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Preliminary communication

Para-hydrogen-induced polarization in rhodium complex-catalyzed hydrogenation reactions

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Abstract

The homogeneous hydrogenation of PhC≡CH catalyzed by $RhClL_3$, $Rh(COD)L_2^+$, and $Rh(COD)dppe^+$ ($L = PPh_3$; COD = 1,5-cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane) has been investigated using *para*-hydrogen-induced polarization (PHIP) which shows that in accord with earlier studies, for $RhClL_3$ the addition of H_2 is reversible, whereas for $Rh(COD)(dppe)^+$ and $Rh(COD)L_2^+$, H_2 addition in hydrogenation catalysis is irreversible.

In 1983 Brown and co-workers [1] investigated the reversibility of H_2 oxidative addition in homogeneous hydrogenations catalyzed by the rhodium complexes $RhClL_3$, $Rh(COD)L_2^+$, and $Rh(COD)(dppe)^+$ ($L = PPh_3$; COD = 1,5-cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane). The first of these, Wilkinson's catalyst, was known to catalyze hydrogenation by H_2 oxidative addition followed by olefin coordination and insertion, with the initial H_2 addition step being reversible [2]. The cationic complex $Rh(COD)(dppe)^+$, on the other hand, acted similarly to $Rh(COD)(chiraphos)^+$, an asymmetric hydrogenation catalyst, which after loss of COD functioned by reversible olefin binding followed by irreversible H_2 addition [3]. The basis of Brown's study was the use of *ortho*- and *para*-hydrogen in non-equilibrium amounts and Raman spectroscopy to monitor the return to equilibrium populations of the two forms of hydrogen. The Brown study showed that $RhClL_3$ promoted $o\text{-}H_2 \rightleftharpoons p\text{-}H_2$ conversion competitive with hydrogenation while the $Rh(dppe)^+$ system equilibrated the two forms of H_2 only after substrate had been consumed.

Recently the use of *para* enriched hydrogen has been found to give rise to enhanced NMR absorptions and emissions in reaction in which H_2 is added or transferred pairwise to a substrate [4,5]. If the reaction occurs fast relative to proton relaxation, then the transferred protons will reflect initially the nuclear spin populations of the starting dihydrogen, leading to the observed dynamic NMR effects. Since para hydrogen induced polarization (PHIP) is easy to observe and gives direct

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information about the hydrogenation product, unlike Raman spectroscopy in the Brown study, we have reexamined that investigation using PHIP and PhC≡CH as substrate. Our results are consistent with the earlier work and show that for cationic systems in which H_2 addition in the catalytic cycle is irreversible, PHIP can be generated in the reaction system for extended periods of time.

Two methods of sample preparation were used in the present study. For flame sealed samples, each tube contained ~ 3 mg of catalyst, 1.5 μl of PhC≡CH and 0.7 ml acetone-d_6 under 1.5 atm H_2. These samples were stored at $-196\,^{\circ}$C for 72 h, during which time the hydrogen atmosphere became *para* enriched. The samples were then thawed immediately prior to reaction and NMR observation. For sample tubes with teflon valves, reagents, solvent and 2–3 atm of independently prepared para enriched hydrogen [6a*] were added just prior to sample placement in the NMR spectrometer. During each hydrogenation reaction, the sample tube was periodically removed from the spectrometer and shaken to promote H_2 mixing between gas and solution phases.

