was orange with some copper plating the walls of the vial. ^{1}H NMR analysis showed $[(Ph_3P)CuH]_6$, 4-phenyl-2-butanol, and both cyclohexanol and cyclohexanone (86:14).

B. With Added Phosphine. General procedure B was used with a reaction pressure of 1500 psi for 48 h. 4-Phenyl-3-buten-2-ol (42 mg, 0.28 mmol) was added prior to solvent. ^{1}H NMR analysis of the resulting bright red homogeneous solution showed $[(Ph_3P)CuH]_6$, 4-phenyl-3-buten-2-ol, and cyclohexanol.

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Supplementary Material Available: High-field (500-MHz) ^{1}H NMR spectral data for the reduced products (2 pages). Ordering information is given on any current masthead page.

Single-Crystal X-ray and Neutron Diffraction Studies of an η^2-Dihydrogen Transition-Metal Complex: *trans*-$[Fe(\eta^2\text{-}H_2)(H)(PPh_2CH_2CH_2PPh_2)_2]BPh_4$

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Abstract: The H–H distance in the η^2-H_2 ligand in $[Fe(\eta^2\text{-}H_2)H(dppe)_2]BPh_4$, **1**-$BPh_4$, dppe = $PPh_2CH_2CH_2PPh_2$, is 0.816 (16) Å as determined by neutron diffraction on a crystal of volume 2.62 mm^3 at 20 K: 1-BPh_4 is monoclinic, space group $C2/c$, a = 16.999 (7) Å, b = 16.171 (2) Å, c = 22.114 (5) Å, β = 102.52 (2)°, U = 5934.4 (2) Å^3, and D_c = 1.315 g cm^{-3} for Z = 4; $R(F)$ = 0.071, $R(F^2)$ = 0.110, $R_w(F^2)$ = 0.113 for 4116 reflections with $I \geq 3\sigma(I)$. The H–H separation is 0.87 (3) Å as determined by X-ray diffraction at 298 K: monoclinic, $C2/c$, a = 17.327 (3) Å, b = 16.407 (4) Å, c = 22.224 (3) Å, β = 102.87 (1)°, U = 6159.2 (1) Å^3, and D_c = 1.267 g cm^{-3} for Z = 4; $R(F)$ = 0.038, $R_w(F)$ = 0.034, for 3673 reflections ($I \geq 3\sigma(I)$). These η^2-H_2 distances agree with the X-ray value of 0.89 (11) Å reported for the tetrafluoroborate salt, **1**-BF_4. As was found for **1**-BF_4, **1**-BPh_4 contains an η^2-H_2 ligand that is symmetrically side-on bonded to the iron and trans to the terminal hydride such that the Fe has a distorted octahedral configuration. These diffraction studies serve to calibrate H–H distances obtained by the T_1 NMR method for dihydrogen complexes in solution where the H_2 ligand is suggested to be rapidly spinning. The H–H distance is the same as that in $W(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ despite the fact that the tungsten complex has a more labile H_2 ligand. The terminal hydride–iron distance of 1.535 (12) Å as determined by neutron diffraction is shorter than the distances to the dihydrogen ligand (H–Fe = 1.616 (10) Å). This is the first experimental demonstration of this expected difference in metal bonding to hydride and H_2. There is no disorder of ligands apparent in the structure at 20 K.

Neutron diffraction studies have played a crucial role in the characterization of polyhydride complexes in the solid state.[2] Of some 30 structures examined, none had revealed a short H–H distance attributable to H–H bonding until the η^2-dihydrogen complexes $M(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$, M = Mo, W, were reported in 1984.[3] The H–H bond length in the tungsten complex is 0.82 (1) Å. In 1985, the Morris group reported the preparation and characterization of the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(dppe)_2]$-$BF_4$, M = Fe, Ru.[4] The Fe complex displayed properties that were somewhat different from those reported for the Mo and W complexes, including a lower lability of H_2 with respect to exchange with hydrogen gas, deprotonation of H_2 by strong bases, intramolecular exchange of H atoms between dihydrogen and hydride ligands, a slightly smaller ^1J(H,D) coupling constant in the η^2-HD complex (32[5] versus 34 Hz), and a longer minimum T_1 value for the H_2 ligand (8.5 ± 1.0 ms at 200 MHz for (H_2)Fe and ≤ 4 ms at 250 MHz for (H_2)W).[4,5] The H–H distance from X-ray diffraction of 0.89 (11) Å is not precise enough to say whether the bond is longer than that in the above W complex, as might have been expected judging by some of these properties. An NMR method for determining H–H distances in polyhydride complexes based on spin–lattice relaxation times[6] provided an ambiguous answer since the distance could be 1.09 Å if rotation of the dihydrogen group were slow compared to the tumbling of the molecule (i.e., if the dihydrogen correlation time were less than that of the terminal hydride ligand) or it could be 0.86 Å if the

