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One-Hydrogen Polarization in Hydroformylation Promoted by Platinum−Tin and Iridium Carbonyl Complexes: A New Type of Parahydrogen-Induced Effect

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Received April 26, 2002

Parahydrogen-induced polarization in NMR spectra (PHIP) is now recognized as a powerful tool for mechanistic studies of reactions involving molecular hydrogen.[1−4] By virtue of its signal enhancing capabilities, PHIP has been used in hydrogenation catalysis to observe and identify catalytic intermediates. However, to date no reports have appeared involving PHIP for the study of hydroformylation, in which molecular hydrogen is also a reactant. Here we report the use of parahydrogen in examining hydroformylation and a new enhancement effect in which the C*H*O proton of the product exhibits a single hydrogen net polarization. The basis of this effect, which we refer to as one-hydrogen PHIP (oneH-PHIP), involves strong coupling of hydride resonances prior to aldehyde reductive elimination from the catalyst.

Platinum phosphine complexes activated by $SnCl_2$ comprise a set of hydroformylation catalysts, exhibiting good chemoselectivity and flexibility of design.[5−12] Mechanistic investigations of these systems have led to an understanding of the principal steps of the reaction, and catalytically relevant complexes including Pt(II) acyl species have been isolated and studied.[5,13−15] While these acyl species were not observed to form Pt(IV) acyl dihydrides under H_2, they do generate aldehydes. In the present study, we find that *trans*-$PtCl(COEt)(PPh_3)_2$ with $SnCl_2$ in acetone or benzene-acetone under 3 atm of para-enriched hydrogen produces propanal at +20−30 °C with the aldehydic proton in emission as shown in Figure 1a.[16] Unlike other PHIP results reported to date, this unusual polarization involves only a single proton. The absence of polarization when normal hydrogen is employed, and the observation of polarization when the reaction is carried out in the presence of a radical trap (9,10-dihydroanthracene or hydroquinone), support the notion that the C*H*O polarization has a parahydrogen origin. Similar polarization is observed when the hydroformylation of 1-hexene is carried out using *cis*-$PtCl_2(CO)(PPh_3)$-$SnCl_2$ as the catalyst. The emission polarization occurs in the C*H*O proton of the heptanal product. The use of ^{13}CO in the catalysis leads to incorporation of the label into the aldehydes without affecting the polarization (J_{CH} = 171 Hz).

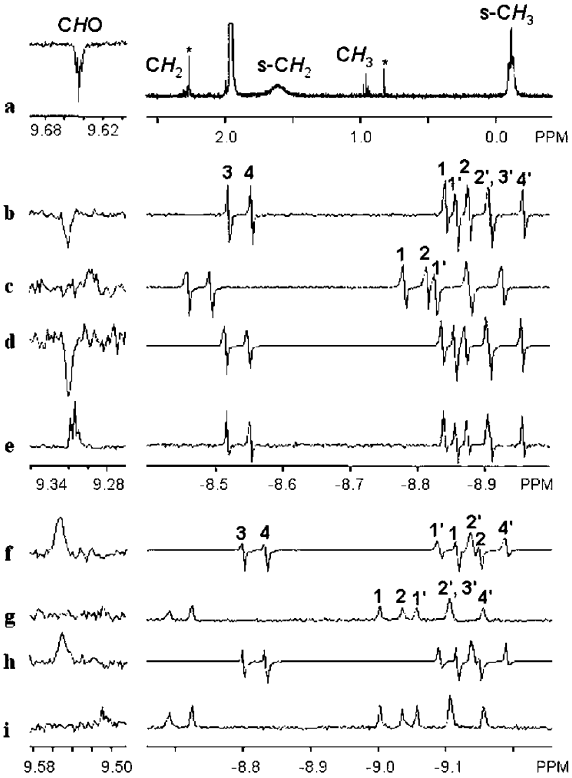
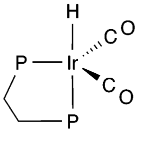


Figure 1. (**a**) Spectrum showing oneH-PHIP of aldehyde proton during the reaction of para-enriched hydrogen (3 atm) with $[PtCl(COEt)(PPh_3)_2]$ + 3 equiv of $SnCl_2$ in C_6D_6-acetone-d_6 (4:3) at +20 °C (signals of the propanal are marked as C*H*O, C*H*$_2$, and C*H*$_3$ and the starting Pt-acyl complex as *s-CH*$_2$ and *s*-C*H*$_3$; asterisks denote impurity peaks); (**b**−**e**) spectra showing effect of parahydrogen on the aldehyde proton and the hydride resonances of **2** in 5 mM in C_6D_6 solutions (for numbering of hydride resonances, see text): (**b**) initial moment; (**c**) immediately after shaking; (**d**) 1.5 min inside the probehead at +80 °C; (**e**) 6 min at +80 °C; (**f**−**i**) same as b−e except with C_6D_6-acetone-d_6 (7:3 v/v) as solvent and at +75 °C unless noted: (**f**) start of the experiment, after 1.5 min at +75 °C; (**g**) after rapid cooling, spectrum at +30 °C; (**h**) heating again for 1.7 min at +75 °C; (**i**) after rapid cooling, spectrum at +30 °C.

