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Structural and Spectroscopic Characterization of Iridium Trihydride Complexes: Evidence for Proton–Proton Exchange Coupling

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Abstract: Protonation of the neutral iridium dihydrides $(\eta\text{-}C_5H_5)Ir(L)H_2$ with $HBF_4{\cdot}Et_2O$ affords cationic trihydride complexes of the form $[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4$ (L = various phosphine and phosphite ligands). The ^1H NMR spectra of the cations in the hydride region at low temperature display AB_2X spin systems ($X = {}^{31}P$), which are simplified to AB_2 spin systems in the $^1H\{^{31}P\}$ spectra. The values for J_{A-B} derived by computer fitting of the observed spectra are extremely large, ranging from 61 to 1565 Hz. In general, J_{A-B} is inversely proportional to the basicity of the ligand L. The J_{A-B} values are strongly temperature dependent, increasing rapidly over the temperature range 150–200 K. Coupling constants have not been evaluated at temperatures higher than 200 K due to the onset of A/B site exchange, which causes line broadening and eventual coalescence of the two resonances. In derivatives partially labeled with deuterium in the hydride ligands, no H–D coupling was resolved. In a tritiated derivative, ^3H NMR was used to detect J_{H-T}, which was substantially reduced from the expected value. A neutron diffraction study of $[(\eta\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) has been carried out. Compound **21** crystallizes in the space group $P2_12_12_1$ ($Z = 4$) with $a = 8.840$ (2) Å, $b = 9.971$ (1) Å, $c = 14.278$ (2) Å, and $V = 1258.5$ (5) Å^3 (130 K). The structure of **21** in the solid state is best described as a normal pseudo seven-coordinate trihydride, with the cyclopentadienyl ligand capping a square pyramid comprising the three hydride ligands and the P ligand. The shortest H–H distance between the hydride ligands is 1.674 (14) Å. These results are interpreted in terms of the operation of quantum mechanical exchange coupling between the hydrogen nuclei in these complexes.

The structure and reactivity of transition-metal polyhydride complexes is an area of great interest to organometallic chemists due to the central importance of such species in catalytic processes. In this context, the reaction of H_2 with transition-metal complexes via oxidative addition to give dihydrides has been very extensively studied. While many theoretical studies of the interaction of H_2 with metal complexes have been carried out, it was not until the seminal discovery by Kubas[3] that an isolable dihydrogen complex was available for study. Subsequently, a number of dihydrogen complexes have been reported,[4] including several examples of polyhydrides now believed to contain both dihydrogen and hydride ligands.[5] In particular, several metal trihydrides are clearly established to have dihydrogen/hydride structures.[6]

The formal similarity between H_2 and H_3^+ as potential ligands is readily apparent. A lucid theoretical treatment of these and related polyhydrogen "ligands" has been reported by Burdett and co-workers.[7] While it is well established that H_3^+ in the gas phase

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has an equilateral triangle structure,[8] the calculations of Burdett indicate that, for the model system $Cr(CO)_5$, coordination of H_3^+ in an "open" mode is energetically preferred.

We have recently reported preliminary evidence for the existence of a coordinated trihydrogen ligand in complexes of the general formula $[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4$ (L = phosphine or arsine ligand).[9] The principal indicators at that time for bonding interactions between the "hydride" ligands in these species were the exceptionally large ^{1}H–^{1}H coupling constants. These coupling constants show a remarkable temperature dependence. Simultaneous with our original report, Chaudret and co-workers reported similar observations for the *neutral* ruthenium complexes of the form $(\eta\text{-}C_5Me_5)Ru(L)H_3$ (L = phosphine),[10] which had also been studied by Bercaw and Paciello.[11] Subsequently, Morris, Chaudret, and co-workers observed similar large, temperature-dependent coupling constants in niobium complexes $[NbH_3(\eta\text{-}C_5H_{5-n}R_n)_2]$ (n = 1, 2; R = $SiMe_3$).[12]

We have continued to study this problem, with particular emphasis on understanding the origin of the large coupling constants and their remarkable temperature dependence. The observed temperature dependence could be explained as a manifestation of an equilibrium between two structural forms, one having an ordinary trihydride structure (with a low J value) and another form having a "trihydrogen" structure, with a very large J value. This rationalization fails to explain the fact that the large proton–proton couplings observed in some cases actually exceed the value for H_2 itself,[13] which should be the largest such coupling possible by the usual Fermi contact mechanism, unless very unusual electronic structures are invoked.

In an attempt to ascertain the structure of a representative compound, an X-ray diffraction study of $[(\eta\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) has been carried out.[9] Unfortunately, the results were inconclusive in that the hydride ligands could not be located. In order to obtain definitive structural data, we have also carried out a neutron diffraction study, which has revealed that the solid-state structure of **21** is probably best described as a normal trihydride, with relatively short H–H distances, but no bonding interactions between the hydride ligands.

These considerations have prompted us to study the NMR properties of isotopically substituted derivatives, wherein hydride ligands are substituted with deuterium and tritium, in principle allowing the observation of coupling between H and D or T. While H–D couplings have not been observed, H–T couplings are observed, which are substantially diminished from the expected values based on the values of γ_T. We propose that the large magnitude of the H–H couplings, the temperature dependence, and the striking isotope effects observed in these couplings are in fact manifestations of exchange coupling. Exchange coupling is well-known in ESR spectroscopy[16] and is also observed in the NMR spectrum of solid ^{3}He.[17] In this paper, we describe spectroscopic and structural studies of a number of iridium trihydride complexes and outline an interpretation of these observations in terms of exchange coupling. A preliminary account of this interpretation has been previously communicated.[18]

Experimental Section

General Procedures. All syntheses and chemical manipulations were conducted under nitrogen or argon by standard Schlenk, drybox, or vacuum line techniques. Elemental analyses were performed by Galbraith Laboratories. Infrared spectra were recorded on either a Perkin-Elmer 337 grating instrument or a Nicolet 5-SX Fourier transform infrared spectrometer. Samples were examined in solution in 0.1-mm path length CaF_2 or NaCl cells or as KBr pellets. ^{1}H NMR spectra were obtained on Bruker WM-250, -490, and -500 MHz spectrometers. Chemical shifts are recorded in parts per million relative to residual protio solvent. ^{2}H and ^{31}P NMR spectra were recorded on a Bruker WM-500 spectrometer at 76.77 and 202.48 MHz, respectively, with chemical shifts relative to internal CD_2Cl_2 and external 85% H_3PO_4, respectively. Tritium NMR spectra were recorded on a Bruker WM-490 MHz spectrometer modified to operate at 522.3 MHz.

Variable-temperature ^{1}H NMR experiments were performed with a Bruker B-VT1000 controller with a copper/constantan thermocouple. All temperatures were calibrated by using ^{1}H chemical shifts of methanol. Simulations for ^{1}H NMR spectra were obtained with the Bruker program PANIC (Parameter Adjustment in NMR by Iterative Calculation). Simulations of proton line shapes of the partially deuterated isotopomers were done according to Pople[19] on an IBM PC/AT. Relaxation rate (T_1) experiments employed the saturation recovery method (180–τ–90 pulse sequence).

Unless otherwise stated, all solvents and reagents were obtained commercially and used without further purification. Toluene, THF, diethyl ether, pentane, and heptane were predried with 4-Å molecular sieves and purified by distillation from alkali metal/benzophenone under nitrogen. Absolute methanol and glacial acetic acid were purged with nitrogen before use. Zinc metal (80 mesh) was used as received (J. T. Baker). Liquid phosphines and phosphites (Strem Chemicals) were degassed and stored in vessels equipped with Teflon high-vacuum stopcocks. Solid phosphines, arsines, and stibines were used without further purification, except triphenylphosphine, which was recrystallized from heptane. The caged phosphite, 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane, (MPTB) was prepared according to the published procedure.[20] (**Caution:** *this phosphite is extremely toxic.*) $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) was prepared in the same manner as $[Ir(COD)Cl]_2$[21] (COD = 1,5-cyclooctadiene) except by substituting COE for COD.

$(\eta\text{-}C_5H_5)Ir(C_2H_4)_2$. $[Ir(COE)_2Cl]_2$ (2.90 g, 3.24 mmol) was added to 50 mL of THF in a 250-mL Schlenk flask. The orange slurry was freeze-pumped three times, after with ethylene was passed through the slurry at 0 °C for 0.5 h. This resulted in a clear orange solution. To this solution was added an ethereal solution of KC_5H_5 (0.73 g, 7.00 mmol) at 0 °C. A pale orange solution and a colorless precipitate of KCl was observed. After stirring, the solution was filtered through a 2.5-cm bed of Celite packed in a medium-pore frit and the Celite washed with 2 × 15 mL of diethyl ether. The filtrate was reduced to dryness on a rotary evaporator. The off-white residue was sublimed onto a water-cooled probe (1 × 10^{-3} mmHg, 25 °C) to afford colorless crystals. Yield 1.80 g, 90%. Spectroscopic data are consistent with those reported in the literature.[22]

$(\eta\text{-}C_5H_5)Ir(L)I_2$. In a typical synthesis, a 250-mL Schlenk flask was charged with 200 mg (0.64 mmol) of $(\eta\text{-}C_5H_5)Ir(C_2H_4)_2$ and 30 mL of CH_2Cl_2. Iodine (178 mg, 0.70 mmol) was added to the colorless solution, resulting in the immediate formation of a red precipitate of $[(\eta\text{-}C_5H_5)IrI_2]_x$. After 30 min of stirring, 1.1 equiv of the appropriate ligand was added. The reaction mixture was stirred for 1–2 h, giving a red solution. The solvent was removed on a rotary evaporator and the residue recrystallized from CH_2Cl_2/heptane (50:50) to give red microcrystals of analytically pure $(\eta\text{-}C_5H_5)Ir(L)I_2$ (**1–10**) in ca. 95% yield. (See supplementary material for analytical and spectroscopic data for **1–10**.)

