Definitive Evidence for a Pairwise Addition of Hydrogen to a Platinum Bis(phosphine) Complex Using **Parahydrogen-Induced Polarization**

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Summary: Through the use of parahydrogen-induced polarization (PHIP), conclusive evidence has been obtained that H₂ addition to Pt(Ph₂PCH₂CH(Me)OPPh₂) proceeds in a concerted, pairwise manner. PHIP has also been used in conjunction with a 2D HMQC sequence to obtain ³¹P and ¹⁹⁵Pt NMR spectra from submilligram samples in 2–5 min.

The activation of dihydrogen by metal complexes in solution is a key step in homogeneous hydrogenation.¹⁻³ For most late metal catalysts, the activation proceeds by oxidative addition in a concerted manner leading to a dihydride product of metal oxidation state two greater than in the starting compound. For d⁸ complexes such as $IrCl(CO)(PPh_3)_2$ and IrBr(CO)(dppe) (dppe = bis-(diphenylphosphino)ethane), oxidative addition of H₂ has been studied extensively and the dihydride products have been shown conclusively to form in a concerted, pairwise manner with hydride ligands mutually cis.^{4–9} For d^{10} complexes of Pt(0), the addition of H₂ is presumed to take place in an analogous manner, but evidence in this regard is less compelling. While Pt(II) dihydrides have long been known,¹⁰ their formation often involved reductions using hydride sources, and in cases where the reaction was done under H₂, the possible addition of hydrogen was not studied mechanistically. However, from Trogler's study of the cistrans iosmerism of PtH₂(PMe₃)₂ and subsequent reductive elimination of $H_{2,1,1,1,2}$ a pairwise addition mechanism can be inferred mainly on the basis of a kinetic isotope effect for the elimination. In other studies designed to maintain a cis disposition of the hydride ligands in PtH_2L_2 complexes, chelating bis(phosphine) ligands

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(diphos) were employed, ^{13–16} but it was found that many of the PtH₂(diphos) systems reversibly lost hydrogen with concomitant formation of [PtH(diphos)]₂ dimers. In a recent investigation of these systems, Andersen observed that, in addition to monomer-dimer equilibria, mixtures of PtH₂(diphos) and PtD₂(diphos) led to facile generation of the d₁ isotopomer.¹⁷ Far from establishing the concerted addition of H_2 to Pt(0), the studies of PtH₂-(diphos) systems have generated uncertainty about the presumed mechanism of addition.

In this communication, we present definitive evidence for the pairwise addition of dihydrogen to a platinum center using parahydrogen-induced polarization (PHIP) and show that with the aid of PHIP extremely rapid detection of ³¹P and ¹⁹⁵Pt NMR resonances can be achieved from submilligram samples of complex. As described previously,¹⁸⁻²⁵ PHIP arises when H₂ enriched in the para spin state adds to a metal center in a manner such that spin correlation is maintained between the two protons, leading to enhanced absorptions and emissions in the product dihydride resonances. A key to observing PHIP is that the transferred protons become magnetically distinct in the product.

In order to remove the equivalence of the hydride ligands in PtH₂L₂ systems, the unsymmetrical bidentate ligand Ph₂PCH₂CH(Me)OPPh₂((dpp)₂mop) has been prepared from propylene oxide, LiPPh₂, and PClPh₂, and the corresponding Pt dihydride complex 1 has been synthesized according to eq 1.26 The identity of 1 is established unequivocally by ¹H, ³¹P, and ¹⁹⁵Pt NMR spectroscopies.²⁷ When 0.4 mg of 1 is dissolved in toluene- d_8 under ca. 2 atm of para-enriched H₂, the spectrum shown in Figure 1 is obtained within 67 s after

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Figure 1. ¹H PHIP NMR spectrum of $((dpp)_2mop)PtH_2$, **1**, obtained from the reaction of 0.4 mg of **1** and paraenriched H₂ in toluene- d_8 at 298 K, showing antiphase doublets due to H_a and H_b. Other peaks due to solvent (s) and dissolved orthohydrogen (*) are labeled.



shaking the sample and introducing it into the spectrometer. The signals corresponding to H_a and H_b at δ –0.282 and –0.014 ppm, respectively, exhibit doublet of doublets patterns due to ³¹P coupling, ¹⁹⁵Pt satellites, and enhanced absorption/emission (A/E) polarization with a separation between absorption and emission extrema of 2.4 Hz corresponding to $J_{\rm HH}$. The phase of the polarization (A/E) indicates that the sign of the $J_{\rm HH}$ coupling constant is positive.¹⁹ Hydride H_a also exhibits an additional coupling to one of the methylene protons of the (dpp)₂mop ligand.

