylene complex **4** leading to

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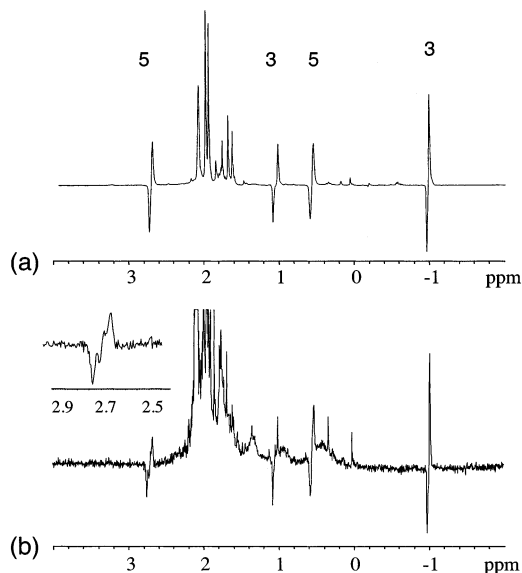
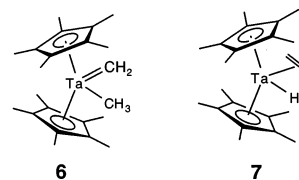


Figure 1. (a) ¹H NMR spectrum of Cp*₂Ta(CH₂)(H) (**4**) with para-enriched hydrogen in toluene-*d*₈ at 20 °C. Hydride resonances of **5** and **3** are indicated. (b) ¹H NMR spectrum of Cp*₂Ta(¹³CH₂)(H) (**4**-¹³C) with para-enriched hydrogen in toluene-*d*₈ at 20 °C. Inset shows ¹³C coupling more clearly.

the common final product Cp*₂TaH₃ (**3**) are also analyzed to give information about the relative reactivity of the intermediate species formed.



Results and Discussion

H₂ Addition to Cp*₂Ta(CH₂)(H) (4**).** Complex **4** reacts rapidly with dihydrogen at room temperature in solution (benzene-*d*₆ or toluene-*d*₈) to yield methane (δ 0.15) and Cp*₂TaH₃ (**3**) as determined by ¹H NMR spectroscopy.²⁵ The PHIP experiments for this reaction were conducted under ca. 3 atm of para-enriched hydrogen using a 45° pulse angle and 8 or 16 scans per spectrum. Similar conditions were used for all other PHIP experiments described in this paper. Above 255 K, polarized signals are observed at δ 2.73, 0.57 (antiphase doublets, *J* = 16 Hz), 1.11 (antiphase triplet with central line missing, *J* = 13 Hz), and -0.91 (antiphase doublet, *J* = 13 Hz), as shown in Figure 1a. The signals at δ 1.11 and -0.91 correspond to the hydrides of **3** and have the same polarization as was previously reported for eq 1.²¹ The signals at δ 2.73 and 0.57 are very similar to those observed for the hydride ligands of the phenyl dihydride complex **2** (δ 2.5 and 0.95) and are thus assigned to the methyl dihydride complex **5**, marking the first time that this species has been spectroscopically seen and characterized.

In the addition of *p*-H₂ to **4**, both sets of resonances attributed to the hydrides in the methyl dihydride **5** and the final product **3** are in polarization at every temperature at which PHIP is observed (-15–50 °C); no reaction is seen to occur at lower temperatures. This is in contrast to the reaction of **1** with *p*-H₂

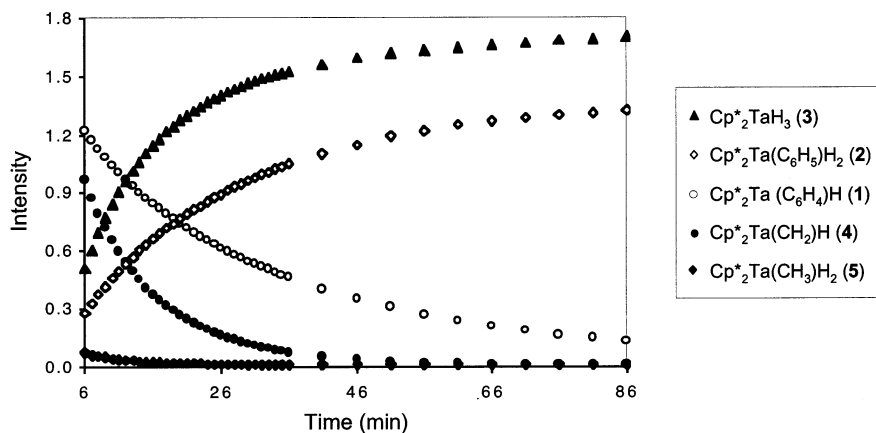


Figure 2. Same sample comparison of H₂ addition to Cp*₂Ta(C₆H₄)(H) (**1**) and Cp*₂Ta(CH₂)(H) (**4**) in benzene-*d*₆ at 20 °C.