With $RhClL_3$ as catalyst [6b*], relatively weak PHIP is observed which disappears completely within 7–10 minutes. Figure 1 shows the results for one typical run in which the sample was removed from the spectrometer for agitation 3 times over a 6 minute period. The initial polarization in the *gem* and *trans* resonances [6c*] of the styrene product is weak and of the multiplet type whereas net polarization occurs after removal from the probe and placement back into the field. This change in polarization arises from a magnetic field dependent effect and is discussed elsewhere [7]. The key points here are that: (1) PHIP does occur, albeit weakly; (2) it dies out quickly; (3) mixing of the solution with the H_2 atmosphere does not bring back PHIP after 7–10 min (and in the case of Fig. 1, after 5 min); and (4) styrene resonances increase throughout the period monitored (~ 10 min). The results indicate that *ortho-para* H_2 equilibration is occurring competitive with hydrogenation and is achieved within 7–10 minutes. Since *ortho-para* conversion is promoted by oxidative addition/reductive elimination, the results are consistent with reversible H_2 addition required by the published mechanism of catalysis and found by Brown, et al. [1].

The PHIP results using $Rh(COD)(dppe)^+$ as catalyst are strikingly different. The magnitude of polarization after each shaking is substantially larger, the decay of polarization is slower, and the time during which PHIP can be generated is much greater. In Fig. 2, spectra b, c and d show the *para*-hydrogen-induced polarization when the sample is shaken after 45, 75 and 110 min of reaction, respectively. The decay of polarization after each agitation lasts up to 8 min, indicating that transfer of para enriched H_2 to PhC≡CH continues well after the sample is placed back in the probe. The multiplet polarization seen throughout Fig. 2 is also consistent with this notion [7]; no net polarization is observed with $Rh(COD)(dppe)^+$ and PhC≡CH as substrate.

The third catalyst examined in the present study is the cationic system Rh(diolefin)$L_2{}^+$ reported by Schrock and Osborn [8]. These investigators found that under H_2 the system readily forms the *cis* dihydride bis(solvate) cation $RhH_2(sol)_2L_2{}^+$ and its neutral conjugate base, which are both active alkyne

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* Reference numbers with asterisks indicate notes in the list of references.