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(η-C_5H_5)IrPMe$_3$H$_2$ (11). A 150-mL Schlenk tube was charged with 353 mg (0.60 mmol) of (η-C_5H_5)IrPMe$_3$I$_2$ (**1**) and 15 mL of absolute methanol. To the red slurry was added 0.5 g of Zn (80 mesh) and 1.0 mL of glacial acetic acid. The resulting mixture was stirred for 2 h, giving a pale yellow solution. Saturated aqueous NaCl solution (10 mL) was added. After 3 × 20 mL toluene extractions, the toluene extracts were combined and the solvent was removed in vacuo. The off-white residue was recrystallized from CH_2Cl_2/Et_2O (20:80) to give colorless crystals of **11**. Yield 170 mg, 85%. The neutral dihydrides **12–20** were prepared in the same manner in yields of 80–90%. The corresponding neutral dideuterides were readily prepared by employing methanol-d_1, CH_3COOD, and D_2O in the above procedure. It should also be noted that neutral dihydrides **11** and **15–17** may be easily purified by vacuum sublimation onto a water-cooled probe (1×10^{-3} mmHg, 40 °C).

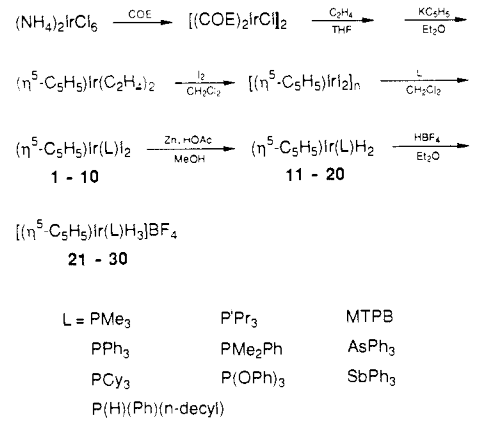
(η-C_5H_5)IrPMe$_3$H$_3$$^+BF_4$$^-$ (21). A 25-mL Schlenk flask was charged with 60 mg (0.22 mmol) of **11** and 5 mL of diethyl ether. The colorless solution was cooled to 0 °C. To this solution was added ethereal HBF_4 (20 μL) dropwise, resulting in the formation of a white precipitate. The solution was filtered and the solid residue washed with 3 × 10 mL of Et_2O and recrystallized from Et_2O/CH_2Cl_2 (10:90) to give **21** as colorless cubes. Yield 70 mg, 92%. A similar procedure was used in preparing compounds **23–25**.

(η-C_5H_5)IrPPh$_3$H$_3$$^+BF_4$$^-$ (22). A 25-mL Schlenk flask was charged with 30 mg (0.06 mmol) of **12** and 5 mL of CH_2Cl_2. This solution was cooled to 0 °C and 10 μL of $HBF_4 \cdot Et_2O$ added dropwise. The colorless solution was stirred for 10 min and the solvent volume reduced in vacuo (ca. 50%). The salt was precipitated with Et_2O, washed with 3 × 10 mL of Et_2O, and recrystallized from concentrated CH_2Cl_2 solution to afford colorless microcrystals of analytically pure **22**. Yield 30 mg, 81%. A similar procedure was used in preparing compounds **26–30**.

Neutron Diffraction Analysis. The crystal employed was a colorless prism weighing 1.35 mg (volume 0.63 mm^3). This specimen was mounted on an aluminum pin oriented approximately along crystallographic (10$\bar{1}$), sealed under a helium atmosphere in an aluminum container, and placed in a closed-cycle helium refrigerator[23] mounted on a four-circle diffractometer[24] at the Brookhaven High Flux Beam Reactor. A germanium (220) single-crystal monochromator was used to obtain a neutron beam of wavelength 1.15930 (12) Å based on KBr (a_0 = 6.6000 Å at T = 298 K[25]). The sample temperature was maintained at 130.0 (5) K[26] during data collection. Initially, the crystal was cooled to 20 K, but there was some indication of split peak profiles at 80 K and below, which were not present at 130 K.

Unit cell dimensions, determined by least-squares fit of the averaged 2θ values of eight reflections, each of which was centered for four different forms, are listed in Table IV together with other relevant experimental details. Intensity data were obtained over the hk$\bar{l}$ octant except for a few reflections, inaccessible due to restrictions introduced by the refrigerator system, which were scanned as h$\bar{k}$l or $\bar{h}$0$\bar{l}$. Intensities of two reflections were monitored every 100 measurements to check experimental stability, which was judged satisfactory.[27] Data were obtained in θ:2θ step-scan mode with the counting time per step determined by a preset monitor count of the incident neutron beam (ca. 8 s). Integrated intensities were calculated with the assumption that 10% of the steps at either extremity of the scans represent background. Lorentz and absorption corrections were applied, the latter calculated by means of numerical integration[28,29] over a Gaussian grid of 16 × 12 × 8 points along a, b, and c, respectively, with the crystal approximated by 10 faces belonging to forms {110}, {101}, {011}, and {001}. The validity of the absorption correction was checked by comparison with azimuthal scan intensity data for reflection 4$\bar{1}$4. Averaging data for equivalent reflections and deleting space group absences yielded 1499 unique F_o^2 values for use in the structure refinement, of which 33 subsequently were judged to be contaminated by scattering due to the aluminum sample container and refrigerator shrouds and accordingly were discarded.

Scheme I



For the initial structure model, coordinates of non-hydrogen atoms were taken from the room-temperature X-ray study.[9] Cyclopentadienyl hydrogens were placed at calculated positions, and methyl and hydride hydrogens were located from successive difference Fourier syntheses. The structure was refined by full-matrix least squares, based on F_o^2, including in the final model anisotropic thermal parameters for all 32 atoms, a scale factor k, and a parameter for an isotropic type I extinction correction[30] with Lorentzian mosaic,[31] for a total of 290 variable parameters (N_o/N_v = 5.1). Neutron scattering lengths were taken to be b_C = 0.6648, b_H = -0.371, b_B = 0.535, b_F = 0.565, b_{Ir} = 1.060, and b_P = 0.513 (all × 10^{-12} cm).[32] The refinement was terminated when the maximum |shift/error| was <0.05. The final R_{F^2} values and goodness of fit (S) are somewhat higher than normal, due to the relatively weak intensity obtained from the small sample and the consequent need for long counting times, which lead to a relatively high contribution from background aluminum scattering. The conventional R value, based on F for 1002 reflections with $I > 3\sigma(I)$ is 0.057. A difference Fourier synthesis computed following the refinement was devoid of significant features, with the largest positive residual being less than 5% of a typical carbon peak and the most negative residual being smaller than 10% of a typical hydrogen. All calculations were carried out on MicroVAX computers, using programs described by Lundgren.[33]

Reaction of 22 with D_2. In an NMR tube fitted with a Kontes high-vacuum stopcock was placed 6.5 mg of **22**. CH_2Cl_2 or CD_2Cl_2 (0.4 mL) was vacuum transferred into the tube followed by three freeze–pump–thaw cycles. The tube was then pressurized to 30 psi with D_2. Light was excluded. The reaction was essentially complete in 18 h, giving >95% isotopically pure **22**-d_3. Various levels of isotopic enrichment may be obtained by varying the reaction time. Similar procedures were followed for **27** and **28**.

Preparation of (η-C_5H_5)Ir(PPh$_3$)(CO)H$^+$BF$_4$$^-$ (31). A 10-mL Pyrex bomb was charged with 12 mg of **22** and 2 mL of CH_2Cl_2 (vaccum transfer). The solution was subjected to three freeze–pump–thaw cycles and then charged with 40 psi of CO gas. The reaction was monitored by IR and was complete in 1 h: IR (ν_{CO}, CH_2Cl_2) 2057 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m, PPh$_3$), 5.82 (s, 5 H), -14.4 (d, J_{H-P} = 24.4 Hz, 1 H). A similar procedure was used to prepare (η-C_5H_5)Ir(AsPh$_3$)(CO)H$^+$BF$_4$$^-$ (**32**) and (η-C_5H_5)Ir(SbPh$_3$)(CO)H$^+$BF$_4$$^-$ (**33**), although much longer reaction times were needed for the preparation of **33**. Characterization of **32**: IR (ν_{CO}, CH_2Cl_2) 2058 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.68–7.30 (m, AsPh$_3$), 5.90 (s, 5 H), -14.53 (s, 1 H). **33**: IR (ν_{CO}, CH_2Cl_2) 2051 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, SbPh$_3$), 5.97 (s, 5 H), -14.79 (s, 1 H).