(eq 1), where the only polarization initially observed corresponds to the phenyl dihydride species **2** which is stable below 0 °C. The subsequent hydrogenolysis of **2** that yields benzene and the trihydride **3** takes place at higher temperatures, and, at later stages of the reaction, only **3** is in polarization. While the resonances at δ 2.73 and 0.57 for the methyl dihydride complex **5** have similar chemical shifts to those of the phenyl dihydride **2**, an ambiguity was perceived to exist regarding whether the polarized resonances correspond to two Ta–H protons, or to one Ta–H and one Ta–CH₃ proton. Because either was a possibility, depending on the mechanism of H₂ addition as shown in Scheme 1, two experiments were undertaken to distinguish between the two possibilities.

In the first of these, H₂ addition to the methyl methylene complex Cp*₂Ta(CH₂)(CH₃) (**6**)²⁴ was examined using PHIP. Upon addition of *p*-H₂ to a solution of **6** in benzene-*d*₆, PHIP is not observed until 90 °C, and then only very minor polarized resonances are seen for **3** and an unknown species (δ 0.3, antiphase doublet, $J_{\text{H-H}} = 15$ Hz). With extended heating, no additional reactivity is observed other than conversion to the ethylene complex Cp*₂Ta(C₂H₄)(H) (**7**) as previously reported.²³ The difference in reactivity between the two methylene complexes **4** and **6** with H₂ correlates with the difference in α -insertion rates – **4** proceeds 10⁷ faster than **6** – found previously by magnetization transfer,²³ strongly supporting the notion that H₂ addition occurs via a Ta(III) intermediate. In contrast, if H₂ addition were proceeding via Path B of Scheme 1 through a four-centered transition state, then such a difference in reactivity between **4** and **6** would not be expected.

The second experiment, that served to establish unequivocally the path of H₂ addition to the methylene hydride complex, involved preparation of the ¹³C-labeled complex, Cp*₂Ta(¹³-CH₂)(H) (**4**-¹³C), to determine the magnitudes of J_{CH} for the added hydrogen atoms. One-bond ¹ J_{CH} values, which would be expected for one of the hydrogens in Path B, are typically in the 125–140 Hz range. Under *p*-H₂, the polarized resonances for **5** at δ 2.73 and 0.57 are observed with additional couplings (Figure 1b), but the magnitudes of these couplings (δ 2.73, $J_{\text{C-H}} \approx 11$ Hz; δ 0.57, $J_{\text{C-H}} \approx 3$ Hz) are too small to represent the one-bond coupling that would result from Path B. The two polarized resonances for Cp*₂Ta(¹³CH₃)(H)₂ (**5**-¹³C) are thus due to tantalum hydrides.

Together, the PHIP studies with **4**, **4**-¹³C, and **6** all point to the major mechanism for H₂ addition as being via a Ta(III)

intermediate [Cp*₂Ta(CH₃)] rather than by a direct addition across the Ta=CH₂ bond. This is the same mechanistic pathway found for the benzyne complex **1**. It is interesting that formation of a Ta(III) intermediate followed by H₂ addition is preferred over H₂ addition across the Ta–C bond in light of the high reactivity of carbene and benzyne fragments in organic chemistry.