The emission polarization of Figure 1a contrasts with PHIP previously reported in which pairwise addition of para-H_2 to a metal center or organic substrate leads to antiphase polarization (A/E or E/A) in the resonances of the two protons that were originally part of the same H_2 molecule. The possibility of single hydrogen polarization was raised by Natterer who suggested that it may be observable if the two protons of the H_2 molecule formed a strongly coupled system at the catalyst.[17a] In the case of hydroformylation catalysis, such a strongly coupled system would be found in the acyl dihydride intermediate. To probe this notion, the model hydroformylation system $Ir(COEt)(CO)_2(dppe)$ (**1**; dppe = bis(diphenylphosphino)ethane), which produces propanal above 70 °C under H_2 and for which the corresponding acyl dihydride intermediate (**2**) has been characterized, was examined.[18]



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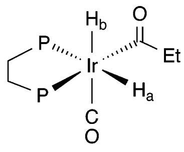

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10.1021/ja026698t CCC: $22.00 © 2002 American Chemical Society

When Ir(COEt)(CO)$_2$(dppe) (**1**) in C_6D_6 is placed under 3 atm of para-enriched hydrogen at 80 °C, the single pulse spectrum shown in Figure 1b is produced.[16] PHIP with its antiphase resonances is clearly seen in the hydride region with J_{HH} positive from the A/E phase, while the propanal C*H*O resonance exhibits net emission similar to that found in Figure 1a. Normal J_{PH} couplings permit assignment of the -8.696 resonance to H_a and the -8.905 resonance to H_b. Each A/E doublet is actually part of an AB or AX subsystem[17b] for the two hydrides that can be identified by its respective ^{31}P spin labels. For H_a and H_b, respectively, doublets 1 and 1′ correspond to the AB subsystem labeled as $\alpha\alpha$ for $^{31}P_{trans}{}^{31}P_{cis}$ based on negative cis J_{PH} and positive trans J_{PH} coupling constants. Likewise, doublets 2 and 2′ correspond to the $\alpha\beta$ subsystem, 3 and 3′ to the $\beta\alpha$ subsystem, and 4 and 4′ to the $\beta\beta$ subsystem. Spectral simulation clearly reveals that doublets 1 and 1′ at 80 °C are close enough in frequency to give evidence of significant second-order effect ($\Delta\delta/J_{HH} = 4$) with 1′ slightly upfield from 1 (doublets 2 and 2′ also exhibit second-order mixing but to a greatly reduced extent because of a larger $\Delta\delta/J_{HH}$) (see the Supporting Information).

The sign of the observed oneH-PHIP originates from preferential correlation of the singlet parahydrogen spin function with the one of the zero-spin levels ($\alpha\beta$ or $\beta\alpha$) of H_aH_b in **2** which has greater singlet or ($\alpha\beta$-$\beta\alpha$) character by virtue of second-order mixing. The overpopulation of this level results in an excess of β spins for the proton corresponding to the high-field member of the AB subsystem and an excess of α spins for the low-field component. In the present case, reductive elimination of the acyl with H_b in **2** then leads to the observed aldehyde proton emission. The excess of α spins that is expected for the other product of reductive elimination, IrH(CO)(dppe), is not seen, possibly because of relaxation effects and rapid reaction to form IrH(CO)$_2$(dppe). After propanal is produced, formation of IrH$_3$(CO)(dppe) is also seen with PHIP similar to that of **2**. Our analysis of oneH-PHIP necessitates that cis reductive elimination of aldehyde from an acyl dihydride species is stereospecific, because the dppe P donors in **2** cannot become mutually trans, thus eliminating the path for propanal formation that would generate RCH_aO.

The observation of oneH-PHIP is maintained if the rate of aldehyde production is high enough to provide a steady state concentration of polarized aldehyde. When the sample is removed from the probe and shaken to restore an equilibrium concentration of parahydrogen in solution, polarization disappears because of a decrease in sample temperature and consequent separation of H_a and H_b resonances in **2** (Figure 1c). Polarization reappears when the sample temperature reaches 80 °C as propanal production resumes and the hydride doublets 1 and 1′ approach each other close enough for a significant second-order effect (Figure 1d). Eventually, the aldehyde resonance from normal or relaxed propanal dominates over any polarized signal once the reaction has progressed to a considerable extent (Figure 1e).

