

Measurements were carried out both at a constant ionic strength of 0.5 M and also in the absence of any added electrolyte. The equilibrium constant increases with decreasing temperature. Lower  $\Delta H^0$  values are observed for the more acidic hydrides, while the negative values of  $\Delta S^0$  are expected due to greater solvation of the ionic products. Thermolysis of the iron vinylidene cation ( $\text{BF}_4^-$  counterion) in  $\text{CH}_3\text{CN}$  at  $57^\circ\text{C}$  releases *tert*-butylacetylene and leads to the formation of  $(\text{C}_5\text{H}_5)(\text{CO})(\text{PMe}_3)\text{Fe}(\text{CH}_3\text{CN})^+\text{BF}_4^-$ , which was isolated as red needles in 78% yield.<sup>3</sup>

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**Supplementary Material Available:** Spectroscopic and analytical data for  $1^+$  ( $\text{PF}_6^-$ ,  $\text{Cr}^-$ ,  $\text{Mo}^-$ ,  $\text{W}^-$  salts),  $2^+\text{PF}_6^-$ ,  $3^+\text{PF}_6^-$ ,  $(\text{C}_5\text{H}_5)(\text{CO})(\text{PMe}_3)\text{Fe}-\text{C}\equiv\text{C}-\text{CMe}_3$ ,  $(\text{C}_5\text{H}_5)(\text{CO})(\text{PMe}_3)\text{Fe}=\text{C}=\text{C}(\text{H})\text{CMe}_3^+\text{BF}_4^-$ , and  $(\text{C}_5\text{H}_5)(\text{CO})(\text{PMe}_3)\text{Fe}(\text{CH}_3\text{CN})^+\text{BF}_4^-$  (3 pages). Ordering information is given on any current masthead page.

## Para Hydrogen Induced Polarization in Hydrogenation Reactions

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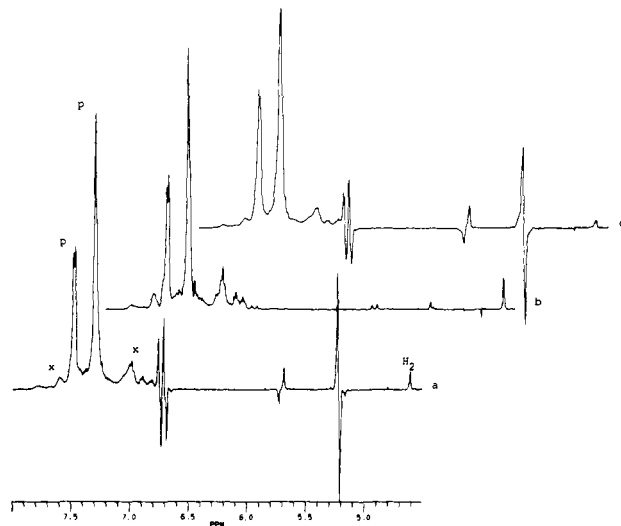
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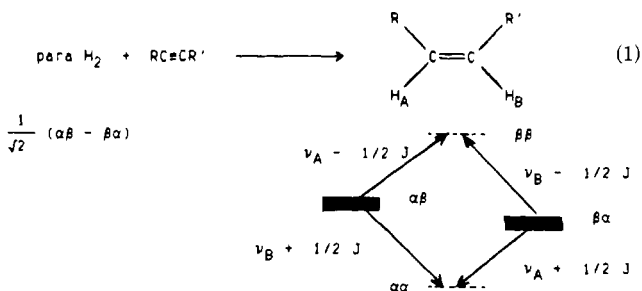
Since 1969, the occurrence of enhanced NMR absorptions and emissions known as CIDNP has been viewed as definitive evidence of a radical pair mechanism.<sup>1-3</sup> Recently, we reported that the binuclear complex  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  hydrogenates alkynes with CIDNP observed in the product olefin resonances.<sup>4</sup> Through the use of  $^{13}\text{C}$  and  $^2\text{H}$  labeled substrates, we showed that the polarization process did *not* involve the intermediacy of organic radicals, thus differing from other observations of CIDNP in hydrogenation