Results

Synthesis. In contrast to the readily available halide-bridged dimer [(η-C_5Me_5)IrCl$_2$],[34] the cyclopentadienyl analogues are

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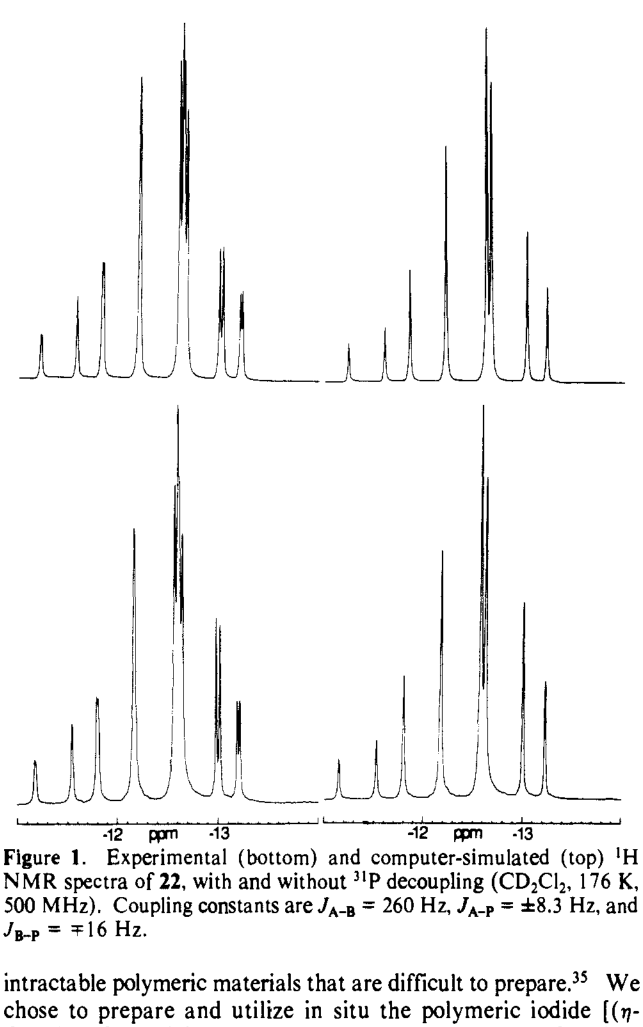

Figure 1. Experimental (bottom) and computer-simulated (top) ^{1}H NMR spectra of **22**, with and without ^{31}P decoupling (CD$_2$Cl$_2$, 176 K, 500 MHz). Coupling constants are J_{A-B} = 260 Hz, J_{A-P} = ±8.3 Hz, and J_{B-P} = ∓16 Hz.

intractable polymeric materials that are difficult to prepare.[35] We chose to prepare and utilize in situ the polymeric iodide [(η-C$_5$H$_5$)IrI$_2$]$_n$, which was prepared by treatment of (η-C$_5$H$_5$)Ir(ethylene)$_2$ with iodine. While the iodide polymer has very limited solubility, reactions with a wide variety of ligands proceed readily to afford excellent yields of the monomeric complexes (η-C$_5$H$_5$)Ir(L)I$_2$ (see Scheme I).

Conversion of metal halides to hydrides can be accomplished with a wide variety of reagents. In the pentamethylcyclopentadienyl analogues such as (η-C$_5$Me$_5$)Ir(PMe$_3$)Cl$_2$, conversion to the dihydrides is conveniently achieved with a variety of borohydride or aluminum hydride reagents.[36] In our cyclopentadienyl complexes, we have found that such reagents give low yields of hydride products. Excellent yields of the dihydrides **11–20** were obtained by the zinc/acetic acid/methanol procedure of Moss and Graham[37] (eq 1). The dihydrides are colorless, thermally

$$(\eta\text{-C}_5\text{H}_5)\text{Ir(L)I}_2 + \text{Zn/CH}_3\text{COOH/MeOH} \rightarrow (\eta\text{-C}_5\text{H}_5)\text{Ir(L)H}_2 \quad (1)$$

stable, and crystalline. They are mildly air sensitive in the solid state and quite air sensitive in solution. A summary of the analytical and spectroscopic data for these compounds is given in Table I. Compounds **11**[38] and **12**[39] have been briefly reported, while **13–20** are previously unknown.

Protonation (HBF$_4$·Et$_2$O) of the neutral dihydrides in Et$_2$O affords the salts [(η-C$_5$H$_5$)Ir(L)H$_3$]BF$_4$ (**21–30**) in good yields (eq 2). These complexes are colorless, moderately air stable solids, which are air sensitive in solution. Analytical and ^{1}H NMR data are given in Table I.

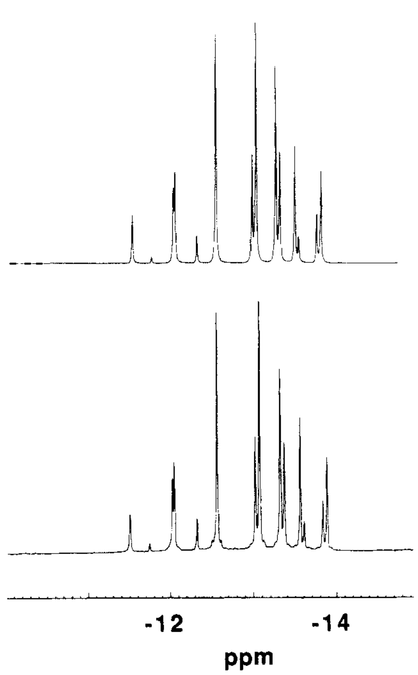

Figure 2. Experimental (bottom) and computer-simulated (top) ^{1}H{^{31}P} NMR spectra of **30** (CD$_2$Cl$_2$, 176 K, 500 MHz). Coupling constants are J_{A-B} = 281 Hz, J_{A-C} = 268 Hz, and J_{B-C} = 3.4 Hz.

$$(\eta\text{-C}_5\text{H}_5)\text{Ir(L)H}_2 + \text{HBF}_4\cdot\text{Et}_2\text{O} \rightarrow [(\eta\text{-C}_5\text{H}_5)\text{Ir(L)H}_3]\text{BF}_4 \quad (2)$$

^{1}H NMR Observations. In addition to appropriate ligand resonances and cyclopentadienyl resonances, compounds **21–30** exhibit a single resonance in the hydride region (ambient temperature). In most cases, coupling to the coordinated P nuclei of the phosphine or phosphite ligand is resolvable, leading to a doublet with J_{H-P} = 8–10 Hz (see Table II). The observation of a single hydride resonance indicates that the different hydride environments are undergoing an exchange process that is rapid on the NMR time scale.

Low-temperature ^{1}H NMR spectra of **21–27** reveal extremely complex patterns in the hydride region, best described as AB$_2$X spin systems. Computer simulation is consistent with this description. With ^{31}P decoupling, the spectra are simplified to AB$_2$ spin systems (see Figure 1). The most significant feature of these spectra is the *extremely* large values for J_{A-B} (see Table II). While the observed spectra differ slightly at different applied fields (250 or 500 MHz), the values of J_{A-B} derived from computer simulation of the observed spectra are *field independent*.

The values for the chemical shifts of the A and B sites derived from the above analysis show no significant temperature dependence. The chemical shift of the single hydride resonance observed at ambient temperature is precisely the population-weighted average of the low-temperature chemical shifts (see Table II).

Temperature Dependence of J_{A-B}. In the course of our observations of the low-temperature ^{1}H NMR spectra of several of these species, we noted that the values of J_{A-B} are highly temperature dependent. For example, in complex **26** (L = P(OPh)$_3$), J_{A-B} = 358 Hz at 176 K, increasing steadily to 526 Hz at 196 K. Observations could not be made at higher temperatures due to the onset of line broadening caused by the H$_A$/H$_B$ exchange process. Similar trends were observed in all complexes studied (see Table III). In all cases examined, the observed coupling constant increases with increasing temperature.

Secondary Phosphine Complex: An ABC Spin System. In the hope of obtaining more detailed structural information, the neutral dihydride **20** (L = P(Ph)(n-decyl)(H)) was prepared. The ^{1}H NMR spectrum in the hydride region is an ABX spin system, (X = ^{31}P) with J_{A-X} = J_{B-X} = 31.9 Hz and J_{A-B} = 6.9 Hz. Pro-

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Table I. ^1H NMR Data and Analyses for **11–30**[a,b]

					calcd		found	
	L	assignment	δ,[c] ppm	coupling[d]	C	H	C	H
11	PMe_3[e,g]	C_5H_5	5.03 (s)					
		PCH_3	1.37 (d)	$^2J_{PH} = 10.5$				
		IrH_2	-17.49 (d)	$^2J_{PH} = 31.4$				
12	PPh_3[f,g]	PC_6H_5	7.7–7.0 (m)					
		C_5H_5	5.01 (d)	$^3J_{PH} = 0.9$				
		IrH_2	−16.95 (d)	$^2J_{PH} = 30.5$				
13	PCy_3	C_5H_5	5.17 (s)		51.18	7.47	51.55	7.36
		PC_6H_{11}	2.0–1.1 (m)					
		IrH_2	-18.98 (d)	$^2J_{PH} = 29.0$				
14	P^iPr_3	C_5H_5	5.19 (d)	$^3J_{PH} = 1.0$	40.08	6.74	40.21	6.91
		$PCHMe_2$	3.0–2.8 (m)					
		$PCCH_3$	1.05 (dd)	$^3J_{PH} = 14.0$ $^3J_{HH} = 7.2$				
		IrH_2	-19.00 (d)	$^2J_{PH} = 29.0$				
15	PMe_2Ph	PC_6H_5	7.8–7.2 (m)		39.28	4.57	39.27	4.48
		C_5H_5	5.26 (s)					
		PCH_3	2.07 (d)	$^2J_{PH} = 10.5$				
		IrH_2	-17.87 (d)	$^2J_{PH} = 30.8$				
16	$P(OPh)_3$	POC_6H_5	7.4–7.1 (m)		48.50	3.89	48.53	4.00
		C_5H_5	4.69 (d)	$^3J_{PH} = 2.0$				
		IrH_2	−18.20 (d)	$^2J_{PH} = 36.4$				
17	MPTB[h]	C_5H_5	5.33 (d)	$^3J_{PH} = 2.1$	29.48	3.96	29.49	3.98
		$POCH_2$	4.16 (d)	$^3J_{PH} = 5.3$				
		$POCH_2CCH_3$	0.72 (s)					
		IrH_2	−17.94 (d)	$^2J_{PH} = 37.0$				
18	$AsPh_3$[g]	AsC_6H_5	7.7–7.0 (m)		48.55	3.92	48.77	4.08
		C_5H_5	5.03 (s)					
		IrH_2	-16.88 (s)					
19	$SbPh_3$	SbC_6H_5	7.6–7.3 (m)		45.11	3.62	45.29	3.65
		C_5H_5	5.29 (s)					
		IrH_2	−17.91 (s)					
20	P*[i]	PC_6H_5	7.7–7.3 (m)		49.49	6.74	49.39	6.59
		PH	6.11 (dm)	$^1J_{PH} = 367$				
		C_5H_5	5.18 (s)					
		$PC_{10}H_{21}$	2.0–0.9 (m)					
		IrH_A	−17.76 (dd)	$^2J_{PH} = 31.9$ $^2J_{HH} = 6.9$				
		IrH_B	−17.96 (dd)	$^2J_{PH} = 31.9$ $^2J_{HH} = 6.9$				
21	PMe_3	C_5H_5	5.97 (s)		22.71	4.06	22.70	3.99
		PCH_3	1.99 (d)	$^2J_{PH} = 12.5$				
		IrH_3	−13.24 (d)	$^2J_{PH} = 10.0$				
22	PPh_3	PC_6H_5	7.6–7.3 (m)		54.33	3.80	45.56	3.93
		C_5H_5	5.92 (s)					
		IrH_3	−12.39 (d)	$^2J_{PH} = 7.9$				
23	PCy_3	C_5H_5	5.97 (s)		44.02	6.59	44.21	6.83
		PC_6H_{11}	2.1–1.1 (m)					
		IrH_3	-13.77 (d)	$^2J_{PH} = 9.2$				
24	P^iPr_3	C_5H_5	6.01 (s)		33.14	5.77	33.18	5.79
		$PCHMe_2$	2.25 (m)					
		$PCCH_3$	1.17 (dd)	$^3J_{PH} = 16.3$ $^3J_{HH} = 7.1$				
		IrH_3		$^2J_{PH} = 9.5$				
25	PMe_2Ph	PC_6H_5	7.7–7.4 (m)		32.17	3.95	32.30	4.10
		C_5H_5	5.90 (s)					
		PCH_3	2.29 (d)	$^2J_{PH} = 12.0$				
		IrH_3	-12.94 (d)	$^2J_{PH} = 9.6$				
26	$P(OPh)_3$	POC_6H_5	7.5–7.2 (m)		42.02	3.53	42.28	3.61
		C_5H_5	5.50 (d)	$^3J_{PH} = 1.9$				
		IrH_3	−12.48 (d)	$^2J_{PH} = 8.5$				
27	MPTB[h]	C_5H_5	6.00 (d)	$^3J_{PH} = 1.5$	24.25	3.46	24.22	3.54
		$POCH_2$	4.40 (d)	$^3J_{PH} = 5.7$				
		$POCH_2CCH_3$	0.85 (s)					
		IrH_3	-12.25 (br s)					
28	$AsPh_3$	AsC_6H_5	7.6–7.3 (m)		42.28	3.55	42.59	3.65
		C_5H_5	5.98 (s)					
		IrH_3	−12.69 (s)					
29	$SbPh_3$	SbC_6H_5	7.6–7.3 (m)		39.45	3.31	39.52	3.28
		C_5H_5	6.06 (s)					
		IrH_3	-13.45 (s)					
30	P*[i]	PC_6H_5	7.7–7.3 (m)		42.21	5.92	42.36	6.01
		PH	6.33 (dm)	$^1J_{PH} = 430$				
		C_5H_5	5.95 (s)					
		$PC_{10}H_{21}$	1.8–0.9 (m)					
		IrH_3	−12.83 (br s)					

