is not possible and a donating solvent, such as THF, must be invoked.

At present, X-ray diffraction analysis provides the most efficient method for obtaining structural models for the reactions in Figure 2. Consequently, we will continue to seek structural information for additional molecular aggregates that will elaborate on the complexes depicted in Figure 2 and expand upon the role of "molecular preorganization"[13] and/or "complex induced proximity effects"[14] in the aldol reaction.

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Supplementary Material Available: Full crystallographic details including atomic coordinates, thermal parameters, bond angles, bond lengths, and a thermal ellipsoid plot (8 pages). Ordering information is given on any current masthead page.

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Parahydrogen and Synthesis Allow Dramatically Enhanced Nuclear Alignment

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Recently we have predicted that very large nuclear spin magnetizations can be obtained on molecules formed by molecular addition of parahydrogen (p-H_2) such that the dihydrogen protons become magnetically inequivalent.[1] In this communication we report the experimental observation of this effect. The reaction studied is the hydrogenation of acrylonitrile, CH_2CHCN, to propionitrile, CH_3CH_2CN, catalyzed by tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst[2]) at ambient temperature and pressure. Large transient proton nuclear magnetic resonance (NMR) signals are observed both in propionitrile transitions and in the hydride region[2,3] of the hydrogenated catalyst.

Figure 1a shows the proton NMR spectrum (ν_0 = 200 MHz) of a deuteriobenzene solution 0.76 M in acrylonitrile and 0.035 M in $Rh(PPh_3)_3Cl$ obtained by Fourier transformation of the free-induction decay after a 6 μs $\pi/2$ pulse. Figure 1b was obtained from the same sample after H_2 enriched to 50% in the para nuclear spin state was bubbled for 1.1 s through a capillary submerged in the spinning NMR sample, ending 0.8 s before the rf pulse to allow the turbulence to subside. Figure 1c was obtained 200 s later with no further addition of H_2 and shows that the reaction-induced state which leads to the intense antiphase multiplets of Figure 1b is transient in nature. When the time between the H_2 burst and the rf pulse is varied, an exponential decay of the antiphase amplitude is observed with a time constant T_J^S = 7 ± 2 s, where the subscript J indicates the nature of the nonequilibrium population differences present[1] and distinguishes this quantity from the usual relaxation time T_1 for longitudinal magnetization. The superscript indicates the chemical species. The frequencies of the transient lines are those expected for the hydrogenation product propionitrile. Since the propionitrile is