**Figure 1.**  $^1\text{H}$  NMR spectra at 400 MHz showing para  $\text{H}_2$  induced polarization in the resonances of styrene from the reaction of  $[\text{Rh}_2\text{Cl}_2\text{H}_2(\text{CO})_2((\text{Ph}_2\text{PCH}_2)_2\text{PPh})_2]^+$  with  $\text{PhC}\equiv\text{CH}$  in  $\text{CDCl}_3$  under  $\text{H}_2$ : (a) after storage at  $-196^\circ\text{C}$  under  $\text{H}_2$ ; (b) after storage at  $-196^\circ\text{C}$  under vacuum followed by addition of tank  $\text{H}_2$ ; (c) after storage at  $-196^\circ\text{C}$  under vacuum followed by addition of para enriched  $\text{H}_2$ . The resonances marked "x" are due to the catalyst complex and those marked "p" are due to excess  $\text{PhC}\equiv\text{CH}$ .

tions involving mononuclear organometallic hydrides.<sup>5-8</sup> We now report results with other complexes and substrates including simple olefins and show that the polarizations we observe, and those described earlier,<sup>4</sup> arise from para  $\text{H}_2$ . The notion that hydrogenation reactions using para  $\text{H}_2$  can generate polarized products has recently been proposed and demonstrated by Weitekamp.<sup>9</sup> This means of developing polarization, which does not require radicals of any type, promises to be a highly useful tool for the study of hydrogenation reactions and  $\text{H}_2$  oxidative additions.

According to the Weitekamp proposal,<sup>9</sup> para  $\text{H}_2$  induced polarization can arise when  $\text{H}_2$  is transferred pairwise to a substrate to yield a product in which the two transferred protons are magnetically distinct. If the reaction occurs fast relative to proton relaxation, then the transferred protons will initially reflect the nuclear spin populations of the starting dihydrogen. This is shown schematically in eq 1 for hydrogenation of an internal alkyne with



para  $\text{H}_2$ . Since only the  $\alpha\beta$  and  $\beta\alpha$  states of the product olefin correlate with the para  $\text{H}_2$  nuclear spin function, these states will be overpopulated relative to a normal Boltzmann distribution (as shown in the diagram of eq 1), giving rise to polarized A/E or

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E/A transitions similar to a multiplet effect.

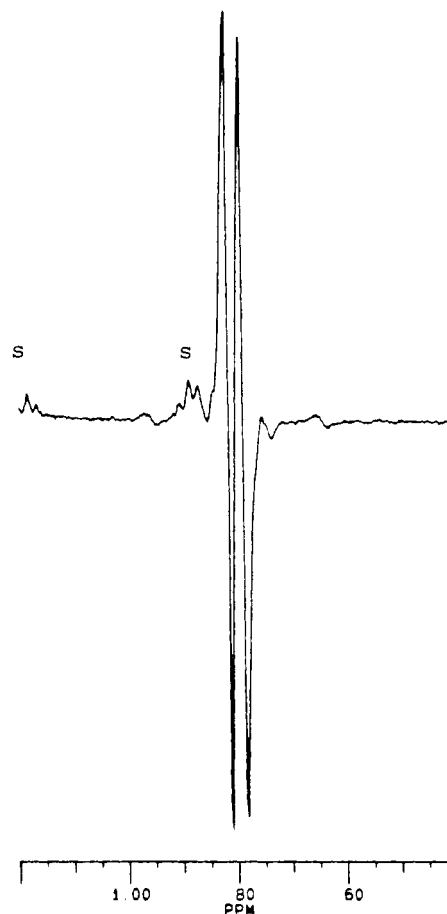
The procedure for generating para  $H_2$  induced polarization is relatively simple. The sample for study is prepared under  $H_2$  and stored for 8 h or more in liquid  $N_2$  prior to reaction. While ortho/para  $H_2$  conversion is slow in the gas phase, it is promoted, albeit inefficiently by many species including the platinum group element complexes used in the present study. At 80 K, the equilibrium composition of  $H_2$  is 48.39% para and 51.61% ortho compared with 25.13% para and 74.87% ortho at 273 K.<sup>10</sup> Upon warming, the sample is shaken and inserted immediately into the NMR probe with data collection commencing within 20 s.