[a] Unless otherwise specified, spectra of the neutral dihydrides $(\eta^5C_5H_5)Ir(L)H_2$ **11–20** were obtained in $CDCl_3$ at ambient temperature, 250 MHz. [b] Spectra of the cationic trihydrates $[(\eta^5\text{-}C_5H_5)Ir(L)H_3]BF_4$ **21–30** were obtained in CD_2Cl_2 at ambient temperature, 500 MHz. [c] Chemical shifts are referenced to residual protiated solvent. [d] Coupling constants are reported in Hz. [e] $(\eta^5\text{-}C_5H_5)IrPMe_3H_2$ has previously been reported, ref 38. [f] $(\eta^5\text{-}C_5H_5)IrPPh_3H_2$ has previously been reported, ref 39. [g] Measured in benzene-d_6, 250 MHz. [h] MPTB = 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane. [i] P* = P(H)(Ph)(*n*-decyl).

Table II. Low-Temperature ^{1}H NMR Data (Hydride Region) for **21**–**29**[a]

	L	δ_{H_A}[b]	δ_{H_B}[b]	$^2J_{A-B}$[c]	$^2J_{PH_A}$[c]	$^2J_{PH_B}$[c]
21	PMe_3	−12.43	−13.90	114	±8.3	∓19.0
22	PPh_3	−11.80	−12.75	320	±8.3	∓16.0
23	PCy_3	−13.35	−14.10	68.0	±5.6	∓17.0
24	P^iPr_3	−13.25	−14.10	69.0	±5.7	∓17.0
25	PMe_2Ph[d]	−12.21	−13.56	191	±4.8	∓16.8
26	$P(OPh)_3$	−11.76	−13.09	432	0	∓12.5
27	MPTB[e]	−11.31	−12.83	1274	0	∓9.7
28	$AsPh_3$[f]	−12.02	−13.17	512		
29	$SbPh_3$	−12.82	−13.89	158		

[a] Unless otherwise specified, spectra were obtained in CD_2Cl_2 at 186 K, 500 MHz. [b] Chemical shifts are referenced in the residual protiated solvent. [c] Coupling constants are reported in Hz. [d] Measured in CD_2Cl_2 at 250 MHz. [e] MPTB = 1-methyl-4-phospha-3,6,8-trioxabicyclo[2.2.2]octane. [f] Measured in CD_2Cl_2 at 490 MHz.

Table III. Temperature and Ligand Dependence on J_{A-B}[a,b]

	L	176 K	181 K	186 K	191 K	196 K
23	PCy_3	61	64	68	73	77
24	P^iPr_3	63.5	66.5	69	71.5	75
21	PMe_3	96	106	114	122	135
29	$SbPh_3$	147	158	171	180	196
25	PMe_2Ph[c]	161	175	191	210	237
22	PPh_3[d]	260	291	320	355	397
26	$P(OPh)_3$	358	397	432	469	526
28	$AsPh_3$[e]	376	419	460	512	570
27	MPTB[f,g]	972	1119	1274	1425	1565

[a] Unless otherwise specified, spectra were obtained in CD_2Cl_2, 500 MHz. [b] Coupling constants are reported in Hz. [c] Measured in CD_2Cl_2, 250 MHz at 180, 183, 186, 191, and 196 K. [d] Further measurements were obtained in $CHFCl_2/CD_2Cl_2$ mixture (4:1), 490 MHz: 228 (171 K), 213 (167 K), 198 (163 K), 187 (160 K), 176 (157 K), 162 (153 K), and 151 Hz (150 K). [e] Measured in CD_2Cl_2, 490 MHz at 176, 180, 183, 186, and 189 K. [f] MPTB = 1-methyl-4-phospha-3,6,8-trioxabicyclo[2.2.2]octane. [g] Measured in CD_2Cl_2, 490 MHz at 176, 181, 186, 191, and 196 K.

Table IV. Experimental Details of the Neutron Diffraction Analysis of $[(\eta^5\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**)

formula	$C_8H_{17}BF_4IrP$
crystal system	orthorhombic
space group	$P2_12_12_1$
Z	4
mol wt, g mol^{-1}	423.2
T, K	130.0 (5)
a, Å	8.840 (2)
b, Å	9.971 (1)
c, Å	14.278 (2)
V, Å^3	1258.5 (5)
ρ(calc), g cm^{-3}	2.23
no. of reflcns, N_o	1466
no. of vbl params, N_v	290
R_{F^2}[a]	0.106
R_{wF^2}[a]	0.081
goodness of fit, S[a]	1.64

[a] $R_{F^2} = \sum(F_o^2 - kF_c^2)/\sum F_o^2$. $R_{wF^2} = \sum w(F_o^2 - k^2F_c^2)^2/\sum wF_o^4$. $S = [\sum w(F_o^2 - k^2F_c^2)^2/k^2(N_o - N_v)]^{1/2}$.

tonation of **20** affords $[(\eta\text{-}C_5H_5)Ir(P(Ph)(n\text{-decyl})(H))H_3]BF_4$ (**30**). The low-temperature ^{1}H NMR spectrum of **30** is an ABCX spin system, which simplifies to an ABC spin system with ^{31}P decoupling. For the analysis of this complex spin system, initial parameters were derived by the method of Castellano and Waugh.[40] Final iterative fitting of observed and calculated spectra was carried out using PANIC (see Figure 2). The ABC spin system is completely defined by three coupling constants and three chemical shifts. The coupling constants in this case are J_{A-B} = 281 Hz, J_{A-C} = 268 Hz, and J_{B-C} = 3.4 Hz (176 K). While J_{A-B} and J_{A-C} increase rapidly with increasing temperature, as noted above for the AB_2 cases, J_{B-C} is independent of temperature.

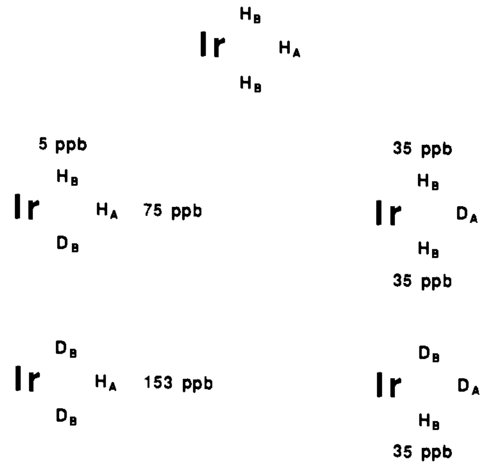

Figure 3. Isotope effects on the chemical shifts of the various isotopomers of partially deuterated **22**. Shifts are reported in parts per billion (ppb) and are upfield from the chemical shift of the pure protio species.

