allow tunnelling, and so the picture is self-consistent. The collapse of the AB_2 pattern to a single line[5,7] is brought about in part by the increased tunneling as higher energy states are occupied before classical barrier crossing becomes important. The intermediate line shapes are not those predicted from the usual models of chemical exchange[17] in which a thermally activated barrier crossing (hopping) motionally averages the chemical shifts at a fixed coupling constant.

In summary, anomalous scalar couplings observed for metal trihydrides in solution are explicable as exchange couplings but not as indirect couplings. They do not indicate large electron density between protons but rather weak delocalization by pairwise proton tunnelling. The details of the potential and explication of its apparent variation with metal or ligands is a challenging problem.

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Note Added in Proof. A similar exchange mechanism has been proposed by Zilm et al. to explain these NMR observations. See the following communication in this issue.

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Proton–Proton Exchange Couplings in Transition-Metal Polyhydrides

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We have previously reported the synthesis and anomalous NMR properties of a series of cationic iridium trihydride complexes of the general formula $[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4$ (L = PMe_3, **1**; L = PPh_3, **2**; L = $AsPh_3$, **3**).[1] The low-temperature $^1H\{^{31}P\}$ spectra of these compounds in the hydride region are AB_2 patterns with extremely large, temperature-dependent and field-independent values of J_{AB}. Similar observations have been made by others on *neutral* trihydrides such as $(\eta\text{-}C_5Me_5)Ru(PR_3)H_3$[2] and $(\eta\text{-}C_5H_{5-n}R_n)_2NbH_3$[3] (R = $SiMe_3$; $n = 1, 2$). Attempts to interpret these observations in terms of a structural model have invoked either dihydrogen/hydride structures[2] or trihydrogen complexes[1,3] such as those suggested by Burdett and co-workers.[4] The magnitude of reported J_{AB} (up to 570 Hz) and the fact that these couplings are very sensitive to temperature is unprecedented in solution NMR. The exponential temperature dependence reported[1] previously can at face value be rationalized by an equilibrium between two species, with one having a small J_{HH} and the second having a large J_{HH}. However, the sheer magnitude of the required large J_{HH}'s cannot be readily accounted for by any of the factors giving rise to a normal J coupling[5] unless a very unusual electronic structure is invoked. This communication describes a compound which displays an even larger J_{AB} and a tritium labeling experiment whose result provides the key to the origin of these couplings.

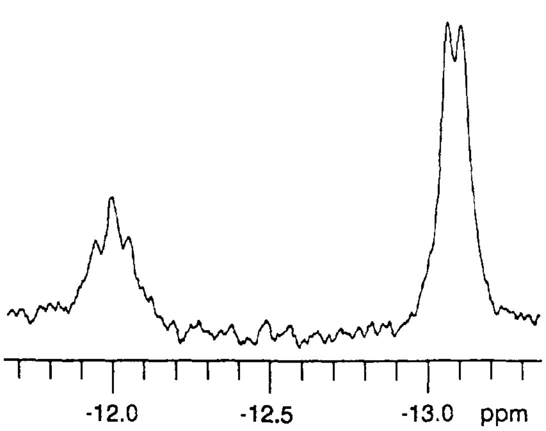

Figure 1. Tritium NMR spectrum of partially tritiated **3** recorded at 185 K on a 490 MHz proton instrument modified to operate at 522 MHz. Tritium incorporation was accomplished by a procedure analogous to the deuterium labeling procedure.[8]

As previously reported,[1] no H–D coupling has been observed in partially deuterated samples of complex **1**. Computer simulation of the ^1H line shape[6] confirms that the rapid quadrupolar relaxation of the ^2D nucleus ($T_1 \approx 25$ ms) at 193 K could preclude observation of the expected 19 Hz J_{HD} in **1** (J_{HH} = 122 Hz). The related complex **4** (L = MPTB[7]) has also been prepared. Since complex **4** gives an AB_2 spectrum at low temperature with J_{AB} values ranging from 1053 Hz (181 K) to 1397 Hz (196 K), it seemed almost certain that partial deuteration[8] would produce a resolvable H–D coupling. None was observed, and it seems unlikely that the ^2D T_1 could be sufficiently short to render the expected (150–200 Hz) J_{HD} unobservable unless the ^2D quadrupole coupling is also unusually large. In the absence of T_1 data, a definitive conclusion then cannot be drawn from this result. Because of these complications due to rapid deuterium relaxation and chemical exchange in the deuterium isotopomers, it was decided that conclusive results would only be obtained by using ^3T. The ^3T NMR of partially tritiated **3** at 185 K is shown in Figure 1. The ^3T_A–^1H_B and ^3T_B–^1H_A couplings are 29 and 24 Hz, respectively, rather than the ca. 530 Hz expected from the J_{HH} observed at this temperature.

This observation is quite remarkable and strongly suggests that the large J_{HH} couplings *are not magnetic in origin but are in fact exchange couplings*.[9-13] The model which best fits the NMR data for these trihydrides involves such couplings between the unique proton A and the two other protons B. In both NMR and ESR it has long been recognized that quantum mechanical tunneling[14-17] and exchange interactions[9-13] produce spectral features

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(7) MPTB = 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane. Complex **4** was prepared by methods analogous to those reported previously[1] for **1**–**3**.

