Organometallics **1996,** *15,* 2863−2865 2863

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

Meehae Jang,[†] Simon B. Duckett,[‡] and Richard Eisenberg*,[†]

Departments of Chemistry, University of Rochester, Rochester, New York 14627, and
University of York, Heslington, York, England YO1 5DD

Received April 18, 1996[⊗]

Summary: Through the use of parahydrogen-induced polarization (PHIP), conclusive evidence has been obtained that H_2 addition to $Pt(Ph_2PCH_2CH(Me)OPPh_2)$ proceeds in a concerted, pairwise manner. PHIP has also been used in conjunction with a 2D HMQC sequence to obtain ^{31}P and ^{195}Pt 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 d^8 complexes such as $IrCl(CO)(PPh_3)_2$ and $IrBr(CO)(dppe)$ (dppe = bis(diphenylphosphino)ethane), oxidative addition of H_2 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 H_2 is presumed to take place in an analogous manner, but evidence in this regard is less compelling. While Pt(II) dihydrides have been long known,[10] their formation often involved reductions using hydride sources, and in cases where the reaction was done under H_2, the possible addition of hydrogen was not studied mechanistically. However, from Trogler's study of the cis−trans iosmerism of $PtH_2(PMe_3)_2$ and subsequent reductive elimination of H_2,[11,12] 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 (diphos) were employed,[13−16] but it was found that many of the PtH_2(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 PtH_2(diphos) and PtD_2(diphos) led to facile generation of the d_1 isotopomer.[17] Far from establishing the concerted addition of H_2 to Pt(0), the studies of PtH_2(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 ^{31}P and ^{195}Pt NMR resonances can be achieved from submilligram samples of complex. As described previously,[18−25] PHIP arises when H_2 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 PtH_2L_2 systems, the unsymmetrical bidentate ligand $Ph_2PCH_2CH(Me)OPPh_2$((dpp)$_2$mop) has been prepared from propylene oxide, $LiPPh_2$, and $PClPh_2$, and the corresponding Pt dihydride complex **1** has been synthesized according to eq 1.[26] The identity of **1** is established unequivocally by ^1H, ^{31}P, and ^{195}Pt NMR spectroscopies.[27] When 0.4 mg of **1** is dissolved in toluene-d_8 under *ca.* 2 atm of para-enriched H_2, the spectrum shown in Figure 1 is obtained within 67 s after

---

[†] University of Rochester.
[‡] University of York.
[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

(1) James, B. R. *Homogeneous Hydrogenation*; John Wiley and Sons: New York, 1973.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 51.

(4) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679−680.

(5) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511−3514.

(6) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386−392.

(7) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772−7774.

(8) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148−3160.

(9) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147−1161.

(10) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 365−366.

(11) Packett, D. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 5036−5038.

(12) Packett, D. L.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1768−1775.

(13) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063−2073.

(14) Clark, H. C.; Smith, M. J. H. *J. Am. Chem. Soc.* **1986**, *108*, 3829−3830.

(15) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554−1556.

(16) Scrivanti, A.; Campostrini, R.; Carturan, G. *Inorg. Chim. Acta* **1988**, *142*, 187−189.

(17) Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014−4025.

(18) Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645−2648.

(19) Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541.

(20) Eisenschmid, T. C.; Kirss, R. U.; Deutsch, P. P.; Hommeltoft, S. I.; Eisenberg, R.; Bargon, J.; Lawler, R. G.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 8089−8091.

(21) Kirss, R. U.; Eisenschmid, T. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1988**, *110*, 8564−8566.

(22) Bargon, J.; Kandels, J.; Kating, P.; Thomas, A.; Woelk, K. *Tetrahedron Lett.* **1990**, *31*, 5721−5724.

(23) Bargon, J.; Kandels, J.; Woelk, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 58−59.

(24) Eisenberg, R. *Acc. Chem. Res.* **1991**, *24*, 110−116.

(25) Eisenberg, R.; Eisenschmid, T. C.; Chinn, M. S.; Kirss, R. U. *Adv. Chem. Ser.* **1992**, *No. 230*, 47−74.

