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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 complexes[2] or palladium colloids[3] 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)($CHPhCH_2Ph$)(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*-[$Pd(PEt_3)_2(OTf)_2$].[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 $Pd(PH_3)(H)(C_2H_5)$ have considered the role of monophoshine species in alkene hydrogenation.[9]

A number of 9 μM solutions of *cis*-[$Pd(PEt_3)_2(OTf)_2$] (**1**) in MeOD-d_4 containing a 25-fold excess of diphenylacetylene-d_{10} under 2−4 atm of 100% *p*-H_2 have been examined by 700 MHz NMR spectroscopy. This reaction would be expected to provide a route to the analogous Pd(0) species $Pd(PEt_3)_2$.[10] The resulting ^{1}H 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 ^{13}C≡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*-H_2 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 ^{1}H 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 ^{31}P nuclei which resonate at δ 8.40 (J_{PP} = 54 Hz) and 25.90 (J_{PP} = 54 Hz). Use of ^{13}C≡C-enriched diphenylacetylene-d_{10} (310 K) revealed that the ^{1}H resonance of **2** at δ 4.47 connected to a ^{13}C 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 $Pd(PEt_3)_2(CHPhCH_2Ph)(H)$. 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 ^{1}H NMR spectra was, however, the observation of a PHIP-enhanced hydride signal at δ −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 ^{1}H−^{31}P HMQC spectrum revealed three ^{31}P signals for **3** at δ 3.41 (d, J_{PP} = 75 Hz), 4.63 (d, J_{PP} = 75 Hz), and 7.64. A ^{1}H−^{13}C HMQC measurement yielded two ^{13}C signals for **3**, one due to CH_2 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 $Pd(PH_3)_3(H)(CH_2CH_3)$ is unsta-

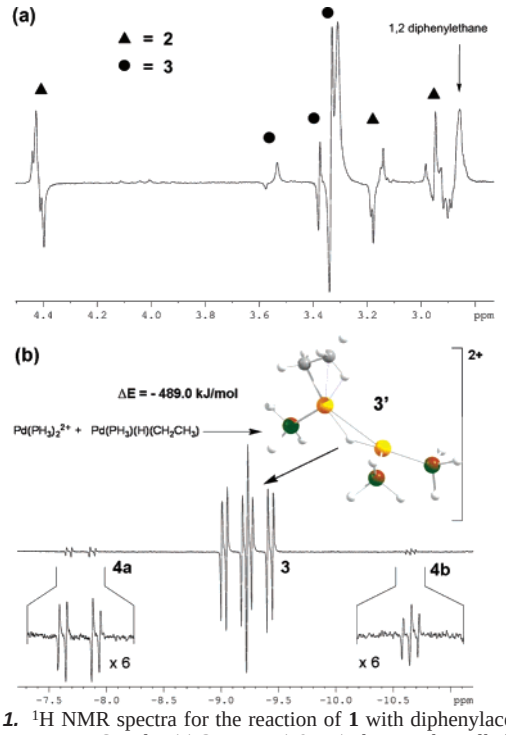
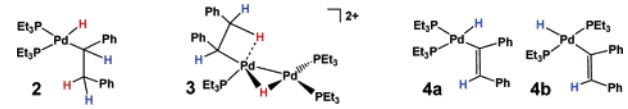


Figure 1. ^{1}H NMR spectra for the reaction of **1** with diphenylacetylene-d_{10} and *p*-H_2 in MeOD-d_4: (a) 32 scans (295 K) showing key alkyl proton resonances; (b) 1224 scans (312 K) showing hydride resonances of **3**, **4a**, and **4b**, with the DFT model for **3** (**3′**) inset.