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with no classical analogues. There is ample evidence from dynamic NMR,[18,19] kinetic data,[20] and inelastic neutron scattering[21] that the labile hydrogen nuclei in related systems exhibit quantum mechanical behavior at the temperatures involved ($T > 170$ K). Exchange couplings are well-known in ESR.[9-12] The formal mathematical description of the exchange interaction is in fact the same for any pair of indistinguishable spin 1/2 particles be they electrons, protons, or ^{3}He nuclei. The effect of the exchange interaction is to add a pseudo-magnetic coupling term to the spin Hamiltonian of the required form $-2\mathbf{J}\mathbf{I}_1{\cdot}\mathbf{I}_2$ where $2\mathbf{J}$ is the difference in energy of the symmetrical and antisymmetrical two particle orbital wave functions, i.e.

$$2\mathbf{J} = E_\mathrm{S} - E_\mathrm{A} = \langle\Psi_\mathrm{S}(1,2)|\mathcal{H}(1,2)|\Psi_\mathrm{S}(1,2)\rangle - \langle\Psi_\mathrm{A}(1,2)|\mathcal{H}(1,2)|\Psi_\mathrm{A}(1,2)\rangle \quad (1)$$

$\mathcal{H}(1,2)$ is given by

$$\mathcal{H}(1,2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(1) + V(2) + v(1,2) \quad (2)$$

where $V(1)$, $V(2)$ are single particle potentials, and $v(1,2)$ is the pairwise potential between the particles.[13]

The observation that the ^{3}T spectrum of **3** displays J_HT's that are only 24 and 29 Hz, 20 times less than expected, is a direct consequence of this model. If the J_HH coupling is largely an exchange coupling, it is expected to disappear in the partially tritiated isotopomer as the configurations $\mathrm{H_AT_B}$ and $\mathrm{T_AH_B}$ are not degenerate in energy. The small couplings observed in the tritium spectrum are then principally the usual magnetic scalar couplings. The same situation must hold for the deuterium isotopomers as well. However the smaller J_HD values, now known to be ca. 4 Hz on the basis of the above result, will invariably be unresolved due to the short ^{2}D T_1's. While exchange couplings are familiar to chemists in the context of ESR,[9] such effects have not been identified before in solution NMR. It has been recognized for some time that the NMR of solid ^{3}He is dominated by nuclear exchange couplings[13] which can be as large as 10 MHz. The size of this coupling is a very sensitive function of the amplitude of the ^{3}He lattice vibrations. This is borne out by the fact that **J** varies three orders of magnitude in solid ^{3}He, from 10^{-2} to 10 MHz, over the molar volume range of 17-24 cm^3. It is reasonable to assume that the potential the protons experience in the trihydrides considered here is fairly flat given their fluxional nature. Thus the required large amplitude motion is quite plausible. To estimate the size of these couplings, Landesman's model[13b,c] for exchange has been applied with parameters suitable for a pair of protons. In this model, which assumes a hard spheres potential, **J** is given by

$$\mathbf{J} \approx -\frac{3}{4}\sqrt{\frac{3}{\pi}}\frac{\hbar}{m}\left(\frac{a}{\delta^3}\right)\exp-\left\{\frac{3}{4}\,\frac{a^2 + \lambda^2}{\delta^2}\right\} \quad (3)$$

where a is the internuclear distance, δ the amplitude of the vibrational motion, λ the range of the interaction potential between the two protons, and m the proton mass. Preliminary solid-state NMR line shape[22] data for **2** give the AB distances as both 1.65 ± 0.05 Å and the BB distance as 2.20 ± 0.15 Å. Assuming λ the order[23] of 1 Å, J can be estimated for various values of δ. In a simple harmonic approximation, the zero-point motion amplitude δ (Å) for reasonable vibration frequencies of 410, 460, and 560 cm^{-1} are 0.35, 0.33, and 0.30 Å, respectively.[24] For these values J is calculated as 7200, 760, and 3 Hz in qualitative agreement with the observed range of such couplings. In addition when a is increased to the BB distance of 2.2 Å, J decreases by over a factor of 10^6. As the above rough calculation indicates, the value of J is an extremely sensitive function of the vibrational amplitude δ. At elevated temperatures there will also be thermally activated contributions to δ. In the temperature range in question $\langle\delta^2\rangle$ is expected to be directly proportional[24] to T. For small changes in T the observed exponential dependence is easily seen to be qualitatively predicted as a consequence of eq 3. Furthermore, fits of the temperature dependence are consistent with the above structural parameters and choice of λ.[25]

The ^{3}T NMR data reported here provides the first conclusive experimental evidence for pseudo-magnetic exchange couplings in solution ^{1}H NMR. A simple theory has been put forward which qualitatively accounts for the magnitude, temperature dependence, and isotope dependence of these couplings. Experiments are in progress to further test predictions of this model. Further theoretical work is also in progress to provide a better quantitative understanding of these couplings.

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Note Added in Proof. A similar exchange mechanism has been proposed by Jones et al. to explain these NMR observations. See paper in this issue.

Registry No. **1**, 113161-52-7; **2**, 113161-54-9; **3**, 113180-40-8; **4**, 119326-87-3.

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Carbon-Carbon Bond-Forming Reactions of Organotransition Metals with α- or γ-Haloorganolithium Reagents[1]

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Migratory insertion is one of a very limited number of fundamentally different patterns of organometallic transformations permitting the formation of carbon-carbon and carbon-heteroatom bonds, some of the others being reductive elimination, carbo-

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