Deuterium Exchange Reactions. Since partial deuteration has been highly informative in studies of dihydrogen complexes, we sought convenient procedures for incorporating deuterium into these complexes. A D_2/H_2 exchange reaction reported by Shapley and co-workers[39] for compound **12** was attempted (eq 3). In our hands, we found that no deuterium incorporation occurs under the reported conditions.

$$(\eta\text{-}C_5H_5)Ir(PPh_3)H_2 + D_2\ (20\ \text{psi}) \rightarrow (\eta\text{-}C_5H_5)Ir(PPh_3)D_2 + H_2 \quad (3)$$

In contrast, the cationic trihydride readily exchanges (eq 4). Thus, it seems likely that the previously reported exchange reaction occurred via the cationic species, perhaps catalyzed by adventitious acid.

$$[(\eta\text{-}C_5H_5)Ir(PPh_3)H_3]BF_4 + D_2 \rightarrow [(\eta\text{-}C_5H_5)Ir(PPh_3)D_3]BF_4 + H_2 \quad (4)$$

NMR Studies of Partially Deuterated Trihydride Cations. Contrary to our expectations, we were unable to observe any evidence of H–D coupling in the ^{1}H NMR spectra of partially deuterated samples of the cations. Observations were made on several compounds at a variety of temperatures from room temperature down to 176 K. In the low-temperature spectra, (^{31}P-decoupled) resonances due to isotopomers of composition H_2D and HD_2 are slightly broader ($\nu_{1/2}$ = 12 Hz) than resonances due to the perprotio species ($\nu_{1/2}$ = 2–3 Hz). Although no H–D coupling was observed, large temperature-independent upfield isotope effects on the chemical shifts upon deuterium substitution were noted. These large isotope shifts allow resonances due to each isotopomer to be assigned. The results are exemplified by data for compound **22**, which is shown in a pictorial format in Figure 3. The four possible isotopomers have composition H_3, H_2D, HD_2, and D_3. The first three are observable in the ^{1}H NMR spectrum. The HD_2 isotopomer has two positional isomers, with H in the A site or one of the B sites, which we designate as $H_A(D_B)_2$ and $H_BD_AD_B$, respectively. Each of these species gives one resonance in the ^{1}H NMR spectrum. Similar considerations apply to the isotopomer H_2D, where the positional isomers are now designated as $(H_B)_2D_A$ and $H_AH_BD_B$. The former species exhibits one resonance while the latter gives a four-line spectrum typical of an AB spin system.

Interestingly, the J_{A-B} values derived from analysis of the AB spin system differ significantly from the J_{A-B} values obtained from the AB_2 spectrum of the H_3 isotopomer. The substitution of one D into one of the B sites causes the proton–proton coupling constant J_{A-B} to *increase by 5–6%.*

In an attempt to ascertain the reason for our failure to observe resolvable H–D couplings in these complexes, we have investigated the ^{2}H NMR spectra of selected complexes. For example, the low-temperature (193 K) ^{2}H NMR spectrum (76.77 MHz, CH_2Cl_2) of **21**-d_3 (>95% D) exhibits two resonances in the hydride

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(40) Castellano, S.; Waugh, J. S. *J. Chem. Phys.* **1961**, *34*, 295–309.

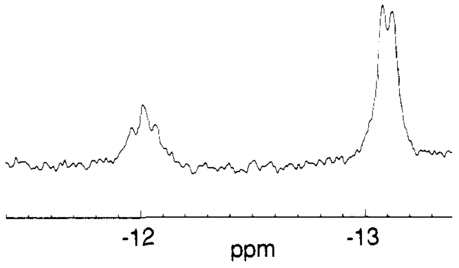


Figure 4. Experimental ^3H NMR spectrum of partially tritiated **28** (CD_2Cl_2, 185 K, 522.3 MHz). Coupling constants are $J_{T_A-H_B} = 29$ Hz and $J_{T_B-H_A} = 24$ Hz.

Table V. Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) for $[(\eta^5\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) at $T = 130$ K

atom	x	y	z	B_{iso}
Ir1	1896 (3)	807 (2)	2293 (2)	1.54 (0.05)
P1	3811 (5)	332 (5)	1285 (3)	1.47 (0.10)
C1	1596 (5)	3026 (4)	2259 (4)	3.03 (0.11)
C2	1023 (6)	2536 (5)	3127 (3)	3.08 (0.12)
C3	−214 (5)	1678 (5)	2929 (3)	3.10 (0.12)
C4	−395 (6)	1651 (5)	1949 (3)	3.48 (0.13)
C5	701 (5)	2459 (5)	1536 (3)	3.30 (0.13)
C6	4585 (6)	−1325 (5)	1442 (4)	3.06 (0.12)
C7	5409 (5)	1443 (4)	1378 (3)	2.06 (0.10)
C8	3268 (6)	408 (5)	71 (3)	2.45 (0.11)
B1	3602 (5)	5185 (5)	477 (3)	1.61 (0.10)
F1	4743 (7)	5824 (7)	7 (4)	4.21 (0.16)
F2	3531 (8)	3848 (5)	210 (4)	4.17 (0.17)
F3	2249 (6)	5792 (8)	265 (5)	4.66 (0.18)
F4	3824 (7)	5265 (6)	1442 (3)	3.49 (0.14)
H1	2501 (12)	3708 (10)	2152 (10)	6.03 (0.35)
H2	1461 (18)	2806 (13)	3816 (7)	7.10 (0.42)
H3	−902 (15)	1171 (13)	3430 (10)	7.16 (0.42)
H4	−1232 (13)	1059 (16)	1574 (10)	7.30 (0.44)
H5	825 (17)	2615 (13)	789 (7)	6.82 (0.41)
H6A	5037 (13)	−1408 (11)	2149 (7)	5.23 (0.31)
H6B	5474 (13)	−1489 (11)	925 (7)	5.01 (0.30)
H6C	3716 (15)	−2060 (10)	1334 (9)	5.36 (0.31)
H7A	6212 (11)	1142 (11)	873 (6)	4.16 (0.25)
H7B	5042 (11)	2463 (9)	1240 (7)	4.43 (0.27)
H7C	5878 (10)	1379 (10)	2084 (6)	3.71 (0.23)
H8A	4209 (11)	105 (11)	−354 (6)	4.24 (0.27)
H8B	2913 (12)	1444 (10)	−105 (6)	4.31 (0.27)
H8C	2320 (12)	−270 (12)	−55 (7)	4.89 (0.30)
H1Ir	1997 (13)	−505 (9)	2923 (6)	4.37 (0.26)
H2Ir	3343 (10)	675 (10)	2946 (5)	3.74 (0.22)
H3Ir	1414 (11)	−541 (9)	1790 (7)	4.29 (0.25)

Table VI. Significant Bond Distances and Angles[a] for $[(\eta^5\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) at $T = 130$ K

	Distances, Å		
Ir1–H1Ir	1.591 (8)	Ir1–Cp[c]	1.889 (5)
Ir1–H2Ir	1.588 (8)	Ir1–C1	2.229 (5)
Ir1–H3Ir	1.583 (9)	Ir1–C2	2.232 (5)
Ir1–H_{mean}	1.587 (3)	Ir1–C3	2.249 (5)
		Ir1–C4	2.247 (5)
H1Ir···H2Ir	1.67 (1)	Ir1–C5	2.235 (5)
H1Ir···H3Ir	1.70 (1)	Ir–C_{mean}	2.238 (5)
H2Ir···H3Ir	2.66 (1)		
		C–C_{mean}	1.412 (6)
Ir1–P1	2.273 (5)		
		C–H_{mean}[d]	1.077 (7)
P–C_{mean}	1.801 (1)		
		B–F_{mean}	1.382 (7)
C–H_{mean}[b]	1.084 (4)		
	Angles, deg		
H1Ir–Ir1–H2Ir	63.6 (5)	H1Ir–Ir1–Cp[c]	130.0 (4)
H1Ir–Ir1–H3Ir	64.7 (5)	H2Ir–Ir1–Cp[c]	123.0 (4)
H2Ir–Ir1–H3Ir	114.4 (5)	H3Ir–Ir1—Cp[c]	120.6 (4)
H1Ir–Ir1–P1	98.3 (4)	P1–Ir1–Cp[c]	131.7 (2)
H2Ir–Ir1–P1	75.8 (3)		
H3Ir–Ir1–P1	74.7 (4)		

[a] Mean values calculated as $(\sum(x_i - \bar{x})^2/n(n-1))^{1/2}$. [b] Methyl groups. [c] Ring centroid. [d] Cp ring.

Table VII. Anisotropic Thermal Parameters (Å$^2 \times 10^3$)[a] for $[(\eta^5\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) at $T = 130$ K

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir1	19 (1)	22 (1)	17 (1)	0 (1)	2 (1)	4 (1)
P1	18 (2)	20 (2)	18 (2)	2 (2)	1 (2)	0 (2)
C1	28 (2)	21 (2)	66 (3)	2 (2)	8 (2)	9 (2)
C2	51 (3)	36 (2)	30 (2)	17 (2)	1 (2)	−12 (2)
C3	27 (2)	42 (3)	48 (3)	10 (2)	23 (2)	10 (2)
C4	23 (2)	53 (3)	56 (3)	9 (2)	−9 (2)	−8 (2)
C5	44 (3)	54 (3)	28 (2)	28 (3)	6 (2)	16 (2)
C6	49 (3)	25 (2)	43 (3)	19 (2)	13 (3)	6 (2)
C7	18 (2)	32 (2)	28 (2)	−3 (2)	−3 (2)	−3 (2)
C8	34 (3)	43 (3)	15 (2)	−5 (2)	−5 (2)	−2 (2)
B1	23 (2)	20 (2)	17 (2)	0 (2)	−1 (2)	2 (2)
F1	50 (3)	59 (4)	51 (3)	−5 (3)	15 (3)	18 (3)
F2	84 (5)	29 (3)	46 (3)	0 (3)	−7 (3)	−8 (2)
F3	26 (3)	87 (5)	63 (4)	22 (3)	−9 (3)	−12 (4)
F4	58 (3)	57 (3)	18 (2)	−24 (3)	−9 (2)	3 (2)
H1	59 (6)	37 (5)	134 (11)	−7 (5)	28 (7)	5 (7)
H2	148 (13)	82 (8)	39 (5)	15 (9)	−31 (7)	−23 (5)
H3	87 (9)	65 (7)	120 (11)	28 (7)	63 (9)	37 (7)
H4	40 (6)	122 (11)	115 (11)	−12 (7)	−27 (7)	−25 (9)
H5	119 (11)	101 (10)	39 (5)	71 (9)	22 (6)	30 (6)
H6A	83 (8)	68 (6)	48 (6)	29 (6)	11 (6)	15 (5)
H6B	75 (7)	57 (6)	58 (6)	26 (6)	22 (6)	8 (5)
H6C	86 (8)	27 (4)	90 (7)	−5 (6)	21 (7)	−8 (5)
H7A	46 (5)	74 (7)	38 (5)	−14 (5)	16 (4)	−8 (5)
H7B	57 (6)	34 (5)	78 (7)	0 (5)	10 (5)	6 (5)
H7C	43 (5)	69 (6)	29 (4)	−10 (5)	−7 (4)	−6 (4)
H8A	57 (6)	80 (7)	24 (4)	−1 (5)	3 (5)	−8 (4)
H8B	65 (6)	63 (7)	36 (5)	10 (5)	−7 (5)	15 (5)
H8C	49 (6)	89 (8)	48 (6)	−28 (6)	−14 (5)	−16 (6)
H1Ir	82 (7)	32 (4)	52 (5)	14 (5)	16 (5)	14 (4)
H2Ir	42 (5)	76 (6)	24 (3)	15 (5)	−2 (3)	2 (4)
H3Ir	55 (6)	36 (5)	71 (6)	−8 (5)	12 (5)	−17 (4)