In Figure 1, there are no other resonances observable except for residual ¹H in toluene- d_8 and the signal for dissolved orthohydrogen. The magnitude of the polarization was estimated by measuring the rate of polarization decay and extrapolating back to t = 0. The decay

(27) Complex 1 is isolated as pale yellow powder from THF and *n*-hexane under H₂ (yield, 70%). Both hydride and phosphorus resonances are flanked by ¹⁹⁵Pt satellites. ¹H NMR (methylene chloride- d_2): δ 6.7–8.3 (m, 24H, Ph), 1.09 (d, ³J_{HH} = 5.5 Hz, CH₃), 2.04 (m, 2H, CH₂), 3.96 (m, 1H, CH), -0.282 (ddd, ⁴J_{HH} = 2.8 Hz, ²J_{cmpH} = 17.6 Hz, ²J_{rmspH} = 170 Hz, ¹J_{HPt} = 1204 Hz, 1H, H_a), -0.014 (dd, ²J_{clspH} = 17.6 Hz, ²J_{rmspH} = 199 Hz, ¹J_{HPt} = 1076 Hz, 11, H_b). ³¹P{¹H} NMR (tetrahydrofuran- d_8): δ +125.9 (d, ²J_{cP} = 22 Hz, ¹J_{PPt} = 2300 Hz, P₀), +14.5 (d, ¹J_{PPt} = 2005 Hz, Pc). The ¹H-coupled ³¹P NMR spectrum shows two doublets at +125.9 and +14.5 ppm with ²J_{rmspH} {¹H} NMR (totlene- d_8): δ -820.0 (dd).



Figure 2. Cross peaks and projections from ¹H–X correlation spectra of **1** obtained with para-enriched H₂ in toluene-*d*₈ at 298 K: (a) ¹H–³¹P HMQC spectrum, acquired with $\tau = 1/(2J_{\text{transPH}_a})$ and an acquisition time of 2 min; (b) ¹H–¹⁹⁵Pt correlation spectrum acquired with $\tau = 1/(2J_{\text{PtH}_a})$ and an acquisition time of 5 min, showing cross peaks connecting ³¹P-coupled H_a and H_b resonances to ³¹P-coupled ¹⁹⁵Pt resonances.

of polarization, which is a function of ¹H spin–lattice relaxation times, the rates of H₂ oxidative addition and reductive elimination, and relaxation from a "higher order" spin state resulting from parahydrogen addition,¹⁹ follows clean first-order kinetics with a rate constant of $4.03 \times 10^{-3} \text{ s}^{-1}$. At t = 2.3 min, the observed polarization enhancement was greater than 900-fold. By extrapolation, the magnitude of enhancement is estimated to be greater than 1600-fold, which is close to the theoretical maximum obtainable under our experimental condition (1750) and is the largest PHIP enhancement yet reported. The results establish unequivocally a pairwise mechanism for H₂ addition to form **1**.

When a solution of **1** is placed under D_2 , rapid loss of hydride resonances occurs with *initial* observation of H_2 and a small amount of HD. Upon standing, the relative amount of HD increases while that of H_2 diminishes. These observations indicate that reductive elimination of H_2 from **1** takes place in a pairwise manner, consistent with the PHIP results described above for the reverse addition process.

⁽²⁶⁾ The ligand (dpp)₂mop was purified by chromatography over alumina using benzene (yield, 20%). ³¹P(¹H} NMR (benzene-d₆): δ +107 (s, P₀), -23 (s, P₂). ¹H and ¹H COSY NMR: δ 7.2–7.6 (m, 24H, Ph), 2.68 and 2.24 (dd, ²J_{HH} = 4.5 Hz, ²J_{HP} = 13.8 Hz, 1H, CH₂), 4.22 (qdd, CH), 1.35 (d, ³J_{HH} = 6.1, CH₃). The complex ((dpp)₂mop)PtCl₂ is isolated as a white powder from CH₂Cl₂–cyclohexane (yield, 60%). ³¹P-{¹H} NMR (methylene chloride-d₂): δ +82.7 (d, ²J_{PP} = 17.8 Hz, ¹J_{PPt} = 3842 Hz, P₀), +0.48 (d, ¹J_{PPt} = 3504 Hz, P_c). ¹H NMR: δ 7.2–7.6 (m, 24H, Ph), 1.10 (d, ³J_{HH} = 5.6 Hz, CH₃), 2.31 (m, 2H, CH₂), 3.71 (m, 1H, CH). ¹⁹⁵Pt{¹H} NMR (methylene chloride-d₂): δ –14.8 (dd).

Communications

Previously, parahydrogen-induced polarization has been used in conjunction with pulse sequences such as INEPT+ to enhance signals of less sensitive nuclei.²⁸ Recently, it has been shown that indirect detection of these nuclei can be achieved rapidly through utilization of a 2D-HMQC sequence via parahydrogen polarization transfer.^{29,30} In Figure 2, we show 2D ¹H-³¹P and ¹H-¹⁹⁵Pt correlation spectra of 1, acquired in 2-5 min using less than 1 mg of sample. For these spectra, an initial 45° ¹H pulse is employed with delays for magnetization transfer set as in the Figure 2 caption. The ${}^{1}H-{}^{31}P$ correlation spectrum of **1** is shown in Figure 2a. Four major cross peaks connecting the phosphorus nuclei Po $(\delta = +125.9)$ and P_c ($\delta = +14.5$) to their proton coupling partners, H_a and H_b, are observed. Additional cross peaks for the ¹⁹⁵Pt satellites are clearly visible in this spectrum (¹⁹⁵Pt, $I = \frac{1}{2}$, 33.8%). The corresponding ¹H-

 ^{195}Pt spectrum of 1 in which phase cycling removes signals from products containing other isotopes of platinum is shown in Figure 2b. In the ^{195}Pt dimension, doublet of doublets multiplicity due to coupling to P_o and P_c is centered at -820 ppm.

The results we have described show PHP in platinum hydride complexes for the first time and provide definitive evidence for pairwise H_2 addition to form **1**. Additionally, PHIP has been used in conjunction with 2D HMQC pulse sequences to give indirect detection of ³¹P and ¹⁹⁵Pt in extraordinarily short amounts of spectrometer time.

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