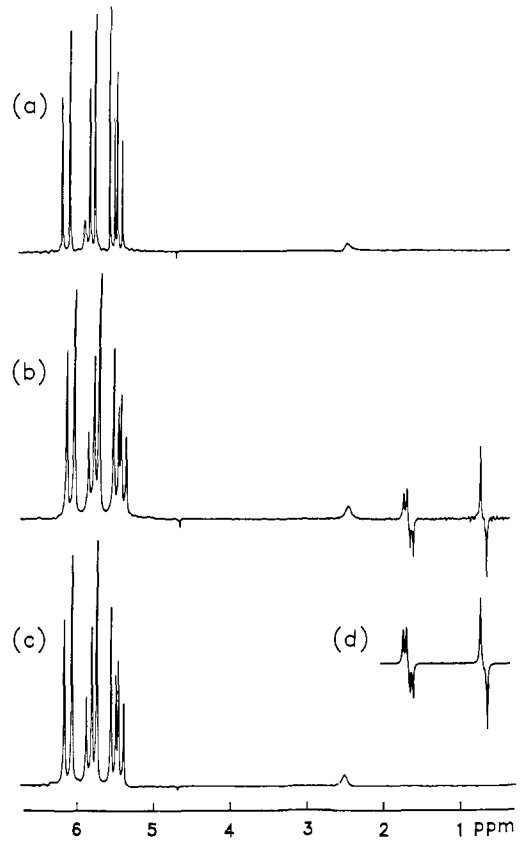

Figure 1. Demonstration that parahydrogen and synthesis allow dramatically enhanced nuclear alignment. Part (a) shows the proton NMR spectrum prior to the reaction. The intense lines are due to the acrylonitrile substrate. Part (b) was obtained subsequent to the hydrogenation to propionitrile but prior to spin-lattice equilibration. The large antiphase propionitrile multiplets in response to a $\pi/4$ pulse are observed only with para-enriched H_2 as reagent. Part (c) is the spectrum of the equilibrated sample and shows that the signal of (b) was a large transient enhancement. Part (d) is a line shape simulation demonstrating the agreement of the theory of ref 1 with the experiment of part (b). The line width is 3.5 Hz due to inhomogeneity of the field, which is degraded by the H_2 capillary.

a stable product, the transient nature of the enhanced NMR response must be a spin-lattice relaxation process from a highly ordered state, which upon irradiation gives signals orders of magnitude greater than the signal due to the equilibrium magnetization of the propionitrile (compare parts b and c of Figure 1).

The expected spectrum may be deduced from the previous theory[1] with minor extensions necessitated by the present system. The H_2 nuclear spin density operator is $\gamma = (1/4) - fI_1 \cdot I_2$, where $f = (1/3)(4x_p - 1)$ and x_p is the fraction of H_2 which is p-H_2. The H_2 gas was passed over a nickel–silica catalyst[4] held in a liquid N_2 bath, in order to achieve f = 0.34, and then warmed to room temperature before use, presumably without significant interconversion of ortho and para states. The multiplet intensities can be predicted analytically in the weak coupling limit. Instead of the usual paramagnetic (3/4,3/2,3/4) pattern for the methyl group (normalized to sum to 3 at zero K), one finds (1/8,0,−1/8) for the f = 1 limit. Similarly, for the methylene group the usual (1/4,3/4,3/4,1/4) multiplet becomes (1/16,1/16,−1/16,−1/16) with interference cancelling two of the three contributions to the inner lines. For comparison to the experiment of Figure 1b an exact numerical simulation of the propionitrile line shape was made (Figure 1d). The initial condition was obtained by deleting[1] oscillating zero quantum density matrix elements, which appear when the H_2 initial condition is expressed in the five-spin eigenbasis of the product. The weak coupling argument given above is

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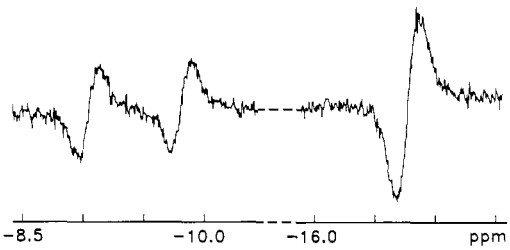
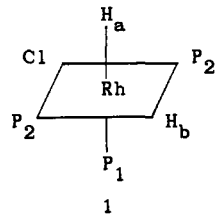


Figure 2. The enhanced transient NMR spectrum of the hydride region of $RhH_2(PPh_3)_3Cl$ (structure **1** of text) formed from parahydrogen in deuteriobenzene. Because of ligand exchange, the only resolved J splitting is for the coupling of the proton at -9.4 ppm to the trans ^{31}P (ref 2 and 3). The unique information is in the phase of the multiplets which shows that the unresolved scalar coupling between the hydride protons is negative.

confirmed qualitatively, and the agreement with experiment is excellent.

An experimental enhancement factor S_{obsd}/S_{eq}, arbitrarily based on the outer lines of the methyl triplet, is defined as the ratio of the transient signal after the H_2 burst to the signal from the equilibrium magnetization (at 300 K) of the molecules formed from that burst. To make this measurement accurately the sequence of H_2 burst, $\pi/4$ pulse, and data acquisition was delivered repeatedly. After each repetition and a delay of 45 s to allow full equilibration, the total propionitrile produced up to that point was measured by acquiring the response to a $\pi/2$ pulse. Enhancement factors of 100–200 were measured on several samples with either deuteriobenzene or deuteriochloroform as solvent. The variability between samples is greater than the 10% accuracy of measurement on each.

