

Palladium-Catalyzed Hydrogenation: Detection of Palladium Hydrides. A Joint Study Using Para-Hydrogen-Enhanced NMR Spectroscopy and Density Functional Theory

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Palladium complexes containing two monodentate phosphine ligands are widely used in homogeneous catalysis.¹ Their conversion during catalysis to palladium monophosphine complexes² or palladium colloids³ means that identifying the active catalyst is not straightforward. In the case of hydrogenation, a role for a palladium hydride is often proposed.⁴ An example of such a species is given by Pd(bcope)(CHPhCH₂Ph)(H),⁵ which was seen through the para-hydrogen-induced polarization (PHIP)⁶ effect. In this Communication, we report on the catalytic activity of *cis*-[Pd(PEt₃)₂(OTf)₂].⁷ Although many palladium-based reactions have been studied by PHIP,^{6,8} we show here for the first time that palladium hydride resonances can themselves be enhanced and, in conjunction with density functional theory (DFT), rationalize the hydrogenation activity of a palladium–bisphosphine based hydrogenation catalyst. Earlier ab initio studies on Pd(PH₃)(H)(C₂H₅) have considered the role of monophosphine species in alkene hydrogenation.⁹

A number of 9 μM solutions of *cis*-[Pd(PEt₃)₂(OTf)₂] (**1**) in MeOD-*d*₄ containing a 25-fold excess of diphenylacetylene-*d*₁₀ under 2–4 atm of 100% *p*-H₂ have been examined by 700 MHz NMR spectroscopy. This reaction would be expected to provide a route to the analogous Pd(0) species Pd(PEt₃)₂.¹⁰ The resulting ¹H NMR spectra at 295 K revealed three new signals at δ 7.25, 6.66, and 2.91, due to the three expected organic hydrogenation products, *trans*-stilbene, *cis*-stilbene, and 1,2 diphenylethane, respectively. The δ 6.66 signal is due to the kinetic *cis*-hydrogenation product and appears in emission due to its formation via an intermediate with inequivalent hydride ligands.¹¹ While the two other signals appear in absorption, they also show PHIP when ¹³C≡C-enriched diphenylacetylene-*d*₁₀ is employed and therefore correspond to products formed via a hydrogenation pathway that places two protons from the same *p*-H₂ molecule on adjacent sites. When this reaction is examined by GCMS, the ratio of *cis*-stilbene:*trans*-stilbene:1,2 diphenylethane was typically 78:11:11.

In these spectra, a number of metal-based species are also detected through the PHIP effect. Notably, three enhanced ¹H NMR signals appear immediately at δ 4.47, 3.22, and 2.99 (Figure 1a). These three coupled signals, arising from species **2** (Chart 1), also couple to two ³¹P nuclei which resonate at δ 8.40 (*J*_{PP} = 54 Hz) and 25.90 (*J*_{PP} = 54 Hz). Use of ¹³C≡C-enriched diphenylacetylene-*d*₁₀ (310 K) revealed that the ¹H resonance of **2** at δ 4.47 connected to a ¹³C signal at δ 67.14 (*J*_{HC} = 157 Hz, *J*_{CP} = 44 Hz), while both the δ 3.22 and 2.99 signals connected to a single δ 35.30 resonance (*J*_{HC} = 130 Hz, *J*_{CP} = 15 Hz). These data confirm that **2** is Pd(PEt₃)₂(CHPhCH₂-Ph)(H). When an EXSY spectrum was recorded at 308 K, magnetization transfer from the δ 4.47 signal of **2** to the δ 7.25 signal of *trans*-stilbene confirmed a role for **2** in the hydrogenation of diphenylacetylene.

The most remarkable feature of these ¹H NMR spectra was, however, the observation of a PHIP-enhanced hydride signal at δ

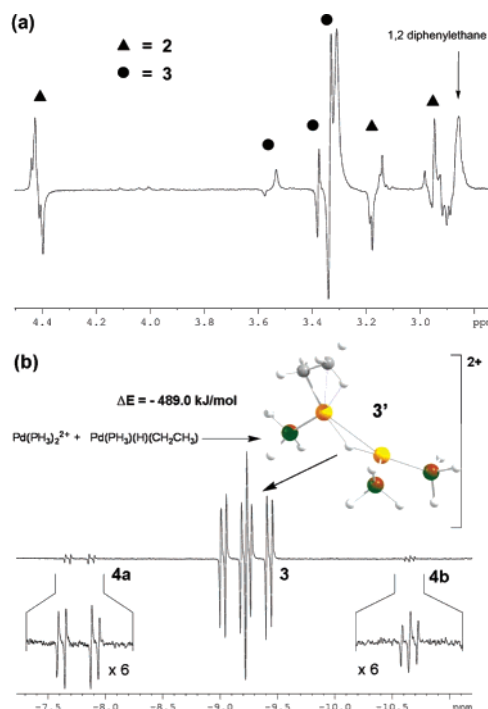
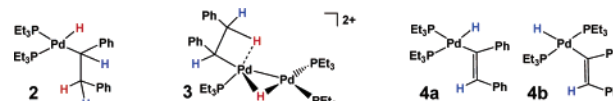