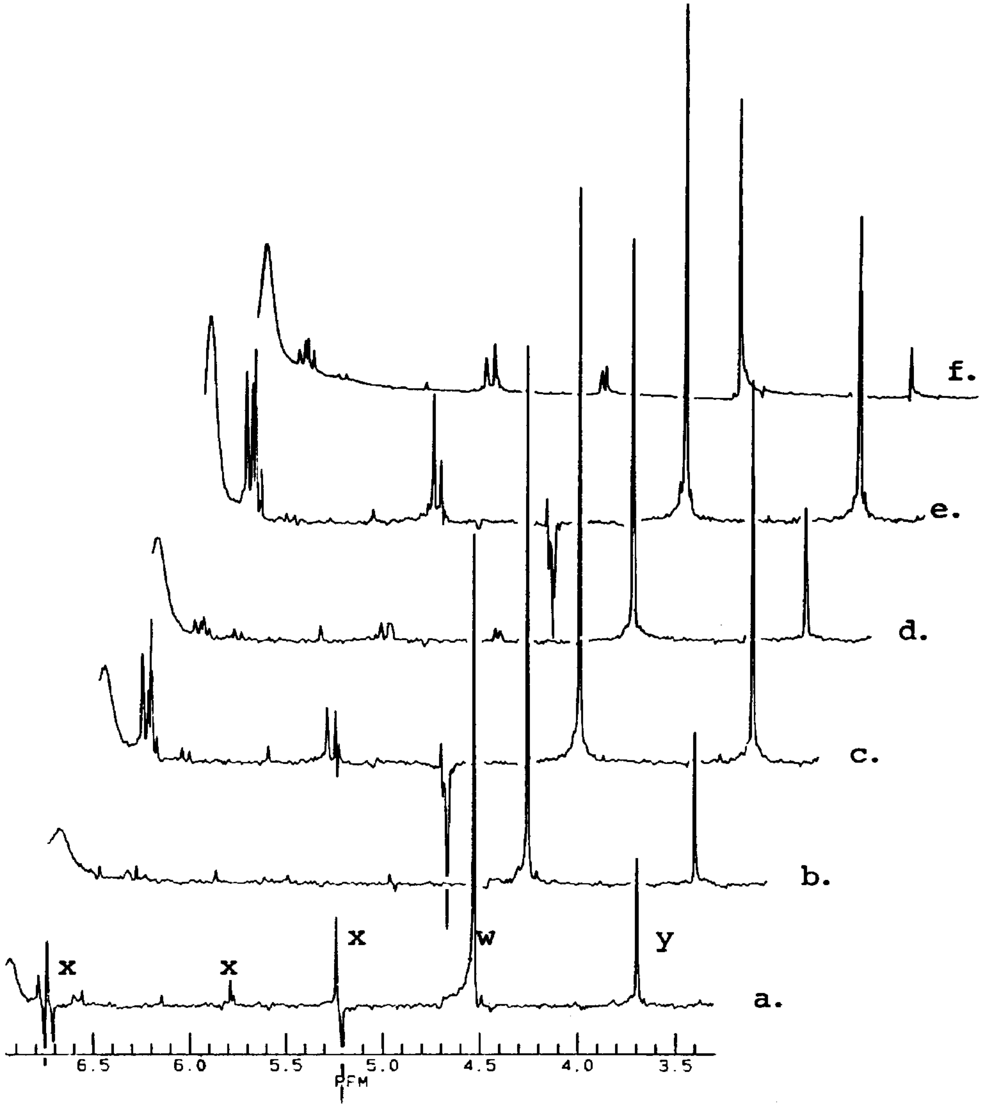

Fig. 1. Hydrogenation of PhC≡CH (27 m*M*) in acetone-d_6 catalyzed by $RhCl(PPh_3)_3$ (12 m*M*) under ~1.5 atm H_2 (~ 50% *para*) at 25° C. The times refer to the total reaction time. (a) 0.25 min; (b) 1 min; (c) 1.25 min, immediately after shaking of sample; (d) 2.0 min; (e) 3.25 min, immediately after shaking; (f) 4.5 min, immediately after shaking. The resonances labelled w = dissolved H_2, x = styrene vinyl protons and y = terminal proton of PhCCH.

hydrogenation catalysts. The results using para enriched H_2 and PhC≡CH show the Schrock–Osborn system to be mechanistically closer to $Rh(dppe)^+$ than to $RhClL_3$. With $Rh(COD)L_2{}^+$ as catalyst, the larger the substrate concentration, the longer the PHIP can be generated by removal from the probe and shaking. The duration of the polarization also depends on the amount of substrate, becoming short when the amount of PhC≡CH becomes small. At that stage, rapid equilibration of *ortho-* and *para*-H_2 occurs by reversible formation of $RhH_2(sol)_2L_2{}^+$. In the Brown study using Raman spectroscopy [1], fast interconversion of *ortho-* and *para*-H_2 was also seen, and this was proposed to happen after complete hydrogenation of the