[a] Thermal parameters are of the form $e^{-2\pi^2}((ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12} + ..))$.

region at −13.8 and −12.4 ppm in the ratio 2:1. The linewidths are ca. 19 Hz. At ambient temperature, a single resonance at −13.2 ppm was observed ($\nu_{1/2} = 9$ Hz).

The rate of deuterium relaxation in **21**-d_3 was investigated by the inversion recovery (180–τ–90 pulse sequence) method. Due to the low sensitivity of deuterium NMR, S/N ratios obtainable in reasonable times are only ca. 10:1. An approximate value for the deuterium T_1 of 25 ms was obtained (193 K). A similar experiment for **27** gave a deuterium T_1 of approximately 65 ms (186 K).

^{3}H NMR Spectroscopy. Tritium was incorporated into compound **28** by stirring a CH_2Cl_2 solution at room temperature under 20 psi pressure of a Ar/T_2 (100:1) gas mixture. Total sample activity was assayed to be ca. 1 mCi. Tritium NMR spectra were obtained at 522.3 MHz on a 490-MHz instrument using a modified ^{19}F probe. Reasonable S/N values were obtained in 3–4 h (ca. 50000 scans). At 185 K, the spectrum shown in Figure 4 was obtained, which gives $J_{T_A-H_B} = 29$ Hz and $J_{T_B-H_A} = 24$ Hz. The expected value of J_{H-T} at this temperature is ca. 530 Hz.

Infrared Spectroscopy. The infrared spectra of these cationic trihydrides revealed weak-medium absorptions attributable to the stretching vibration of the Ir–H bond in the region of 2130–2170 cm^{-1}. For example, the spectra of **21** and **22** measured in CH_2Cl_2 solutions showed broad bands at 2170 cm^{-1} and 2140 and 2170 cm^{-1}, respectively. These assignments as Ir–H stretching modes were verified by deuterium substitution and the subsequent observation of Ir–D stretches. For **21**-d_3, the band at 2170 cm^{-1} was replaced by a new band at 1459 cm^{-1}. Similarly, for **22**-d_3, new bands were observed at 1538 and 1562 cm^{-1}. No bands corresponding to H–H stretching modes or Ir–H bending modes were observed. The IR spectra of **21** and **22** in the solid state (KBr disk) do not differ substantially from the spectra recorded in solution.

Solid-State Structure of 21. Positional and equivalent isotropic thermal parameters for all atoms are given in Table V. Anisotropic thermal parameters are given in Table VII. A view of the

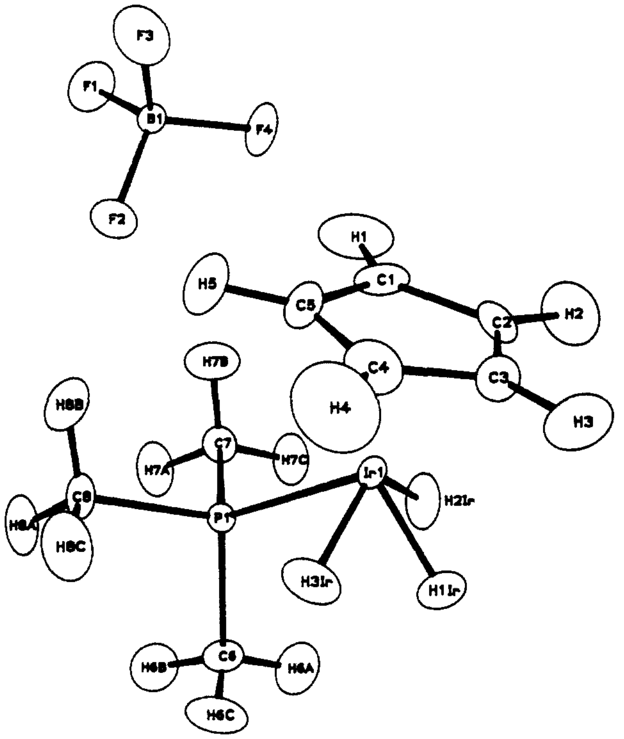


Figure 5. ORTEP diagram of **21** with boundary ellipsoids drawn to enclose 35% probability.

structure of **21** is shown in Figure 5. Selected interatomic distances are listed in Table VI. Other bond distances and angles lie within normal ranges. There are no unusual intermolecular contacts, the closest approaches being H···F, 2.24 Å, and H···H, 2.40 Å.

Reactivity of the Cations. In addition to the facile exchange reaction with D_2 noted above, our preliminary investigation of the reactivity of the trihydride cations has included reaction with CO, which was undertaken in order to obtain some insight into the electronic effects of various ligands. Thus, **22**, **28**, and **29** were exposed to CO (3 atm), leading to incorporation of CO according to eq 5.

$$[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4 + CO \rightarrow [(\eta\text{-}C_5H_5)Ir(L)(CO)H]BF_4 + H_2 \quad (5)$$

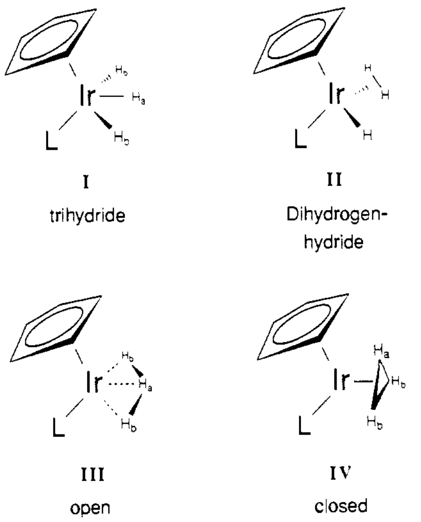
$$(L = PPh_3, AsPh_3, SbPh_3)$$

No reaction was observed with **22** and ethylene (3 atm) over several days at ambient temperature.

Discussion

Structural Models. The overall composition of the cationic "trihydride" complexes is unequivocally established by our observations. The details of the bonding and in particular the extent of H–H interactions among the hydride ligands remain to be fully elucidated. There are four possible structures for these complexes, which are depicted in Chart I. These structures are described as (I) trihydride, (II) dihydrogen/hydride, (III) open trihydrogen complex, and (IV) closed trihydrogen complex. The latter two may be regarded as $Ir(I)H_3^+$ complexes or as H_3^- complexes of Ir(III), depending upon the extent of back-donation from the trihydrogen ligand to the metal. We will now summarize the available data that bears on the structural problem and attempt to draw some conclusions.

Chart I



The most striking feature of the ^1H NMR spectra of **21–30** is the large J_{A-B} values derived from the AB_2 spectra observed at low temperature. The magnitude of J_{A-B} appears to be inversely related to the basicity of the ligand L, as defined by Tolman.[41] As detailed in Table III, the coupling is quite large for $L = PR_3$ (R = alkyl) and increases as alkyl groups are replaced with phenyl groups. Extremely large couplings are observed for phosphite ligands (up to 1565 Hz!) and for $AsPh_3$. Within the series $L = MPh_3$, (M = P, As, Sb) the coupling increases in going from P to As and then decreases abruptly in the antimony derivative. Since there are no Tolman basicity data available for the latter two ligands, we sought to evaluate the electronic environment at the metal center in these complexes by preparing the carbonyl derivatives $[(\eta\text{-}C_5H_5)Ir(L)(CO)H_3]BF_4$. To the extent that the carbonyl stretching frequencies are a reliable qualitative measure of electron density at the metal center, the observed stretching frequencies ($L = PPh_3$, 2057 cm^{-1}; $L = AsPh_3$, 2058 cm^{-1}; $L = SbPh_3$, 2051 cm^{-1}) are consistent with the observed J values being determined primarily by electronic factors. Consistent with these trends is the previously reported complex $[(\eta\text{-}C_5Me_5)Ir(PMe_3)H_3]BF_4$, which exhibits an AB_2 spectrum at low temperature with $J_{A-B} = 56.3$ Hz.[42]

In all compounds studied to date (**21–29**), the J_{A-B} values derived by simulation of the AB_2 spin system show a pronounced temperature dependence (see Table III). In every case, J increases rapidly with increasing temperature. Only a narrow temperature range is accessible, since the onset of thermally activated site exchange causes line broadening above about 200 K, but the increase in J over a small temperature range is quite remarkable. Similar temperature-dependent J values have been reported for compounds such as $[NbH_3(\eta\text{-}C_5H_{5-n}R_n)_2]$ ($n = 1, 2$; $R = SiMe_3$),[12] where J_{A-B} varies from 0 to 90 Hz between 200 and 320 K, and in $(\eta\text{-}C_5Me_5)Ru(PR_3)H_3$,[10] where J_{A-B} varies from 60 to 130 Hz between 170 and 200 K. In general, the J values found for the cationic complexes reported here are larger than values previously reported for these neutral niobium and ruthenium complexes. This may be further evidence that J is inversely proportional to the electron density at the metal center, although such comparisons must be made with caution.