In one set of experiments, the trinuclear complex  $[Rh_3Cl_2H_2(CO)_2(Ph_2PCH_2)_2PPh_2]^+^{11}$  (4.5 mM) was employed as the hydrogenation catalyst with  $PhC\equiv CH$  as the substrate (150 mM) in  $CDCl_3$  under 2–3 atm  $H_2$ . When the sample was introduced into the probe at 50 °C, styrene was produced which, as shown in Figure 1a, exhibited strong A/E polarization in the H resonance trans to phenyl ( $\delta$  5.06;  $J_{HH} = 11$  Hz) and A/E/A/E polarization in the H resonance geminal to phenyl ( $\delta$  6.57;  $J_{HH} = 18, 11$  Hz).<sup>12</sup> A weaker E/A polarization in the cis proton signal ( $\delta$  5.59;  $J_{HH} = 18$  Hz) is also observed due to cross-polarization<sup>9</sup> since this proton was never part of the original  $H_2$  molecule.<sup>4,11</sup> To verify that the polarization was indeed para  $H_2$  induced, two other identical samples were prepared and stored under vacuum at  $-196$  °C. To one sample was added  $H_2$  (3 atm) just prior to insertion into the NMR spectrometer while to the other, a similar pressure of para enriched  $H_2$ , prepared separately,<sup>12b</sup> was added. The former showed no polarization (Figure 1b) while the latter (Figure 1c) exhibited polarizations essentially identical with that seen for the sample stored under  $H_2$ .

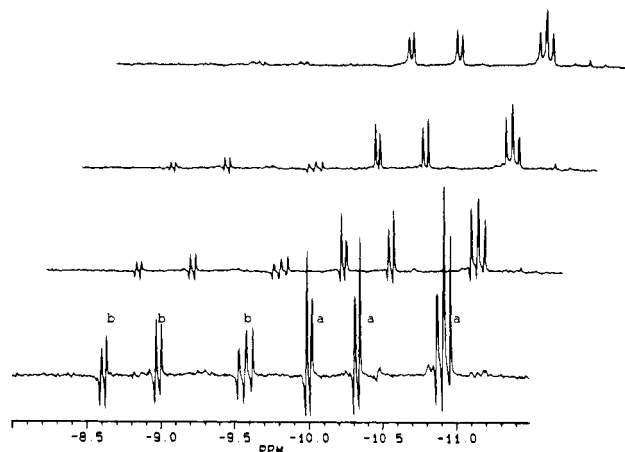
A second set of experiments used the complex  $Pd_2Cl_2(Ph_2PCH_2PPh_2)_2$ <sup>13</sup> as the catalyst. A sample containing the catalyst (2 mM) and  $PhC\equiv CH$  (180 mM) in  $CDCl_3$  under  $\sim 3$  atm  $H_2$  showed a small amount of styrene with no polarization when examined without prior storage at  $-196$  °C. However, polarization similar to that in Figure 1a was seen when the sample was subsequently stored for 24 h in liquid  $N_2$ . After decay of the polarization which occurs within 10–12 min at 80 °C, the process was repeated. Through several cycles, large multiplet polarizations in the styrene resonances were observed when the sample was placed in the NMR probe.

Since the magnitude of the polarization relates in part to the relaxation time of the product protons, deuterated substrates lead to more intense and longer lasting polarizations. This is particularly significant when olefins are used as the substrate, thus allowing for the observation of para  $H_2$  induced polarization in the diproto alkane products. These polarizations have been seen when styrene- $d_8$ , propylene- $d_6$ , and ethylene- $d_4$  have been employed with  $[Rh_3Cl_2H_2(CO)_2(Ph_2PCH_2)_2PPh_2]^+$  as the catalyst. Figure 2 shows the para  $H_2$  induced polarization for  $CHD_2CHD_2$  which, despite the equivalence of the two protons, is a complex  $AA'X_2X'_2$  spin system due to H–D coupling. Thus this method can be used to study hydrogenation of simple olefins and assess whether the catalysis occurs via pairwise transfer of hydrogen atoms.