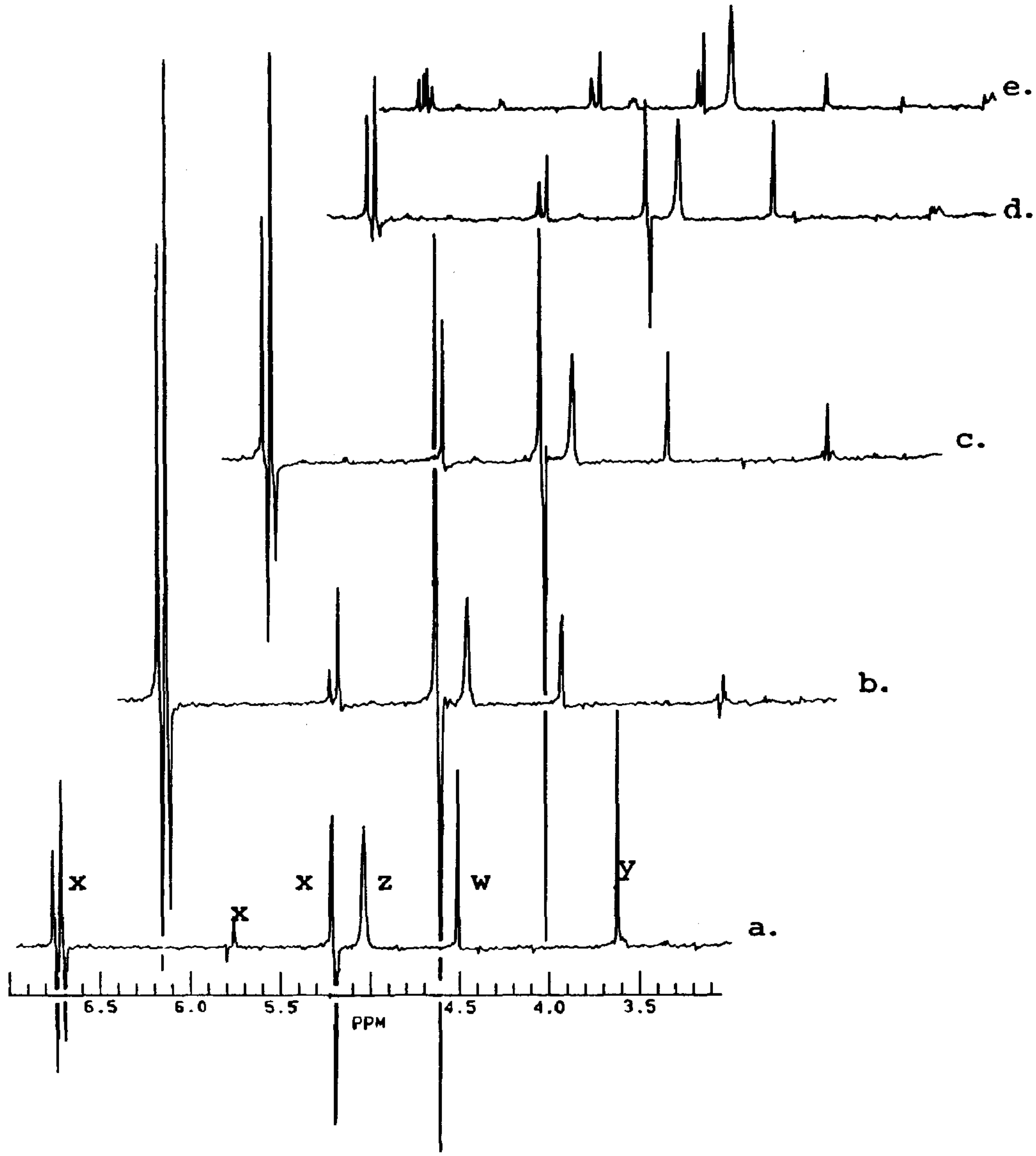

Fig. 2. Hydrogenation of PhC≡CH (27 m*M*) in acetone-d_6 catalyzed by $[Rh(COD)(dppe)^+][PF_6^-]$ (12 m*M*) under ~ 1.5 atm H_2 (~ 50% *para*) at 25 °C. The times refer to total reaction time. (a) 2.5 min, after agitation of sample; (b) 45 min, immediately after shaking; (c) 75 min, immediately after shaking; (d) 101 min, after shaking; (e) 110 min, after relaxation of polarization of (d). The resonances labelled w = dissolved H_2, x = styrene vinyl protons, y = terminal proton of PhCCH, and z = cyclooctene.

substrate Z-benzamidocinnamic acid. Our results are in accord with the earlier work despite the different substrates used.

A significant difference in the PHIP using $Rh(COD)L_2^+$ and $Rh(COD)(dppe)^+$ is that the former exhibits net polarization in the styrene product while the latter shows multiplet polarization. This may relate to the rate at which H_2 addition to the PhC≡CH-catalyst complex takes place in each case, being more rapid for RhL_2^+, but neither quantitation of this difference nor the ability to extract rate constants from the PHIP experiments performed here is possible at this time.