Figure 1. ¹H NMR spectra for the reaction of **1** with diphenylacetylene-*d*₁₀ and *p*-H₂ in MeOD-*d*₄: (a) 32 scans (295 K) showing key alkyl proton resonances; (b) 1224 scans (312 K) showing hydride resonances of **3**, **4a**, and **4b**, with the DFT model for **3** (**3'**) inset.

Chart 1. Structures of **2**, **3**, **4a**, and **4b**

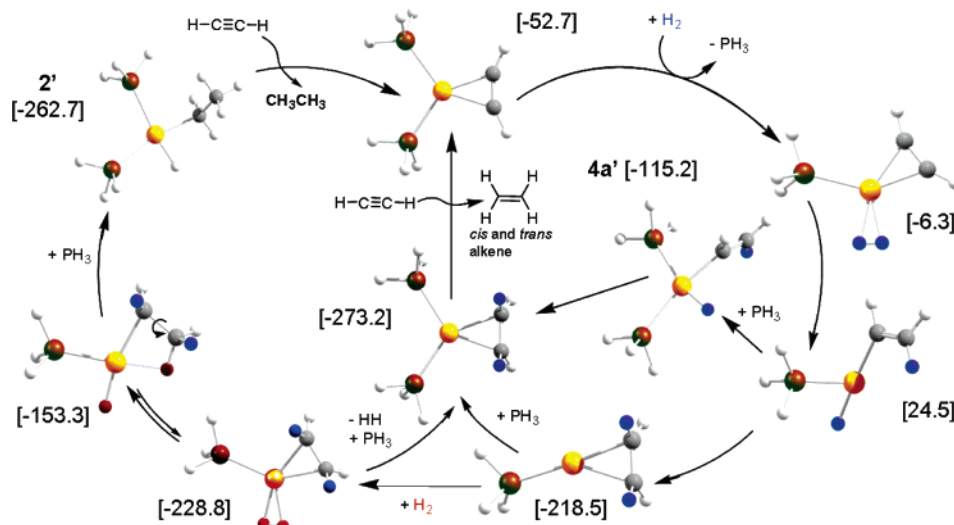


–9.18 due to **3** (Chart 1). This hydride resonance appears as a doublet of doublets of doublets of antiphase doublets due to couplings to three inequivalent phosphine ligands (*J*_{PH} couplings 19, 71, and 89 Hz) and a single proton (*J*_{HH} = –3.50 Hz) (Figure 1b); the proton providing this coupling was located by COSY spectroscopy at δ 3.34 and coupled, in turn, to two signals at δ 3.52 and 3.38. The corresponding ¹H–³¹P HMQC spectrum revealed three ³¹P signals for **3** at δ 3.41 (*d*, *J*_{PP} = 75 Hz), 4.63 (*d*, *J*_{PP} = 75 Hz), and 7.64. A ¹H–¹³C HMQC measurement yielded two ¹³C signals for **3**, one due to CH₂ a moiety at δ 49.70 (*J*_{HC} = 124 Hz) and the other due to a CH moiety at δ 49.58 (dd, *J*_{HC} = 124 and 134 Hz, *J*_{PC} = 24 and 55 Hz). When the hydride resonance of **3** was monitored by EXSY spectroscopy, magnetization transfer into both *cis*-stilbene and 1,2-diphenylethane was seen at 313 K.

Species **3** therefore contains three phosphines, one alkyl ligand, and one hydride ligand. DFT calculations, however, reveal that the monomeric trisphosphine complex Pd(PH₃)₃(H)(CH₂CH₃) is unsta-

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Scheme 1. DFT-Based Reaction Scheme (with Energies) for Hydrogenation by a Palladium–Bisphosphine Complex^a

^a All energies are in kJ/mol and relative to $\text{Pd}(\text{PH}_3)_2 + \text{H}-\text{C}\equiv\text{C}-\text{H} + 2\text{H}_2$; labels **2'** and **4a'** indicate where experimentally observed complexes map onto the DFT model system.