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



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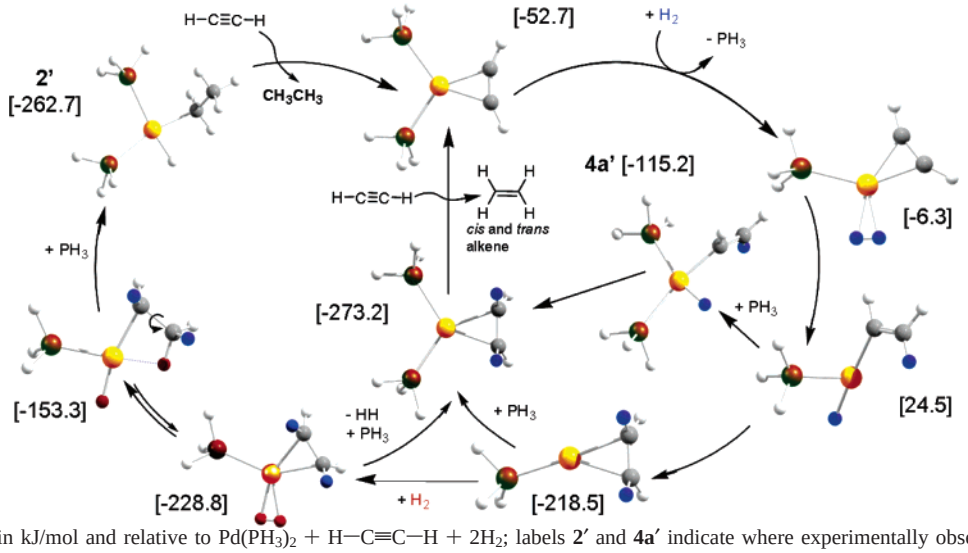
Scheme 1. DFT-Based Reaction Scheme (with Energies) for Hydrogenation by a Palladium−Bisphosphine Complex[a]



[a] All energies are in kJ/mol and relative to $Pd(PH_3)_2$ + H−C≡C−H + $2H_2$; 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 $Pd_2(PH_3)_3(H)(CH_2CH_3)^{2+}$ (**3′**) is stabilized by 489 kJ mol^{-1} relative to $Pd(PH_3)_2^{2+}$ and $Pd(PH_3)(H)(CH_2CH_3)$. Hence, under the reaction conditions where $Pd(PEt_3)_2^{2+}$ 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 δ −7.77 (antiphase ddd with J_{PH} = 82 and 18 Hz) (**4a**) and −10.65 (antiphase dt triplets with J_{PH} = 15.8 Hz) (**4b**).[12] Species **4a** yielded two distinct ^{31}P resonances at δ 11.92 and 10.72, while **4b** produced a single signal at δ 19.29. Additional COSY spectra located a proton at δ 6.35, which accounted for the antiphase J_{HH} splitting of −4 Hz in **4a**, and a further signal at δ 5.35 (J_{HH} = −4 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 be assigned to cis and trans isomers of $Pd(PEt_3)_2(H)(CPh{=}CPhH)$, 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 $Pd(PH_3)_2$ adds H_2 in a high-energy process while coordination of the alkyne is exothermic.[13] The catalytic cycle features palladium−monophosphine species, with $Pd(PH_3)(H)_2(H{-}C{\equiv}C{-}H)$ reacting via hydride transfer to form the three-coordinate vinyl hydride $Pd(PH_3)(H)(CH{=}CH_2)$, which is analogous to $Pd(PH_3)(H)(CH_2CH_3)$.[9] This T-shaped species coordinates phosphine to form cis and trans isomers of $Pd(PH_3)_2(H)(CH{=}CH_2)$ (**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 $Pd(PH_3)(H)(CH{=}CH_2)$ isomerizes to $Pd(PH_3)(CH_2{=}CH_2)$ prior to addition of H_2. The corresponding H_2 addition product then forms the alkyl hydride $Pd(PH_3)(H)(CH_2CH_3)$ after hydride migration. This alkyl species forms $Pd(PH_3)_2(H)(CH_2CH_3)$ 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 δ −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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