The activation of  $H_2$  in homogeneously catalyzed hydrogenations occurs by oxidative addition. To determine whether para  $H_2$  induced polarization can also be seen in the metal complex products of  $H_2$  oxidative addition reactions, we have examined the reaction of  $IrX(CO)(dppe)$ ,  $X = CN$  and  $Br$ ,<sup>14</sup> with para enriched  $H_2$ . These Ir(I) complexes undergo stereoselective  $H_2$

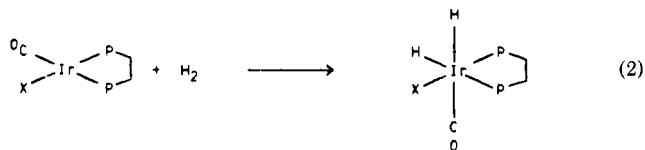


**Figure 2.** Para  $H_2$  induced polarization in the ethane resonances of  $CHD_2CHD_2$ . Resonances marked s are due to impurities in the solvent. The separation between the absorption maxima (and between the emission minima) corresponds to 11.2 Hz while the separation between the central emission and absorption peaks is 3.4 Hz.



**Figure 3.** Para  $H_2$  induced polarization in the hydride resonances of  $IrH_2X(CO)(dppe)$  for  $X = CN$  labeled a and for  $X = Br$  labeled b. The times for the spectra correspond to 1, 2, 3 and 5 min after thawing the sample to commence reaction.

oxidative additions to yield initially the cis dihydride products as shown in eq 2.<sup>14</sup> The results are shown in Figure 3. While each



hydride resonance shows normal P coupling, impressive polari-

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(12) (a) In most cases 16 scans were collected which made the acquisition time for each spectrum 1 min. In some experiments only 8 scans were collected corresponding to an acquisition time of 30 s. A pulse width of 3  $\mu$ s ( $\sim 22^\circ$  pulse angle) was used in all experiments. (b) Para enriched  $H_2$  was prepared by pressurizing a 250-mL bulb to 1 atm  $H_2$  at  $-196$  °C over activated charcoal and iron oxide (rust) and allowing it to stand for 24 h at  $-196$  °C.

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zation is observed in the H-H coupled components, as would be expected for para H<sub>2</sub> induced polarization. In addition, since each P split component exhibits an E/A phase compared with A/E phases in the trans and gem proton resonances of styrene, the sign of  $J_{\text{HH}}$  for IrH<sub>2</sub>X(CO)(dppe) is opposite that of  $^3J_{\text{HH}}$  in styrene and is therefore negative.

The results reported here demonstrate para H<sub>2</sub> induced polarization which should prove useful for the study of hydrogenations, H<sub>2</sub> oxidative additions, and, because of its amplification effect, the detection of catalytically significant hydrides. The effectiveness of the method depends on the pairwise transfer of H<sub>2</sub> to an organic substrate or a metal center and the rate at which this occurs relative to proton relaxation. Finally, unlike previous studies employing ortho/para H<sub>2</sub> conversion to follow hydrogenation and H<sub>2</sub> oxidative addition,<sup>15,16</sup> the method described here monitors the products directly and is capable of much greater sensitivity.

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## Activation of Carbon-Fluorine Bonds by Oxidative Addition

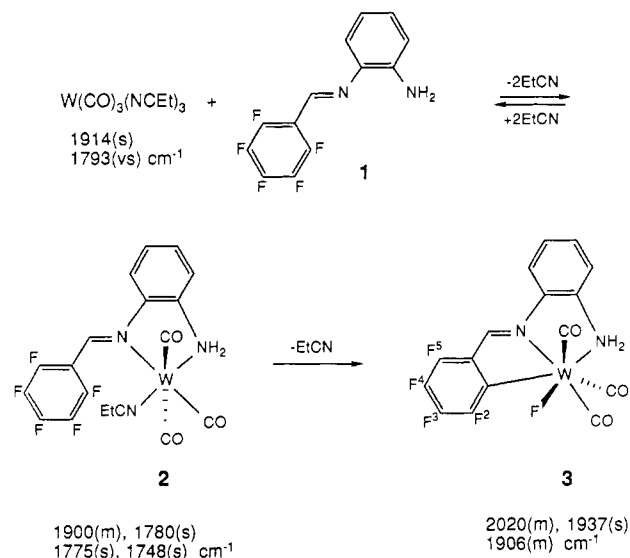
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The oxidative addition of carbon-heteroatom bonds to transition metals has been intensively investigated as a synthetic pathway to new organometallic complexes and employed for the catalytic functionalization of organic compounds.<sup>1</sup> Recent advances have extended the scope of this process to include carbon-hydrogen bond activation.<sup>2</sup> However, few examples of cleavage of carbon-fluorine bonds by oxidative addition to a metal center are known despite the continuing interest in fluoroorganometallic chemistry.<sup>3</sup> The greater abundance of systems capable of activating C-H bonds relative to C-F bonds is perhaps not surprising given the great strength of the C-F bond (125 kcal/mol for Ph-F versus 110 kcal/mol for Ph-H).<sup>4</sup> In this communication we report

Scheme I



that facile oxidative addition of an aromatic C-F bond takes place at tungsten(0).