S0276-7333(96)00295-6 CCC: $12.00

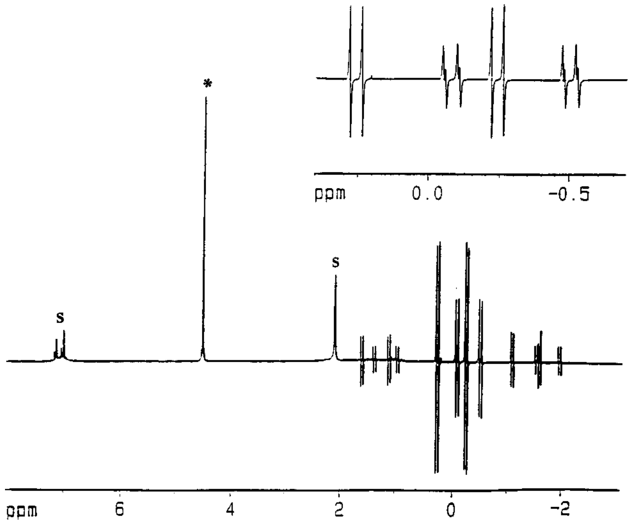
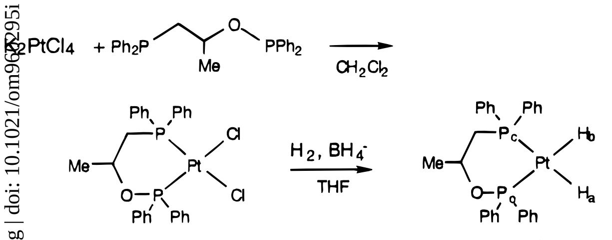


Figure 1. ^1H PHIP NMR spectrum of $((dpp)_2mop)PtH_2$, **1**, obtained from the reaction of 0.4 mg of **1** and para-enriched H_2 in toluene-d_8 at 298 K, showing antiphase doublets due to H_a and H_b. Other peaks due to solvent (s) and dissolved orthohydrogen (*) are labeled.



(1)

1

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 ^{31}P coupling, ^{195}Pt satellites, and enhanced absorption/emission (A/E) polarization with a separation between absorption and emission extrema of 2.4 Hz corresponding to J_{HH}. The phase of the polarization (A/E) indicates that the sign of the J_{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 of polarization, which is a function of ^1H spin–lattice relaxation times, the rates of H_2 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 $4.03 \times 10^{-3}\ s^{-1}$. 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 H_2 addition to form **1**.

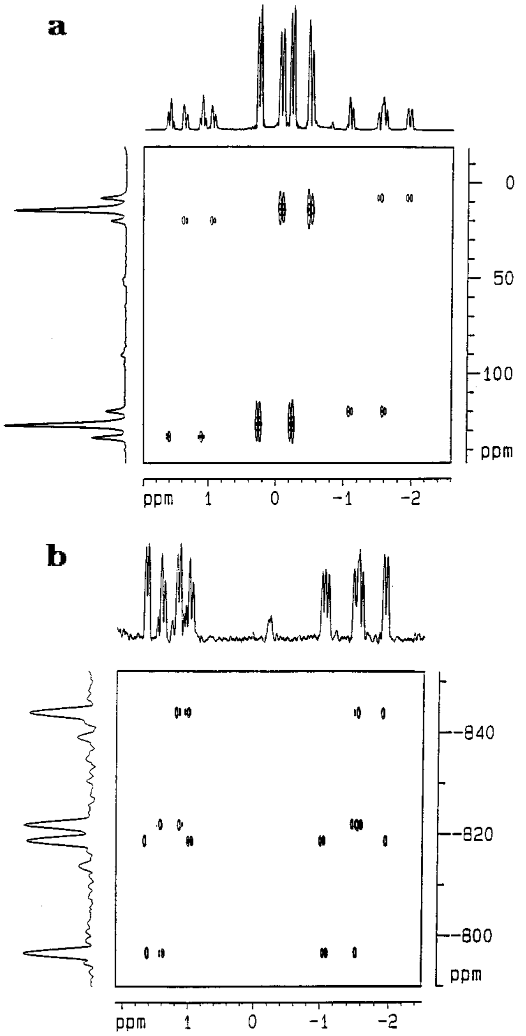


Figure 2. Cross peaks and projections from ^1H–X correlation spectra of **1** obtained with para-enriched H_2 in toluene-d_8 at 298 K: (a) ^1H–^{31}P HMQC spectrum, acquired with $\tau = 1/(2J_{\mathrm{trans}PH_a})$ and an acquisition time of 2 min; (b) ^1H–^{195}Pt correlation spectrum acquired with $\tau = 1/(2J_{PtH_a})$ and an acquisition time of 5 min, showing cross peaks connecting ^{31}P-coupled H_a and H_b resonances to ^{31}P-coupled ^{195}Pt resonances.