Comparison of the Hydrogenolysis of Cp*₂Ta(C₆H₄)(H) (1**) and Cp*₂Ta(CH₂)(H) (**4**).** Complexes **1** and **4** exhibit striking differences in reactivity. While the reaction of **1** with H₂ to form benzene and **3** takes place above room temperature (35 °C), the conversion of **4** to methane and **3** is relatively rapid at 20 °C. To probe the basis of this difference in reactivity – that is, whether it is due different rates of initial H₂ addition or subsequent C–H reductive elimination or some combination thereof – a same sample comparison of the reaction of **1** and **4** with H₂ in benzene-*d*₆ was carried out. Figure 2 shows the distribution of species (**1**–**5**) observed during the first 80 min of reaction at 20 °C, as monitored by the intensities of their respective Cp* resonances in ¹H NMR spectra collected at regular intervals. The curve for the disappearance of benzyne hydride **1** closely mirrors that of the appearance of phenyl dihydride **2**, while the curve for the disappearance of the methylene hydride **4** closely mirrors that for the appearance of the final trihydride product **3**. The intermediate Cp*₂Ta(CH₃)(H)₂ (**5**) is present at very low concentrations at the beginning of the reaction and is undetectable within 20 min. During the first hour of reaction, the formation of **3** is thus attributed solely to the hydrogenolysis of **4**, while the hydrogenolysis of **1** yields only **2** during this time period.

In analyzing the kinetics of the reactions, the disappearances of complexes **1** and **4** are found to be first-order processes, with $k_{\text{obs}} = 3.2 \times 10^{-2} \text{ s}^{-1}$ for **1** and $9.2 \times 10^{-2} \text{ s}^{-1}$ for **4** at 20 °C. That these reactions are first-order can be explained in terms of the mechanism for H₂ addition for **1** and **4**. The first step in the reaction of each of these compounds with H₂ is formation of the Ta(III) intermediate, which subsequently undergoes H₂ oxidative addition. The generation of the Ta(III) intermediate is the rate-determining step in this sequence, rather than H₂ addition. The difference in the k_{obs} rate constants, 2.9 times greater for **4** than for **1**, correlates well with a 2.5 times difference in the rates of Ta(III) formation obtained from the previously reported magnetization transfer studies.²³

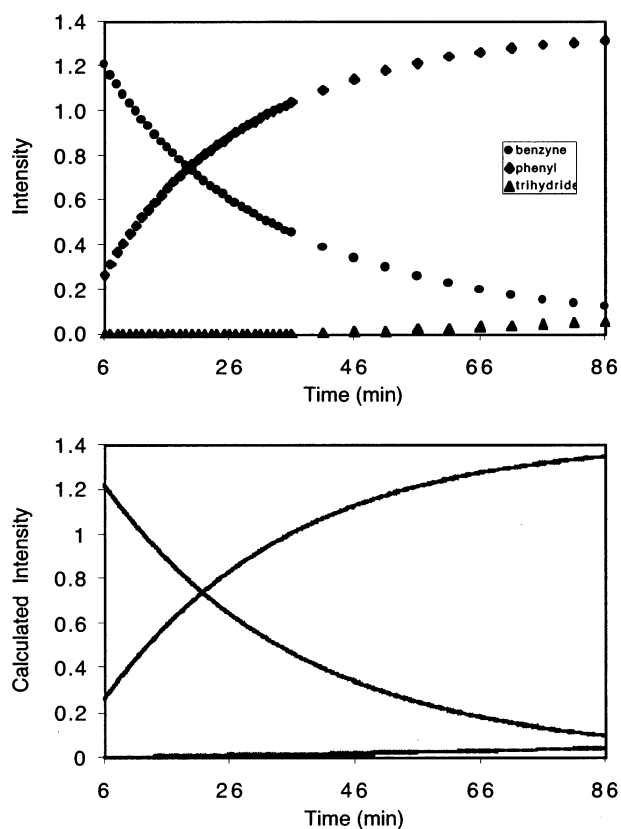
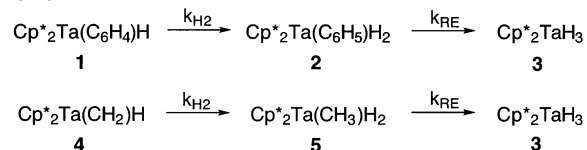


Figure 3. Experimental (top) vs calculated (bottom) intensities for the reaction of H₂ with Cp*₂Ta(C₆H₄)H (**1**) in benzene-*d*₆ at 20 °C.

