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Detection and Reactivity of Pd((C$_8$H$_{14}$)PCH$_2$CH$_2$P(C$_8$H$_{14}$))(CHPhCH$_2$Ph)(H) as Determined by Parahydrogen-Enhanced NMR Spectroscopy

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Palladium complexes are widely used in homogeneous catalysis. They are best known for their C−C bond forming reactions but also feature in oxidation, reduction, isomerization, and carbonylation chemistry.[1] Less well-known is the excellent performance of palladium diphosphine complexes in the hydroformylation of alkenes.[2] The role of palladium hydrides in many of these processes is well established, but the direct observation of palladium hydride complexes in such reactions is extremely rare. Recently, [(1,2-(CH$_2$P-Bu$^t_2$)$_2$C$_6$H$_4$)Pd(H)(MeOH)]$^+$, a key intermediate in the methoxycarbonylation of alkenes, was observed by NMR[3] with subsequent studies detecting the corresponding [(L)$_2$Pd(CH$_2$CH$_3$)]$^+$ species, which features a β-agostic C−H interaction.[4] Deactivated species such as Pd(PPh$_3$)$_2$(H)(Br) or Pd(dippp)(H)(Cl) have also been observed.[5]

The parahydrogen-induced polarization (PHIP)[6] effect enhances the hydride resonances of metal−dihydride complexes directly and those of scalar-coupled ^{31}P and ^{13}C heteronuclei by cross-polarization.[7] The development of selective excitation methods[8] and the use of 2D methods to observe insensitive heteronuclei have also made an impact.[9] Furthermore, PHIP has been harnessed to study the adsorption of H$_2$ onto surfaces,[10] in magnetic resonance imaging (MRI),[11] and to sensitize a hydroformylation product containing a single atom from *p*-H$_2$.[12] Here we employ the PHIP effect to study the reactions of Pd(bcope)(OTf)$_2$ **1** (where bcope is (C$_8$H$_{14}$)PCH$_2$-CH$_2$P(C$_8$H$_{14}$))[13] with alkynes. We show that the resonances of organic components bound within a metal's coordination sphere can be substantially enhanced and hence demonstrate that the PHIP effect can be used to detect metal complexes without the need for enhancement of a hydride resonance.

A 1 μM solution of **1** in CD$_2$Cl$_2$ containing a 50-fold excess of d_{10}-diphenylacetylene was placed under 3 atm of 100% *p*-H$_2$ at 213 K and rapidly introduced into a 400 MHz NMR spectrometer. While a 295 K based ^{31}P NMR spectrum indicated that **1** was the only species present, the corresponding ^{1}H NMR spectrum showed an emission signal at δ 6.66 for the alkene proton of the ^{12}C isotopomer of the kinetic hydrogenation product *cis*-stilbene. Since the two-alkene protons of the cis isomer are magnetically equivalent, the observation of this *p*-H$_2$ enhanced signal indicates the involvement of an undetected intermediate in which the two hydrogen atoms of the *p*-H$_2$ molecule are inequivalent[14] and introduced in a spin-correlated pathway.[9c,d] This intermediate most likely corresponds to Pd(bcope)(CPh=CHPh)(H) as shown in Scheme 1. A weak signal, due to the accumulated thermally polarized trans product, slowly develops in this spectrum at δ 7.18. This product cannot, however, be formed simply from Pd(bcope)(CPh=CHPh)-(H) since the associated hydrogen atoms must remain cis if the process is concerted.

The most notable features of this NMR spectrum, however, correspond to substantially enhanced proton signals at δ 4.94 and 3.13 and a further weakly enhanced signal at δ 2.92 (Figure 1a). These signals contained characteristic anti-phase components due to their origin from *p*-H$_2$ protons, proved to be coupled in a COSY spectrum, and simplified on ^{31}P decoupling. ^{1}H−^{31}P HMQC spectra revealed two ^{31}P doublets at δ 32.3 and δ 42.9 (J_{PP} = 47 Hz) for this species, while a ^{1}H−^{13}C HMQC spectrum produced correlations from the proton resonance at δ 4.94 to a ^{13}C signal at δ 63.0, and the remaining proton resonances to a signal at δ 37.1. It can therefore be concluded that these resonances arise from a ligand that is attached to palladium. When this reaction was reexamined using ^{13}C≡C enriched d_{10}-diphenylacetylene, strong signals were observed in one-dimensional, fully proton coupled ^{13}C experiments at δ 63.0 and δ 37.1; the former showed two ^{31}P splittings of 42 and 14 Hz in addition to a single proton splitting of 147 Hz. The δ 63.0 signal therefore corresponds to a CH group bound directly to palladium. In this spectrum, the δ 37.1 signal appeared as a pseudo-triplet as a consequence of the PHIP effect, with lines of relative intensities 1, 0, and −1, and therefore corresponds to a CH$_2$ moiety. This suggests that *cis*-Ph−CH=CH−Ph has been converted into a PdCHPhCH$_2$Ph group, and the species giving rise to these signals is Pd(bcope)(CHPhCH$_2$Ph)(H), **2** (Scheme 1).[15]

To explore the reactivity of **2**, a series of modified 1D-EXSY experiments were recorded where a single alkyl proton resonance was selected, and magnetization transfer from this site was monitored as a function of mixing time.[6e,16] For the δ 4.94 peak, strong magnetization transfer into the *trans*-stilbene signal at δ 7.18 was observed at 295 K (Figure 1b). When the sample was warmed to 313 K, the intensity of all of the enhanced peaks mentioned previously increased substantially. However, under these conditions, even greater magnetization transfer from the δ 4.94 site into *trans*-stilbene was seen in conjunction with weaker transfer into *cis*-stilbene and into both of the previously described CH$_2$Ph proton sites at δ 3.13 and δ 2.92. Simulation of these experimental traces[17] suggests that the observed rate constants of formation of *trans*- and *cis*-stilbene from **2** were 4 s^{-1} and 0.004 s^{-1}, respectively. This information confirms that the detected PdCHPhCH$_2$Ph group of **2** transforms most readily into *trans*-stilbene and demonstrates that hydride insertion is reversible and involves a discrete Pd(bcope)-(PhCH=CHPh)(H)$_2$ intermediate. These observations thereby account for the isomerization of the kinetic *cis* hydrogenation product into the thermodynamically favored *trans* product, a reaction that can be monitored for more than 50 turnovers based on **1**.