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%). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ +107 (s, P_o), −23 (s, P_c). ^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, CH_2), 4.22 (qdd, CH), 1.35 (d, $^3J_{HH} = 6.1$, CH_3). The complex $((dpp)_2mop)PtCl_2$ is isolated as a white powder from CH_2Cl_2–cyclohexane (yield, 60%). $^{31}P\{^1H\}$ NMR (methylene chloride-d_2): δ +82.7 (d, $^2J_{PP} = 17.8$ Hz, $^1J_{PPt} = 3842$ Hz, P_o), +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, CH_3), 2.31 (m, 2H, CH_2), 3.71 (m, 1H, CH). $^{195}Pt\{^1H\}$ NMR (methylene chloride-d_2): δ −14.8 (dd).

(27) Complex **1** is isolated as pale yellow powder from THF and *n*-hexane under H_2 (yield, 70%). Both hydride and phosphorus resonances are flanked by ^{195}Pt satellites. ^1H NMR (methylene chloride-d_2): δ 6.7–8.3 (m, 24H, Ph), 1.09 (d, $^3J_{HH} = 5.5$ Hz, CH_3), 2.04 (m, 2H, CH_2), 3.96 (m, 1H, CH), −0.282 (ddd, $^4J_{HH} = 2.8$ Hz, $^2J_{\mathrm{cis}PH} = 18.6$ Hz, $^2J_{\mathrm{trans}PH} = 170$ Hz, $^1J_{HPt} = 1204$ Hz, 1H, H_a), −0.014 (dd, $^2J_{\mathrm{cis}PH} = 17.6$ Hz, $^2J_{\mathrm{trans}PH} = 199$ Hz, $^1J_{HPt} = 1076$ Hz, 1H, H_b). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8): δ +125.9 (d, $^2J_{PP} = 22$ Hz, $^1J_{PPt} = 2300$ Hz, P_o), +14.5 (d, $^1J_{PPt} = 2005$ Hz, Pc). The ^1H-coupled ^{31}P NMR spectrum shows two doublets at +125.9 and +14.5 ppm with $^2J_{\mathrm{trans}PH}$ values identical to those obtained from the ^1H NMR spectrum. $^{195}Pt\{^1H\}$ NMR (toluene-d_8): δ −820.0 (dd).

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 $^1H-^{31}P$ and $^1H-^{195}Pt$ 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 $^1H-^{31}P$ correlation spectrum of **1** is shown in Figure 2a. Four major cross peaks connecting the phosphorus nuclei P_o ($\delta = +125.9$) and P_c ($\delta = +14.5$) to their proton coupling partners, H_a and H_b, are observed. Additional cross peaks for the ^{195}Pt satellites are clearly visible in this spectrum (^{195}Pt, $I = ^1/_2$, 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 ^{31}P and ^{195}Pt in extraordinarily short amounts of spectrometer time.

Acknowledgment. Financial support of this work from the National Science Foundation (Grant No. CHE 94-09441) and from NATO is gratefully recognized. In addition, a generous loan of platinum salts from the Johnson-Mathey Aesar/Alfa Co. is thankfully acknowledged.

OM960295I

---

[28] Duckett, S. B.; Newell, C. L.; Eisenberg, R. *J. Am. Chem. Soc.* **1993**, *115*, 1156−1157.

[29] Duckett, S. B.; Barlow, G. K.; Partridge, M. G.; Messerle, B. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3427−3429.

[30] Duckett, S. B.; Mawby, R. J.; Partridge, M. G. *J. Chem. Soc., Chem. Commun.* **1996**, 383−384.