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rotation were sufficiently rapid.[7] The present work provides some answers to these questions and adds one well-characterized dihydrogen complex (without ligand disorder) to the short list of such complexes for which neutron diffraction studies have been undertaken $\{W(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$,[3,8] $Fe(\eta^2\text{-}H_2)(H)_2(PEtPh_2)_3$[9]$\}$. It also provides the first comparison between metal to terminal hydride and metal to dihydrogen distances in the same molecule.

Experimental Section

Preparation of $[Fe(\eta^2\text{-}H_2)(H)(PPh_2CH_2CH_2PPh_2)_2]BF_4$, 1-$BF_4$. Tetrafluoroboric acid etherate (66 μL, 0.50 mmol) was added dropwise to a filtered solution of $FeH_2(dppe)_2{\cdot}2C_7H_8$ (320 mg, 0.31 mmol)[10] in 20 mL of tetrahydrofuran (THF). Light-yellow microcrystals formed over 1 h; this mixture was reduced in volume under vacuum to 10 mL, cooled to −10 °C for 2 h, and then filtered to yield 1-BF_4 (278 mg, 80%). If 40 mL of THF were used instead and the mixture cooled to −10 °C, cubic-shaped crystals suitable for X-ray analysis formed over 12 h. The crystal structure of 1-BF_4 was reported previously.[4] Recrystallization attempts from THF, CH_2Cl_2/ether, or acetone failed to yield crystals suitable for neutron diffraction.

Preparation of $[Fe(\eta^2\text{-}H_2)(H)(PPh_2CH_2CH_2PPh_2)_2]BPh_4$, 1-$BPh_4$. $NaBPh_4$ (27 mg, 0.08 mmol) was placed at the bottom of a long 10-mm tube inside an argon-filled glovebox. A solution of 1-BF_4 (30 mg, 0.03 mmol) in 2 mL of CH_2Cl_2 was filtered into the tube, and then 5 mL of methanol was carefully added as a layer above the CH_2Cl_2 solution. Slow diffusion at 20 °C produced large crystals after 1–3 days.

X-ray Diffraction. This study of 1-BPh_4 was carried out in order to establish the absence of disorder and the suitability of the structure prior to undertaking neutron diffraction measurements. Large, well-formed canary-yellow block-shaped crystals of 1-BPh_4 were cut to size and sealed in Lindemann capillaries in a glovebag under dry argon with the aid of a microscope. All further work was performed on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell dimensions, space group, and intensity measurements were obtained with the options specified in Table I. Lorentz and polarization corrections were applied to all data measured. Absorption corrections were considered unnecessary (μ = 3.9 cm^{-1}).

The structure was solved by use of the Patterson function to locate the Fe atom. Subsequent cycles of least-squares and Fourier calculations then located all remaining non-hydrogen atoms. Hydrogen atoms on the phenyl and CH_2 groups were readily apparent in ΔF maps but were placed in calculated positions with common isotropic thermal parameters. Refinement of this model in two large blocks (all non-H atoms anisotropic) converged to $R[wR]$ = 0.045 [0.045]. The two highest remaining peaks in weighted [or unweighted] ΔF maps, of heights 0.42 and 0.38 e $Å^{-3}$, were both on the crystallographic 2-fold axis passing through Fe at distances of 1.63 and 1.25 Å from Fe. Least-squares refinement of a model with hydrogens placed at both sites and constrained to the 2-fold axis converged with the two atoms 1.71 and 1.45 Å from Fe with B values of 5 (1) $Å^2$ [H(1)] and 3 (1) $Å^2$ [H(2)], respectively. Since either site was a candidate for the location of the H_2 atoms, a test least-squares calculation was conducted before the final refinement cycles were attempted, where each position was displaced slightly off the 2-fold axis; this gave the following results:

	x	y	z	B, $Å^2$	Fe-H	H-H
H(1)	0.0207 (36)	0.2972 (22)	0.2448 (30)	10 (1)	1.52	0.80
H(2)	0.0195 (25)	0.1079 (18)	0.2638 (19)	12 (2)	1.71	0.93