Scheme 2



To gain insight into the relative rates of C–H reductive elimination, the kinetics were modeled using Mathcad software. To simplify the calculations, the reactions are modeled as two sets of consecutive first-order reactions, as shown in Scheme 2. The conversion of **1** to **3** is considered as one system, while the conversion of **4** to **3** is a separate system. The rate constants (k_{H_2}) for the disappearance of **1** and **4** are calculated from experimental data and correspond to the rate constants k_{obs} for initial H₂ addition to yield **2** and **5**, respectively. While this process is composed of two consecutive steps, the first is actually the rate-determining step of unimolecular Ta(III) formation by α -insertion. With values thus obtained for k_{H_2} plus the initial concentrations of **1** and **4**, and the equation for consecutive first-order reactions (see Experimental Section), the rate constants for the second reaction denoted as k_{RE} are obtained by visual fitting of the calculated intensity versus time curves to those obtained from experiment. Figures 3 and 4 show the plots of experimental and calculated data. The rate constants obtained in this manner correspond to the rate constants for reductive elimination of benzene and methane from **2** ($k_{\text{RE}} = 4.7 \times 10^{-4} \text{ s}^{-1}$) and **5** ($k_{\text{RE}} = 1.6 \text{ s}^{-1}$), respectively. From these rate constants, it is seen that the formation of methane from **5** is

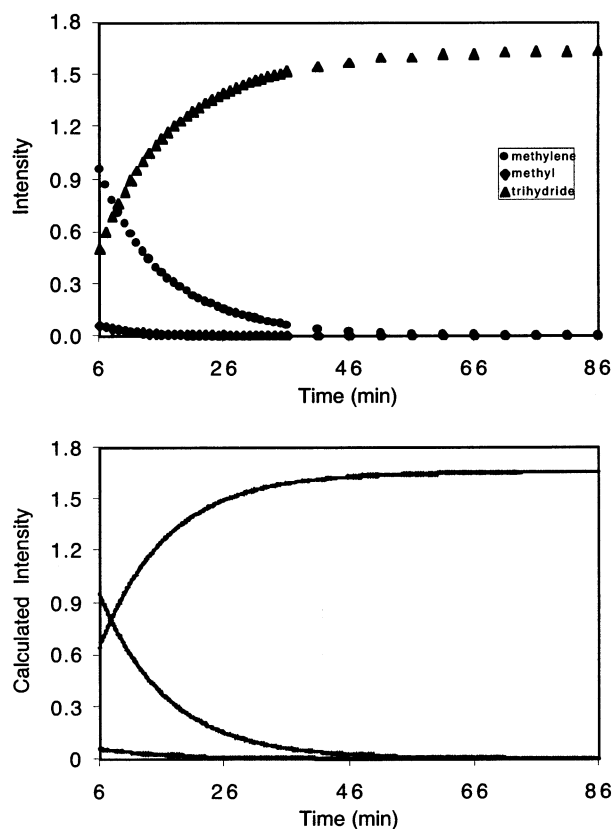


Figure 4. Experimental (top) vs calculated (bottom) intensities for the reaction of H₂ with Cp*₂Ta(CH₂)H (**4**) in benzene-*d*₆ at 20 °C.

approximately 3000 times faster than that of benzene from **2**, leading to a $\Delta\Delta G^\ddagger$ of 4.7 kcal/mol for the reductive elimination process.

The major difference in the reactivities of **1** and **4** comes from the rates of C–H reductive elimination, which agrees well with literature precedent. Methyl-hydride coupling is typically much more facile than phenyl-hydride coupling.^{26–28} The calculated $\Delta\Delta G^\ddagger$ of 4.7 kcal/mol for reductive elimination of benzene versus methane compares relatively well with values previously reported, which are 7.4 kcal/mol (296 K) for Tp’Rh(CN-neopentyl)(R)H (R = Ph, Me)²⁷ and 6.9 kcal/mol (256 K) for Cp*’Rh(PMe₃)(R)H (R = Ph, Me).²⁶ The preference for methane elimination over benzene elimination can in part be rationalized by relative metal–carbon bond strengths. In general, a metal–phenyl bond is approximately 10–15 kcal/mol stronger than a metal–methyl bond.²⁹ In contrast to the expected trend, the early metal complexes (tBu₃SiNH)₃Zr(R) and (tBu₃SiNH)₂(R)Ta(=NSi^tBu₃) (R = Ph, Me) undergo 1,2-RH-elimination reactions in which formation of benzene is *faster* than formation of methane.^{30,31} It is important to note that these reactions involve coupling of a metal-alkyl or -aryl and a hydrogen residing on one of the nitrogen ligands, rather than a classical reductive elimination of a metal-alkyl or

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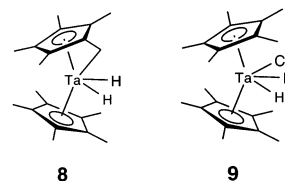
-aryl hydride, which may account for the observed difference in relative rates. Our system provides a rare example of reductive elimination from an *early* transition metal center and a unique opportunity to compare the rates of benzene and methane formation, which is usually only possible with late metal systems.