To test the model for the basis of oneH-PHIP, the dependence of polarization on relative chemical shifts of the hydride protons of **2** was studied. Reversal of the relative positions of the strongly interacting proton transitions in the second-order AB-subsystems should change the sense of the C*H*O polarization from emission to enhanced absorption; in the present case, reversal would have the H_b proton as the low-field component of the second-order interaction. This was achieved experimentally by small changes in the chemical shifts of H_a and H_b through solvent variation. Specifically, dilution of C_6D_6 with 30% of acetone-d_6, which is inert toward **2**, provides the necessary change in chemical shift difference for H_a and H_b at 75 °C. In this situation, the subsystem of 2 and 2′ exhibits the larger second-order effect with $\Delta\delta/J_{HH} = 2.6$ and 2′ as the lower field component (1 and 1′ have a larger $\Delta\delta$ and smaller second-order effect). Experimentally, an enhanced absorption is now seen for the propanal C*H*O proton (Figure 1f). With the H_b component 2′ being at lower field than H_a's component 2, the correlation of the parahydrogen spin function with the H_aH_b spin levels changes so that H_b in the propanal product becomes enriched in the α spin state. Positive polarization of the aldehyde proton is not observable before 2′ becomes definitively downfield of 2, nor after rapid cooling to 30 °C when the production of aldehyde is interrupted (Figure 1g). The observed polarization effect was repeated through a second cycle of heating (Figure 1h), with a low intensity normal signal of propanal observed at the end at +30° (Figure 1i). The oneH-PHIP effect shown in Figure 1 was reproducible several times for samples of slightly different concentrations of starting complex **1**, different temperatures, and different benzene:acetone ratios.

The intensity of oneH-PHIP is much lower than that of conventional PHIP which has been seen to yield signal enhancements of $>10^3$. In the case of **2** described above, the effect is even more attenuated because it occurs only for the subsystem having significant second-order interactions between H_a and H_b components. For the *trans*-PtCl(COEt)(PPh$_3$)$_2$/SnCl$_2$ system, the oneH-PHIP effect appears substantially stronger; Figure 1a gives an enhancement factor for the C*H*O proton of ca. 5. We conclude that oneH-PHIP represents a useful new tool for the study of reactions of dihydrogen, when only one of the protons ends up in a product molecule. The dependence of the sign of oneH-PHIP on the relative chemical shift of the two protons in the dihydride intermediate provides the possibility of directly determining the stereochemistry of the reductive elimination.

Acknowledgment. We thank the National Science Foundation (Grant CHE-0092446) for support of this work.

Supporting Information Available: Details of sample preparation and parahydrogen experiments, and figures of spectral simulations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Eisenberg, R.; Eisenschmid, T. C.; Chinn, M. S.; Kirss, R. U. *Adv. Chem. Ser.* **1992**, *230*, 47−74.
(2) Duckett, S. B.; Sleigh, C. J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *23*, 71−92.
(3) Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645−2648.
(4) Natterer, J.; Bargon, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *31*, 293−315.
(5) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503−512.
(6) Kawabata, Y.; Hayashi, T.; Ogata, I. *Chem. Commun.* **1979**, 462−463.
(7) Schwager, I.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256−267.
(8) Clarke, M. L. *Polyhedron* **2001**, *20*, 151−164.
(9) Consiglio, G.; Pino, P. *Helv. Chim. Acta* **1976**, *59* (2), 642−645.
(10) Gomez, M.; Muller, G.; Sainz, D.; Sales, J.; Solans, X. *Organometallics* **1991**, *10*, 4036−4045.
(11) van der Veen, L. A.; Keeven, P. K.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **2000**, 2105−2112.
(12) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Adv. Chem. Ser.* **1992**, 367−376.
(13) Scrivanti, A.; Botteghi, C. *J. Organomet. Chem.* **1988**, *344*, 261−275.
(14) Scrivanti, A.; Paganelli, S.; Matteoli, U.; Botteghi, C. *J. Organomet. Chem.* **1990**, *385*, 439−446.
(15) Ruegg, H. J.; Pregosin, P. S.; Scrivanti, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* **1986**, *316*, 233−241.
(16) Details of sample preparation, NMR data, and spectral simulations are given in the Supporting Information.
(17) (a) Natterer, J. NMR with Spin Polarized Molecules − Theory and Application. Ph.D. Thesis, University of Bonn, 1997. (b) Becker, E. D. *High-Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980.
(18) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709−718.

JA026698T