The large J values seem inconsistent with structure I and are perhaps suggestive of a structure with direct bonding interactions among the hydride ligands. With the above data in hand, structure type II (dihydrogen/hydride) can probably be ruled out. In other known complexes having this structure, *no* coupling between the coordinated H_2 ligand and the hydride has been observed.[6] A slightly different view of structure type II results if a process of rapid motion of H_A between the two H_B sites is postulated as shown, which could lead to a large coupling constant J_{A-B}. Since H_2 complexes have J_{H-D} of up to 35 Hz, J_{H-H} of up to ca. 230

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Hz is possible.[4] It is hard to imagine that the model considered here could lead to J_{A-B} of more than ca. 120 Hz, which is approximately half the maximum J_{H-H} for a dihydrogen complex, since J_{A-B} would be the weighted average of a large coupling and a near-zero coupling. Our observed values for J_{A-B} greatly exceed this expectation, in some cases by more than an order of magnitude.

The preparation of complex **30**, with L = P(H)(*n*-decyl)(Ph), was undertaken with the intent of distinguishing between structures III and IV. The precursor neutral dihydride **20** exhibits an AB spin system in the hydride region of the $^1H\{^{31}P\}$ NMR spectrum, with a normal J_{A-B} of 6.9 Hz. Protonation of **20** affords **30**, which gives an ABC spin system in the $^1H\{^{31}P\}$ NMR spectrum (see Figure 2). At 176 K, the coupling constants are J_{A-B} = 281 Hz, J_{A-C} = 268 Hz, and J_{B-C} = 3.4 Hz. The values of J_{B-C} are temperature independent, in contrast to J_{A-B} and J_{A-C}, which increase rapidly with temperature. These observations are consistent with structure III, the "open" trihydrogen complex, which has been predicted by Burdett and co-workers[7] to be more stable than structure IV ("closed" trihydrogen) in the case of the hypothetical complex $Cr(CO)_5(H_3)^+$.

The coupling between the hydride ligands and the bound ^{31}P of the phosphorus-containing ligands provides evidence for the overall geometry of these trihydrides. In all compounds reported, J_{H_A-P} is less than J_{H_B-P}. These data are consistent with a cyclopentadienyl capped square pyramidal geometry in which H_A is transoid to PR_3 and the two hydrides designated H_B are cisoid to PR_3. For example, molybdenum complexes $(\eta\text{-}C_5H_5)Mo(CO)_2(PR_3)(H)$ exhibit $^2J_{P-H}$ of 64–73 Hz when the phosphine and hydride ligands are cisoid and $^5J_{P-H}$ of 21–29 Hz when the phosphine and hydride ligands are transoid.[43] Similar observations have also been reported by Gladysz and co-workers for *cis*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)_2]BF_4$.[44]

As mentioned above, the ^1H NMR spectra of partially deuterated **21** gave no resolvable H–D coupling at any temperature. The H–D coupling anticipated at low temperature (193 K) would be ca. 19 Hz. Recalling that the ^2D T_1 for **21** is approximately 25 ms at this temperature, computer simulation of the ^1H line shape[19] shows that the rapid relaxation of the D nucleus would lead to a broadened triplet in which the outer lines are half as intense as the inner lines. If the T_1 value is taken to be 12.5 ms, a single line with $\nu_{1/2}$ = 19 Hz results in the ^1H spectrum. Due to the uncertainty in the ^2D T_1 measurements, the failure to observe J_{H-D} in **21** is suggestive but not conclusive evidence for lack of H–D coupling. For compound **27**, the situation is quite different. Due to the extremely large H–H coupling in this complex, the anticipated H–D coupling at 186 K is 196 Hz. This coupling should be resolvable in the ^1H NMR of the partially deuterated species. Contrary to our expectations, this was not the case. Resonances in the low-temperature ^1H NMR spectra of partially deuterated **27** show no resolvable coupling to deuterium. This failure to observe H–D coupling is inconsistent with the observation of large H–H couplings, if normal coupling mechanisms are operative.

Although no H–D couplings were observed in partially deuterated **21**, **22**, or **27**, large (up to 78 ppb per D substitution) upfield isotope effects were observed, which allowed the various isotopomers to be clearly distinguished in the ^1H NMR spectrum at low temperature. These isotope effects on the chemical shifts show no significant temperature dependence. A tabulation of the shifts observed in the various isotopomers of **22** was given above in Figure 3. Similar shifts were observed for partially deuterated **21** and **27**. The magnitude and direction of these isotope shifts are comparable to those observed in dihydrogen complexes (37 ppb;[45] 30 ppb[46]) and for free dihydrogen (36 ppb[47]). The isotope effects observed here are *asymmetric*, for example, in **22** the isotope shift of the H_A resonance induced by successive replacement of H_B with D is 75–78 ppb per D substitution, while the effect on the H_B resonance of substitution at H_A with D is only 35 ppb. Importantly, substitution of one of the equivalent B sites with D shifts the position of the H_B resonance upfield by only 5 ppb. These observations may be consistent with structure III, in which there is no direct bonding interaction between the two B nuclei. These arguments assume that there is some correlation between the magnitude of the isotope effect on the chemical shift and the degree of bonding interaction between the hydride ligands. It follows that in a metal polyhydride complex where there is clearly no such interaction that the isotope shift would be small. This supposition seems reasonable, but lacks experimental support. The only data that bear on this problem is for $[(\eta\text{-}C_5H_5)Ru(dmpe)(H)(D)]BF_4$, which shows an upfield isotope shift of only 8 ppb,[48] while the closely related $(\eta\text{-}C_5H_5)Ru(PPh_3)H_3$ exhibits upfield isotope shifts of 23 ppb per D substitution.[49] In the absence of a more extensive set of observations regarding isotope effects on chemical shifts in metal hydrides, it is probably premature to make any conclusions regarding structure based on these data.

Examination of the ^1H NMR spectra of partially deuterated **21**, **22**, and **27** at low temperature also reveals that the coupling constant in the isotopomer $H_AH_BD_B$ (an AB spin system) is significantly increased (by ca. 6%) from the value derived from the corresponding AB_2 spectrum of the perprotio species. A secondary isotope effect on a coupling constant of this magnitude is unprecedented. Normal secondary isotope effects on coupling constants are much smaller, with a maximum of ca. 1.5%.[50] These observations were made on the various isotopomers in a single partially deuterated sample, so temperature effects cannot be responsible for this perturbation of the coupling constant. Within the limits of experimental error, the perturbation of the coupling constant is temperature independent. If this effect is a manifestation of isotopic perturbation of *J*, analogous to the well-known isotopic perturbation of resonance (IPR) phenomenon,[51] this would indicate that some rapid equilibrium process is operational, which is perturbed by partial deuteration. Under this reasoning, the isotope shifts discussed above would be manifestations of IPR, rather than intrinsic isotope effects. However, the observed shifts and perturbations are *temperature independent*, which is not consistent with perturbation of an equilibrium.

The above observations are most consistent with structure III, but there are several problems with this explanation. The observed J_{A-B} values actually exceed in some cases the H–H coupling constant of 280 Hz in hydrogen itself (calculated from J_{H-D} = 43.2 Hz[14] or J_{H-T} = 299.3 Hz[15]), which should be the largest such value possible by the normal Fermi contact mechanism.[52] The pronounced temperature dependence of J_{A-B} could be rationalized in terms of a temperature-dependent equilibrium between two structures in solution, perhaps structure III (large *J*) and structure I (small *J*), with structure I thermodynamically favored. This explanation requires even larger limiting values for J_{A-B}.

Attempts to obtain further structural information from infrared spectroscopy were inconclusive. In the case of **21** and **22**, the infrared spectrum in CH_2Cl_2 solution clearly shows the Ir–H stretching band. Attempts to identify H–H stretching modes by using difference methods with **21**-d_3 and **21** were not successful. This result is inconclusive, since such vibrational modes are generally weak or unobserved in the IR spectra of dihydrogen complexes.[4] Similar results were obtained for **22**. The infrared

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spectra obtained for **21** and **22** in the solid state (KBr disk) were in general very similar to the solution spectra. On the assumption that the solid-state structure of a representative compound may help in identifying the solution structure, we have carried out a neutron diffraction study of **21**.