This enhancement in excess of 10^2 relative to the equilibrium magnetization per molecule is already very promising for applications. However, the calculations described above lead to a theoretical maximum enhancement of $fS_{max}/S_{eq} = fkT/3h\nu_o = 3.5 \times 10^3$ possible for this molecule and p-H_2 mole fraction. The catalytic intermediate is believed to have the structure **1** around the Rh center.[2,3,5-7] Since the two protons are already inequivalent, this intermediate is also expected to show antiphase transients when formed from para-enriched H_2. The experimental observation is shown in Figure 2 for a reaction mixture from which substrate was omitted in order to avoid depletion of **1**. Interestingly, the phase of these multiplets gives the *absolute* sign of this coupling as negative, information which is not normally available in spectra derived from a paramagnetic initial condition.



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The inverse of the disappearance rate for the J order of the catalyst dihydride during the period between the H_2 burst and the rf pulse is $T_{1J}^e = 0.28 \pm 0.03$ s. This relaxation time allows a simple explanation for the diminishment factor D defined as the ratio of measured to ideal propionitrile signal enhancement. The largest observed value of $D = S_{obsd}/fS_{max} = 2 \times 10^2/3.5 \times 10^3$ is explained if the rate of transfer of protons from catalyst to substrate is $\simeq 0.2$ s^{-1}. Values in this range have been reported for other alkenes.[7] Additional studies will allow an independent measurement of these rates and an assessment of whether the observed spin dynamics are consistent with the assumed reaction mechanism.[5-7] We have made preliminary observations on another catalytic system; the same phenomenon of large antiphase multiplets is observed on the dihydrido species $H_2Ir(CO)Cl(PPh_3)_2$ formed by addition of para-enriched H_2 to Vaska's compound.[8]

Finally, we note the possibility for a related method of high sensitivity NMR. In the present study ortho–para population differences are converted to nuclear magnetism, which is then measured. The inverse of this phenomenon would be to deduce the nuclear spin order of an ensemble of molecules by measuring the ortho–para population differences of the H_2 formed by their dehydrogenation. Since the spin state is modified by the dynamics under rf pulses and internal couplings, the branching ratio to ortho and para products would depend on the NMR of the dihydrogen precursor.

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Note Added in Proof. The phenomenon reported here and predicted in ref 1 may have been observed elsewhere unwittingly and interpreted as spin sorting of a radical pair intermediate (chemically induced dynamic nuclear polarization or CIDNP). See Hommeltoft et al. (Hommeltoft, S. I.; Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 5346) for such an example and for further references. Professor Eisenberg has informed us that the storage of their samples in liquid nitrogen prior to reaction in the room temperature spectrometer likely created a high concentration of parahydrogen. We thank Professors J. Bargon and R. G. Lawler for bringing this work to our attention.

Registry No. $Rh(PPh_3)_3Cl$, 14694-95-2; acrylonitrile, 107-13-1.

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Methane- and Difluoromethanediphosphonate Analogues of Geranyl Diphosphate: Hydrolysis-Inert Alternate Substrates

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Several groups have conducted mechanistic and structural studies with diphosphate analogues where a bridging oxygen is replaced by carbon (methanediphosphonates) or nitrogen (imidodiphosphates) in situations where it is desirable to repress hydrolysis of P–O–P linkages.[1-3] The major concerns associated with using these analogues are differences between pK_a's and reactivities of the analogues and normal substrates and problems associated with synthesis, especially for imidodiphosphates. Blackburn and co-workers reported that replacement of bridging methylene by a difluoromethylene unit in diphosphonates restored the pK_a's of analogues to values almost identical with those of the natural substrates.[4-6] We recently developed synthetic procedures for introducing methanediphosphonate and difluoromethanediphosphonate moieties into a variety of molecules, including isoprenoids[7] and nucleotides,[8] and now report comparative studies

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