The results we have presented show that PHIP is a useful and convenient mechanistic tool for the study of hydrogenation reactions. When PHIP is both long-lived and capable of being generated for long reaction times, the addition of H_2 to the catalyst in the catalytic cycle is irreversible, whereas when PHIP decays rapidly and can be generated for only short reaction times, catalysis proceeds by reversible addition of H_2 to the catalyst. In either case, the appearance of PHIP is definitive evidence for pairwise transfer of H_2 to substrate.

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References and footnotes

1 J.M. Brown, L.R. Canning, A.M. Forster, J. Organomet. Chem., 255 (1983) 103.

2 (a) J. Halpern, C.S. Wong, J. Chem. Soc., Chem. Comm., (1973) 629; (b) J. Halpern, T. Okamoto, A. Zakhariev, J. Molec. Cat., 3 (1977) 65; (c) C. Rousseau, M. Evrard, F. Petit, J. Molec. Cat., 3 (1978) 309; (d) M.H.J.M. deCroon, P.F.M.T. van Nisselrooij, H.J.A.M. Kuipers, J.W.F. Coeven, J. Molec. Catal., 4 (1978) 325; (e) C.A. Tolman, P.Z. Meakin, D.I. Lindner, J.P. Jesson, J. Am. Chem. Soc., 96 (1974) 2762; (f) Y. Ohtani, M. Fujimoto and A. Yamagishi, Bull. Chem. Soc., Japan, 52 (1979) 69 and ref. therein; (g) D. Wink, P.C. Ford, J. Am. Chem. Soc., 107 (1985) 1794; (h) J.M. Brown, P.L. Evans, A.R. Lucy, J. Chem. Soc., Perkin Trans. II, (1987) 1589.

3 (a) M.D. Fryzuk, B. Bosnich, J. Am. Chem. Soc., 99 (1977) 6262; (b) B. Bosnich, N.K. Roberts, Adv. Chem. Ser., 196 (1982) 337; (c) J.M. Brown, P.A. Chaloner, D. Parker, Adv. Chem. Ser., 196 (1982) 355; (d) A.S.C. Chan, J.J. Pluth, J. Halpern, J. Am. Chem. Soc., 102 (1980) 5952; (e) J.M. Brown, P.A. Chaloner, J. Chem. Soc., Chem. Commun., (1980) 344; (f) P.S. Chua, N.K. Roberts, B. Bosnich, S.J. Okrasinski, J. Halpern, J. Chem. Soc., Chem. Commun., (1981) 1278.

4 (a) C.R. Bowers, D.P. Weitekamp, Phys. Rev. Lett., 57 (1986) 2645; (b) C.R. Bowers, D.P. Weitekamp, J. Am. Chem. Soc., 109 (1987) 5541.

5 T.E. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R. Eisenberg, J. Bargon, R.G. Lawler, A.L. Balch, J. Am. Chem. Soc., 109 (1987) 8089.

6 (a) Prepared by storing a sample of H_2 at −196 °C over a $Fe/SiO_2/C$ catalyst for several hours; (b) Prepared from $[Rh(COD)Cl]_2$ + 10-fold excess PPh_3 in refluxing EtOH followed by recrystallization from C_6H_6/C_6H_{14}; (c) The protons are defined relative to the phenyl group of the styrene product. The *trans* proton is *trans* to the phenyl group and the *gem* proton is geminal to the phenyl group.

7 (a) M.G. Pravica, D.P. Weitekamp, Chem. Phys. Lett., 145 (1988) 255; (b) T.E. Eisenschmid, S.I. Hommeltoft, R. Eisenberg, to be published.

8 R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc., 98 (1976) 2134, 2143.