Literature precedent for C-F bond cleavage includes the low yield synthesis of thermally unstable *trans*-Ni(PET<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)F from C<sub>6</sub>F<sub>6</sub>.<sup>5</sup> Orthometalation of pentafluoroazobenzene by Mn<sub>2</sub>(CO)<sub>10</sub><sup>6a</sup> and of perfluoroazobenzene by CpRu(PPh<sub>3</sub>)<sub>2</sub>Me<sup>6b</sup> has been observed as minor products in refluxing heptane. Photochemical activation of an aromatic C-F bond in a 1,4-bis(pentafluorophenyl)tetrazadiene ligand coordinated to cobalt has also been reported.<sup>7</sup> In the latter three cases, the fate of the cleaved fluorine atom was not determined.

Recently we demonstrated that chelate-assisted oxidative addition of a Ph-X (X = Cl, Br, I) bond in appropriately designed ligands takes place at tungsten(0) under mild conditions.<sup>8</sup> Extension of this chemistry has resulted in the discovery of a ligand in which oxidative addition of a Ph-F bond occurs in high yield to afford a stable tungsten(II) metallacycle with the cleaved fluorine atom bound to the metal center.

Reaction of pentafluorobenzaldehyde with 1.0 equiv of 1,2-diaminobenzene in ethanol affords the yellow crystalline 1:1 Schiff base (**1**) in 92% yield.<sup>9</sup> Treatment of **1** with 1.0 equiv of W(CO)<sub>3</sub>(EtCN)<sub>3</sub><sup>10</sup> in THF at room temperature under nitrogen gives a deep red solution of **3**; IR monitoring (see Scheme I) indicates the reaction is complete in less than 10 min. Addition of hexanes and cooling to -10 °C affords red crystalline **3** in 69% yield as a THF solvate.<sup>11</sup>

The structure **3** is assigned by interpretation of IR, <sup>19</sup>F, and <sup>1</sup>H NMR spectroscopic data and confirmed by single-crystal X-ray diffraction. The <sup>19</sup>F NMR spectrum exhibits four coupled aromatic C-F resonances at -111.44, -138.06, -151.61, and -162.06 ppm versus CCl<sub>3</sub>F in acetone-*d*<sub>6</sub>. A broad peak ( $\nu_{1/2}$  = 23 Hz) at -225.97 ppm is assigned to the fluoride bound to tungsten. This resonance is slightly solvent dependent and shifts to -237.1 ppm when D<sub>2</sub>O is added to the sample suggesting hydrogen bonding to the fluoride.<sup>12</sup> Although <sup>183</sup>W-<sup>19</sup>F coupling has been observed

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(9) NMR data for **1**: <sup>19</sup>F (CDCl<sub>3</sub>, CCl<sub>3</sub>F reference) -142.87 (dd, 2 F), -151.16 (t, 1 F), -162.31 (m, 2 F); <sup>1</sup>H (CDCl<sub>3</sub>) 8.68 (s, 1 H), 7.13 (m, 1 H), 6.78 (m, 3 H), 4.23 (br, 2 H). Anal. Calcd for C<sub>13</sub>H<sub>7</sub>N<sub>2</sub>F<sub>5</sub>: C, 54.56; H, 2.47; N, 9.79; F, 33.19. Found: C, 54.44; H, 2.30; N, 9.75; F, 33.36.

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(11) Anal for **3**·THF. Anal. Calcd for C<sub>20</sub>H<sub>15</sub>N<sub>2</sub>F<sub>5</sub>O<sub>4</sub>W: C, 38.36; H, 2.41; N, 4.47; F, 15.17. Found: C, 38.03; H, 2.27; N, 4.63; F, 15.36.