Addition of H₂ to Cp*₂Ta(C₂H₄)(H) (7). Like the benzyne complex **1**, the ethylene complex Cp*₂Ta(CH₂CH₂)(H)₂ (**7**) can be drawn as either an η²-olefin complex or a Ta(V) metallacycle. Despite this similarity, it was not obvious that **7** would undergo reaction with H₂ via the same mechanism as that established for **1**. In the magnetization transfer studies mentioned previously, the rate of α-H migratory insertion of **7** was reported to be about 10³ times slower than that of **1**.²³ The study of H₂ addition to **7** thus provided yet another opportunity to employ PHIP for examination of the mechanism for H₂ activation via oxidative addition to a Ta(III) intermediate or addition directly across the Ta–C bond.

At room temperature, addition of H₂ to **7** in benzene-*d*₆ does not occur. However, extended heating (3 days at 140 °C) leads to the formation of some trihydride **3** as well as ethane, and minor amounts of Cp*₂Ta(O)(H) (assigned by ¹H NMR comparison to literature data²⁴) and an unknown species (δ 1.8, minor). Under *p*-H₂, PHIP is only observed at elevated temperatures (60–90 °C). Relatively weak polarization is seen in the resonances corresponding to **3** and in a new species at δ 6.7 and 5.1 (antiphase doublets, *J*_{H–H} = 15 Hz). The chemical shifts of the latter resonances posed an initial problem for the structural assignment of this species because they were far removed from the observed hydrides for **2**, **3**, and **5**, and the expected product of H₂ addition, Cp*₂Ta(CH₂CH₃)(H)₂, would be anticipated to have similar hydride resonances. Also, neither of the two resonances could correspond to a methyl proton of the Ta-ethyl ligand which would show normal coupling to unpolarized protons.

In an attempt to determine the identity of the unknown species, several different samples were examined. Complex **7** was prepared by two different routes, and by synthesis from Cp*₂TaCl₂ and 2 equiv of EtMgBr³² and by thermolysis of Cp*₂Ta(CH₂)(CH₃) (**6**).²³ The intensity of the polarization from **7** + *p*-H₂ was found to vary from sample to sample, with no consistent or discernible pattern. Treatment of samples with light yielded no results different from dark controls in terms of polarization, although formation of the known “tucked-in” complex Cp*(η⁶-C₅Me₄CH₂)TaH₂ (**8**)³² was noted on exposure to higher intensity 366 nm light. The identity of the polarized resonances at δ 6.7 and 5.1 was finally established as belonging to Cp*₂TaH₂Cl when the complex Cp*₂TaCl(μ-N₂)TaClCp*₂ was examined with *p*-H₂, which gave strong polarization for the same product at δ 6.7 and 5.1 (antiphase doublets, *J*_{H–H} = 15 Hz) at 75 °C.³³ In addition, the reaction of the complex Cp*₂TaCl(THF) with H₂ at 25 °C showed normal doublets at δ 6.7 and 5.1 (*J*_{H–H} = 15 Hz). These resonances are identified as hydride ligands of the unsymmetric kinetic isomer of Cp*₂TaH₂Cl (**9**). The polarization in the reaction of ethylene complex **7**

with *p*-H₂ due to Cp*₂TaH₂Cl clearly shows the presence of a minor contaminant in the sample of **7** that would not be detected in any other way. In this sense, the results illustrate the extraordinary sensitivity of PHIP in detecting species present in very small concentrations.