ble with respect to phosphine dissociation and the formation of the corresponding PH_3 analogue of **2**, **2'**. The NMR characteristics of the hydride signal of **3**, and in particular the observation of three distinct phosphine resonances without a characteristically large trans PP coupling, support this suggestion and indicate that **3** is most likely a dipalladium species. This is consistent with the fact that the size of the PHIP-enhanced signal for **3** depends critically on the concentration of **1**. DFT calculations on potential dipalladium species reveal that $\text{Pd}_2(\text{PH}_3)_3(\text{H})(\text{CH}_2\text{CH}_3)^{2+}$ (**3'**) is stabilized by 489 kJ mol^{-1} relative to $\text{Pd}(\text{PH}_3)_2^{2+}$ and $\text{Pd}(\text{PH}_3)(\text{H})(\text{CH}_2\text{CH}_3)$. Hence, under the reaction conditions where $\text{Pd}(\text{PEt}_3)_2^{2+}$ is present, the formation of **3** is expected.

Remarkably, in the high metal concentration experiments at 312 K, two further PHIP-enhanced hydride signals (ratio 1:0.7) are detected in the early stages of the reaction, where there are high levels of substrate and H_2 , at $\delta -7.77$ (antiphase ddd with $J_{\text{PH}} = 82$ and 18 Hz) (**4a**) and -10.65 (antiphase dt triplets with $J_{\text{PH}} = 15.8 \text{ Hz}$) (**4b**).¹² Species **4a** yielded two distinct ^{31}P resonances at $\delta 11.92$ and 10.72 , while **4b** produced a single signal at $\delta 19.29$. Additional COSY spectra located a proton at $\delta 6.35$, which accounted for the antiphase J_{HH} splitting of -4 Hz in **4a**, and a further signal at $\delta 5.35$ ($J_{\text{HH}} = -4 \text{ Hz}$) in **4b**. While the weak and transient nature of the NMR signals seen for these species prevented the collection of ^{13}C data, they can be unambiguously assigned to cis and trans isomers of $\text{Pd}(\text{PEt}_3)_2(\text{H})(\text{CPh}=\text{CPhH})$, respectively.

The role of these species in the hydrogenation chemistry of **1** is illustrated in Scheme 1 and has been rationalized through this and other theoretical studies, which reveal that $\text{Pd}(\text{PH}_3)_2$ adds H_2 in a high-energy process while coordination of the alkyne is exothermic.¹³ The catalytic cycle features palladium–monophosphine species, with $\text{Pd}(\text{PH}_3)(\text{H})_2(\text{H}-\text{C}\equiv\text{C}-\text{H})$ reacting via hydride transfer to form the three-coordinate vinyl hydride $\text{Pd}(\text{PH}_3)(\text{H})(\text{CH}=\text{CH}_2)$, which is analogous to $\text{Pd}(\text{PH}_3)(\text{H})(\text{CH}_2\text{CH}_3)$.⁹ This T-shaped species coordinates phosphine to form cis and trans isomers of $\text{Pd}(\text{PH}_3)_2(\text{H})(\text{CH}=\text{CH}_2)$ (**4a'**, **4b'**), which differ in energy by 20.6 kJ mol^{-1} . Experimentally, the observation of NMR signals for **4a** and **4b** in the ratio 1:0.7 suggests that their formation proceeds under kinetic control. In view of the fact that the [**4b**] remains low, C–H bond formation via phosphine dissociation must be rapid.

The DFT studies predict that $\text{Pd}(\text{PH}_3)(\text{H})(\text{CH}=\text{CH}_2)$ isomerizes to $\text{Pd}(\text{PH}_3)(\text{CH}_2=\text{CH}_2)$ prior to addition of H_2 . The corresponding H_2 addition product then forms the alkyl hydride $\text{Pd}(\text{PH}_3)(\text{H})(\text{CH}_2\text{CH}_3)$ after hydride migration. This alkyl species forms $\text{Pd}(\text{PH}_3)_2(\text{H})(\text{CH}_2-$

$\text{CH}_3)$ upon PH_3 coordination, a species that is directly analogous to **2**. The detection of **3**, **4a**, and **4b** is therefore fully consistent with the DFT studies.

An additional hydride resonance appears in these NMR spectra as an emission signal at $\delta -18.69$ which does not contain any ^{31}P splittings. The formation of a cluster containing two equivalent hydrides that are not phosphorus-coupled is therefore indicated. This confirms that phosphine loss occurs. We further note that the addition of free PEt_3 slows down both hydrogenation and cluster formation; activity is totally suppressed by 5 equiv.

The key deductions outlined in this paper are summarized in Scheme 1 and correspond to the mapping of the hydrogenation of an alkyne by a palladium–bisphosphine complex.

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Supporting Information Available: Synthetic and computational details and key NMR observations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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