When the peak at δ 3.13 was selected in the same EXSY experiment at 313 K, exchange into free H$_2$ and weaker exchange into free *cis*- and *trans*-stilbene, as well as into the δ 4.94 position, were observed. However, when the resonance at δ 2.92 was selected, only transfer into *trans*-stilbene was observed. These observations confirm that the proton yielding the resonance at δ 3.13 transfers directly into free H$_2$, while those at δ 4.94 and δ 2.92 move into *trans*-stilbene. The identification of **2** as an alkyl hydride is therefore confirmed (Scheme 1). Since the hydride

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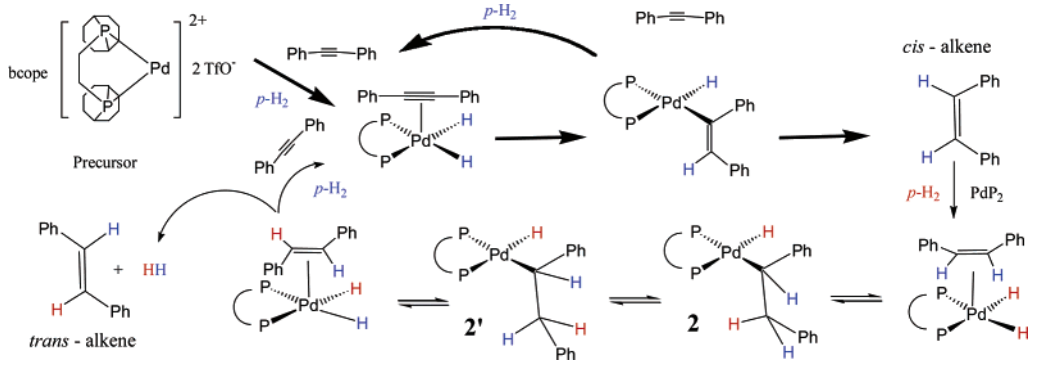
Scheme 1. Hydrogenation by a Palladium Bisphosphine Complex[a]



[a] Color indicates the transformations of individual *p*-H_2 molecules with the dominant catalytic formation of *cis*-stilbene indicated in bold, the secondary isomerization to *trans*-stilbene competes on the NMR timescale.

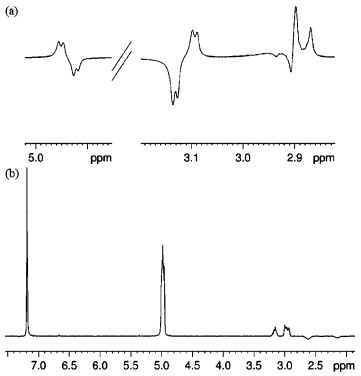


Figure 1. (a) $^1H\{^{31}P\}$ spectrum of **2** in CD_2Cl_2 at 295 K showing key alkyl proton resonances. (b) Magnetization transfer from the alkyl α-H of **2** to the *β*-H protons and free *trans*-stilbene after 800 ms.

ligands transfer on the internal face of the metal-alkene, the original orientation of the hydrogen and phenyl substituents of the alkyl group must match those of the alkene, and hence, rotation about the C−C bond of **2** is necessary to form *trans*-stilbene (Scheme 1). The strongly enhanced signals at *δ* 4.92 and *δ* 3.13 are therefore due to the original hydrogen atoms of *p*-H_2 activated *cis*-stilbene while the weakly enhanced signal at *δ* 2.92 arises because of a species where hydride exchange places two protons from the same *p*-H_2 molecule onto the same carbon of the alkyl; these effects can be reproduced by simulation, and similar exchange effects have been seen in liberated alkenes produced during related hydrogenation reactions.[18] The failure to detect an nOe interaction from the *δ* 4.94 signal to the hydride ligand suggests the phenyl is initially on the internal face of the alkyl, with rotation to **2′** and subsequent *β*-hydrogen transfer leading to alkene isomerization (Scheme 1).

When phenylpropyne was used as a substrate, Pd(bcope)-(CHPhCH_2Me)(H) **3**, was observed with enhanced proton resonances at *δ* 1.55, 1.86, and 4.72. The observation of **2** is therefore not unique. While enhanced ^1H NMR signals were now observed for *cis*- and *trans*-*β*-methylstyrene, no direct magnetization transfer into them from the aliphatic proton signals of **3** was observed, even at 313 K. It can therefore be concluded that **3** is less prone to *β*-hydride elimination than **2**.

This study has demonstrated that PHIP need not be limited to the study of metal dihydrides since the enhancement of organic components within a metal's ligand sphere can be achieved. To observe the PHIP effect in this study, the reactions must be based on (bcope)Pd$(H)_2$ rather than (bcope)Pd(H)$(solv)^+$, since the necessary pairwise H_2 transfer is not possible with the latter complex.[19] It has also been demonstrated that Pd(bcope)(alkene)-$(H)_2$ undergoes reversible hydride transfer to the bound alkene. These deductions are summarized in Scheme 1 and correspond to the mapping of concerted catalytic hydrogenation by a palladium-(II) bis-phosphine complex.

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

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