Conclusion

Through a combination of PHIP and ¹³C-labeling experiments, the mechanism of H₂ addition to Cp*₂Ta(CH₂)(H) (**4**) has been examined. The addition of H₂ takes place following formation of a Ta(III) methyl intermediate by α-insertion, which is similar to the mechanism previously reported for the benzyne complex Cp*₂Ta(C₆H₄)(H) (**1**). In a direct, same sample comparison of the conversion of **1** and **4** to their respective intermediate dihydrides **2** and **5** and the common final product Cp*₂TaH₃ (**3**), it is found that the methylene complex **4** reacts slightly more rapidly than **1**, consistent with previously reported magnetization transfer rates, and that the intermediate dihydrides exhibit a great difference in reactivity on the basis of the relative tendency of each to undergo C–H reductive elimination. Specifically, the reductive elimination of methane from **5** is 3000 times faster than the reductive elimination of benzene from **2** in accord with reports of similar methane and benzene reductive eliminations from complexes of the late transition metals rhodium and palladium.^{26–28}

In examining the series of tantalocene complexes discussed in this paper, it is apparent that H₂ addition is only observed when a Ta(III) intermediate is accessible. Complexes **1** and **4** both readily undergo α-H migratory insertion to form the Ta(III) intermediates [Cp*₂TaR] (R = Ph, Me) and exhibit facile reaction with H₂. When a Ta(III) intermediate is not readily accessible, as in the case of Cp*₂Ta(CH₂)(CH₃) (**6**) and Cp*₂Ta(C₂H₄)(H) (**7**), minimal or no reaction with H₂ is seen, leading to the conclusion that Path B of Scheme 1 involving direct H₂ addition to the Ta(V)–C bond via a four-centered transition state either does not occur at all or is an exceedingly minor alternative process for H₂ addition in these systems.

Experimental Section

General Information. All complexes were prepared using standard inert-atmosphere Schlenk, vacuum line, and drybox techniques. Solvents were dried using Grubb’s purification system. Deuterated solvents were transferred from ampules to activated sieves and stored in the glovebox. The tantalocene complexes Cp*₂Ta(CH₂)(H),²⁴ Cp*₂Ta(C₆H₄)(H),²³ Cp*₂Ta(CH₂)(CH₃),²⁴ and Cp*₂Ta(C₂H₄)(H)²⁵ were prepared as previously reported. Parahydrogen was prepared by cooling high purity hydrogen over FeCl₃ adsorbed onto silica at 77 K.¹⁴ All NMR spectra were recorded on a Bruker Avance-400 spectrometer. ¹H NMR chemical shifts are referenced relative to the residual proton peak(s) of deuterated solvents.

(32) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213–220.

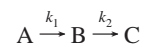
(33) Bregel, D. C.; Oldham, S. M.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 4371–4377.

Addition of Hydrogen to Tantalocene Complexes. In a typical experiment, an NMR tube with a J. Young valve was charged with approximately 1 mg of compound inside a nitrogen atmosphere glovebox. The desired deuterated solvent was added, and the tube was sealed. On a high vacuum line, normal hydrogen (1 atm) or para-enriched hydrogen (ca. 3 atm) was added to the tube at 77 K. Upon warming to room temperature, the reaction was monitored by ^1H NMR. For parahydrogen experiments, a 45° pulse was used, and 8 or 16 scan spectra were collected.

Modeling of Reaction Kinetics for H_2 Addition to $\text{Cp}^*_2\text{Ta}(\text{C}_6\text{H}_4)(\text{H})$ (1) and $\text{Cp}^*_2\text{Ta}(\text{CH}_2)(\text{H})$ (4). An NMR tube with a J. Young valve was loaded with equimolar amounts of **1** and **4** in benzene- d_6 (each ca. 1 mM). The reaction with H_2 (ca. 3 atm) was monitored by ^1H NMR, and the intensities of the Cp^* resonances were recorded every minute for 80 min. The data for disappearance of **1** and **4** were examined with a standard spreadsheet program and found to be first-order for each complex. Mathcad software was used to calculate the rate constants for C–H reductive elimination (k_{RE}).³⁴

(34) Mathcad. *Mathcad 2000 Professional*; Mathsoft Engineering & Education, Inc.: Cambridge, MA, 2000.

The equations for consecutive first-order reactions, shown below, were used to determine k_{RE} .³⁵



$$[\text{A}] = [\text{A}]_0 e^{-k_1 t}$$

$$[\text{B}] = [\text{A}]_0 \frac{k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[\text{C}] = [\text{A}]_0 + \frac{[\text{A}]_0}{k_1 - k_2} [k_2 e^{-k_1 t} - k_1 e^{-k_2 t}]$$

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JA027005B

(35) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.