Solid-State Structure of 21. The structure of **21** in the solid state has been determined by neutron diffraction (see Figure 5). The structure is best described as a distorted capped square pyramid, with the cyclopentadienyl group capping. The hydride ligands can be envisaged as occupying three corners of the base of the square pyramid. The mean Ir–H distance, 1.587 (3) Å, is at the lower end of the range, 1.586 (3)–1.627 (4) Å, of reported terminal Ir–H distances determined by neutron diffraction.[53-56] The H–H distances between the hydride ligands are 1.674 (14), 1.698 (13), and 2.665 (13) Å. In terms of the labeling used to describe the solution NMR spectra, the first two correspond to the distances between the unique hydrogen H_A and the equivalent H_B nuclei. The latter distance is the separation between the equivalent H_B hydrogens. While the former H–H distances are certainly not short enough to be described as bonding interactions, they are perhaps best described as close nonbonding contacts. There is only one example of a polyhydride with shorter H–H contacts, which is $OsH_6(P(iPr)_2Ph)_2$,[57] where the shortest H–H distance is 1.650 (6) Å. Other polyhydrides with relatively short H–H distances are $ReH_7(dppe)$, 1.77 Å;[58] K_2ReH_9, 1.872 (16) Å;[59] $OsH_4(PMe_2Ph)_3$, 1.840 (6) Å;[60] and $(\eta\text{-}C_5H_5)_2TaH_3$, 1.846 (9) Å.[61]

While $(\eta\text{-}C_5H_5)_2TaH_3$ does not show anomalous NMR properties, closely related niobium derivatives exhibit AB_2 spin systems in their ^1H NMR spectra, with large temperature-dependent values of J_{A-B}.[12] While the above bond distance data are entirely from neutron diffraction, which is the most accurate method for locating metal hydrides, it should be pointed out that an X-ray diffraction study of $(\eta\text{-}C_5Me_5)Ru(PPh_3)H_3$ has been reported,[62] which shows a structure qualitatively very similar to that of **21**. Approximate H–H distances as short as ca. 1.6 Å can be calculated from the Ru–H distances of 1.46–1.60 Å and the H–Ru–H angles of 61–65° reported for this ruthenium trihydride. Interestingly, ruthenium trihydrides of this general formula have also been shown to exhibit anomalous NMR properties, with the aforementioned large, temperature-dependent values of J_{A-B}.[10] This indicates that these exceptional couplings may only occur in cases where H–H separations are relatively short.

As noted above, the observations discussed to date are anomalous in several respects. While the solid-state structure of **21** (and presumably the other cations as well) is of type I, the large J_{A-B} values and other observations in solution seem more consistent with structure type III. Implicit in the above discussion of structural models has been the assumption that the couplings are mediated by the normal Fermi contact mechanism.[52] The sheer magnitude of the couplings and the pronounced temperature dependence are difficult to reconcile with this assumption. In addition, the failure to observe H–D coupling in **27** is not consistent with this assumption and the magnitude of the secondary (deuterium) isotope effect on the coupling is unprecedented. We outline below an alternative interpretation, which invokes quantum mechanical exchange of two hydrogen atoms. This coherent exchange process gives rise to an exchange coupling, which can be of appropriate magnitude to explain many of our observations.

Exchange Coupling. In order to obtain further information on the effects of isotopic substitution on the couplings, tritium substitution was undertaken. Analysis by ^3H NMR is straightforward, with incorporation at a low enough level (1 mCi) to pose an insignificant radiation hazard. Under these conditions, the only isotopomer (other than the perprotio species) present in significant amounts has the composition TH_2. Compound **28** (L = $AsPh_3$) was chosen for the initial study since the absence of coupling to ^{31}P simplifies the problem. Recalling that the J_{A-B} value for **28** at 185 K is 500 Hz, a value of ca. 530 Hz would be anticipated for J_{H-T} in this compound at 185 K ($\gamma_T/\gamma_H = 1.06$). The observed ^3H NMR spectrum is shown in Figure 4. The observed H–T coupling constants are $J_{T_A-H_B} = 29$ Hz and $J_{T_B-H_A} = 24$ Hz. This observation demonstrates that there is an isotope effect on the observed coupling of approximately a factor of 20 on replacing H by T in this compound.

These observations can only be interpreted if the large J_{H-H} couplings observed in **21**–**30** are not magnetic in origin but are in fact exchange couplings.[16,17] In both NMR and ESR spectroscopy it is well-known that quantum mechanical tunneling[63-66] and exchange interactions[16,17] lead to spectral features with no classical analogues. Exchange couplings are well established in ESR spectroscopy.[16] 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 ^3He nuclei. In the case of these metal trihydride complexes, the process in question can be envisaged as a *coherent* pairwise exchange of two hydrogen atoms. This process is distinct from the thermally activated A/B exchange process, which occurs at higher temperatures, leading to line broadening in the ^1H NMR. The effect of the exchange interaction is to add a pseudomagnetic 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 (eq 6). The observed coupling J is given by $J = -2\mathbf{J} + J_m$, where J_m is the normal magnetic coupling.

$$2\mathbf{J} = E_S - E_A = \langle\Psi_S(1,2)|\mathcal{H}(1,2)|\Psi_S(1,2)\rangle - \langle\Psi_A(1,2)|\mathcal{H}(1,2)|\Psi_A(1,2)\rangle \quad (6)$$

Where $\mathcal{H}(1,2)$ is given by eq 7:

$$\mathcal{H}(1,2) = -\hbar^2/2m(\nabla_1{}^2 + \nabla_2{}^2) + V(1) + V(2) + v(1,2) \quad (7)$$

In eq 7, $V(1)$ and $V(2)$ are single-particle potentials and $v(1,2)$ is the pairwise potential between the particles.

While exchange couplings involving electrons are well-known in ESR spectroscopy, there is no precedent for such effects involving massive particles such as hydrogen atoms in solution NMR. In solid ^3He, the NMR spectrum is dominated by nuclear exchange couplings, which can be as large as 10 MHz. The magnitude of this coupling is a very sensitive function of the amplitude of the ^3He lattice vibrations, as shown by the fact that J varies from 10^{-2} to 10 MHz, over the molar volume range of 17–24 cm^3.

In the case of metal polyhydrides, as in the case of ^3He, this coupling mechanism requires that the particles involved be undergoing a large amplitude motion, in this case perhaps best visualized as a M–H bending or wag mode. In metal hydrides,[4] such bending modes usually have frequencies of 700–900 cm^{-1}, while in metal dihydrogen complexes,[4] such modes are found at 400–650 cm^{-1}. In spite of a careful search, we were unable to locate such vibrational modes in the IR spectra of our compounds.

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In an attempt to estimate the size of the couplings, the model of Landesman for ^{3}He exchange couplings has been applied, with parameters suitable for a pair of protons. In this model, which assumes a hard-spheres potential, **J** is given by eq 8:

$$\mathbf{J} \cong -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/2}\frac{\hbar}{m}\left(\frac{a}{\delta^3}\right)\exp\left\{-\frac{3}{4}\frac{a^2+\lambda^2}{\delta^2}\right\} \qquad (8)$$

The amplitude of the vibrational motion is given by δ, a is the internuclear distance, m is the proton mass, and λ is the range of the interaction potential between the two protons. The internuclear distance is known from the neutron data to be ca. 1.68 Å. Assuming that λ is on the order of 1 Å,[67] we need only ascertain the amplitude of the vibrational motion δ in order to estimate **J**. As noted above, we were unable to observe such a vibrational mode in the infrared spectra of the cations. In a simple harmonic oscillator approximation, the zero point motion amplitude δ for a reasonable vibration frequency of 450 cm^{-1} is 0.334 Å. For comparison, the neutron diffraction study of **21** gives amplitudes of 0.377–0.407 Å, from the hydride U_{ii} values in Table VII. These values are quite reasonable in the light of the vibrational amplitudes of 0.35–0.40 Å at room temperature reported by Ginsberg[59] for the hydrides in K_2ReH_9. With these values, eq 8 gives **J** = 230 Hz. Clearly **J** will be a very sensitive function of both the internuclear distance a and the vibrational amplitude δ. If a is increased to the B–B separation of 2.6 Å, **J** decreases by a factor of 10^{11}. A decrease in δ to 0.30 Å (consistent with a frequency of 550 cm^{-1}) will decrease **J** to 2 Hz.

This interpretation may also explain the isotopic perturbation of coupling that was noted above. In **22**-d_1 the position isomer $H_AH_BD_B$ exhibits J_{A-B} values ca. 6% greater than the perprotio isomer. This perturbation presumably arises from a subtle isotope effect on the vibrational potential, leading perhaps to a *very* slight increase in δ or a corresponding decrease in a. Presumably similar changes to the vibrational potential are responsible for the observed dependence of J_{A-B} on the nature of the ligand L. The more effective donor ligands (trialkyl phosphines) may lead to slightly stronger and therefore "stiffer" Ir–H bonds.

The above is a very approximate explanation of the factors that will affect the magnitude of the exchange coupling. A more detailed exposition of the theory involved is given in the following paper in this issue.[68]

Conclusions. The solid-state structure of $[(\eta\text{-}C_5H_5)Ir(PMe_3)H_3]BF_4$ (**21**) has been determined by neutron diffraction. While the H–H distances between the hydride ligands are somewhat short, the structural data provide no evidence for bonding interactions and the structure of **21** is best described as a normal trihydride. Compound **21** is representative of a class of cationic trihydride complexes that exhibit large H–H couplings. The couplings are temperature dependent and exhibit quite remarkable primary and secondary isotope effects, which have been explored by deuterium and tritium substitution. The origin of these large couplings and their temperature dependence has been explained in terms of quantum mechanical exchange processes, which apparently require large amplitude motions of the hydride ligands. The coherent exchange process is very sensitive to the vibrational potential experienced by the hydride ligands. The large secondary isotope effects are manifestations of small perturbations to the vibrational potential surface. The lack of observable J_{H-D} in partially deuterated species is now understandable, since the magnetic coupling J_m between hydride ligands in these complexes is quite small.

While the solid-state structure of **21** is a normal trihydride, the solution structure may differ in the extent of H–H interactions, and other structures may be thermally accessible. In particular, it should be noted that the chemical reactivity of the cationic trihydride complexes is consistent with the thermal accessibility of a dihydrogen/hydride structure.

We are continuing studies directed toward the preparation and structural characterization of other polyhydride complexes that may exhibit this novel coupling mechanism. In particular, we note the intriguing possibility that polyhydrides previously thought to be highly fluxional due to facile thermally activated exchange[69] may be further examples of this phenomenon, with *extremely large* exchange couplings. Such a large exchange coupling in effect wipes out any chemical shift differences between chemically distinct hydrides, leading to a single resonance in the ^{1}H NMR for the case of an AB spin system. Such situations will be revealed by appropriate isotope labeling experiments.

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Supplementary Material Available: Listings of complete bond distances and angles for **21** and analytical and spectroscopic data for **1–10** (3 pages); observed and calculated squared structure factors for **21** (9 pages). Ordering information is given on any current masthead page.

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