Similar results were obtained if either H(1) or H(2) was displaced, and the highest remaining peak in the Sim weighted difference Fourier map in the vicinity of the cation was of height 0.12 e $Å^{-3}$. With the results of the neutron structure available, it does appear that H(2) corresponds to the dihydrogen ligand and H(1) to the hydride on the 2-fold axis and that the final temperature factor for H(2) is greater than that of H(1). Further refinements allowed the CH_2 and CH hydrogens to vary from their calculated positions. Least-squares refinement of this model in three large blocks [$\sum w(F_o - k|F_c|)^2$ minimized, all non-hydrogen atoms anisotropic] converged (maximum Δ/σ = 0.083) to the residuals indicated in Table I. A Sim weighted difference Fourier in the region of the cation showed a maximum peak of height 0.13 e $Å^{-3}$, which was at a location 1.1 Å from Fe. Scattering factors were taken from *International Tables for X-ray Crystallography*.[11] The programs used include the Enraf-Nonius SDP package and SHELX76 and ORTEP on PDP 11/23 and Gould 9705 computers.[12]

Table I. Crystal Data and Details of the Intensity Measurements and Structure Refinements for *trans*-$[Fe(\eta^2\text{-}H_2)(H)(PPh_2CH_2CH_2PPh_2)_2]BPh_4$

	X-ray	neutron
crystal system	monoclinic	monoclinic
cell dimensions		
a, Å	17.327 (3)	16.999 (7)
b, Å	16.407 (4)	16.171 (2)
c, Å	22.224 (3)	22.114 (5)
β, deg	102.87 (1)	102.52 (2)
U, $Å^3$	6159.2 (1)	5934.4 (2)
T, K	298	20.0 (5)
fw	1174.9	1174.9
Z/d_{calc}, g cm^{-3}	4/1.267	4/1.315
space group	*C*2/*c*	*C*2/*c*
μ, cm^{-1}	3.9 [Mo Kα]	2.181
reflns in cell detmn	25/22° < 2θ < 32°	16/47° < 2θ < 56°
λ, Å	0.71069	1.0459 (4)
crystal details	yellow block with irregular shape	pale-yellow prism with {001} and {110} boundary faces (8 faces in all)
crystal size, mm	0.32 × 0.36 × 0.15, in the *a*, *b*, *c* directions	1.8 × 1.7 × 0.8, volume = 2.62 mm^3
scan mode	ω:2θ	ω:2θ
scan widths, deg	Δ2θ = (1.20 ± 0.70 tan θ)	Δ2θ = 3.2° [2θ < 55°], Δ2θ = (2.53 + 1.53 tan θ) [55 ≤ 2θ ≤ 112°]
max scan time, s	65	*a*
std reflns [no./interval in s for X-ray or reflns (neutron)]	3/8000[b]	2/200[b]
backgrounds	*c*	*d*
max 2θ/octants	0 < 2θ ≤ 35°/±*h*,±*k*,±*l*; 35 < 2θ < 50°/*h*,*k*,±*l*	112°; *h*,−*k*,±*l*
no. of reflns measd	8523	12772
no. of independent reflns (*n*)	5575[e]	10157
wR_{int}	0.017[f]	0.045
no. of variable parameters	550	692
no. of data [$I \geq 3\sigma(I)$]	3673	4116
$R(F)$ [$I \geq 3\sigma(I)$]	0.038	0.071
$R_w(F)$ [$I \geq 3\sigma(I)$]	0.034	
$R(F^2)[R_w(F^2)]$[$I \geq 3\sigma(I)$]		0.110 [0.113][g,h]
goodness of fit [$I \geq 3\sigma(I)$]	1.55	1.13
weights	$[\sigma^2(F) + 0.00009F^2]^{-1}$	$[\sigma^2(F_o^2)]^{-1} = [\sigma^2_{count} + (F_o^2) + (0.015F_o^2)^2]^{-1}$

[a] The step size was adjusted to give between 65 and 90 steps per scan, and counts were accumulated for ca. 1.5 s/step, the exact time interval being determined by monitoring the incident beam intensity. [b] No significant variations in intensities of the standard reflections were observed over the course of both data collections. [c] By extending the scan by 25% on either side of the peak—measured for half the time taken to collect the peak. [d] First and last tenth of each scan taken as background. [e] 219 standards and 947 systematically absent or zero F_o data rejected. [f] 1782 symmetry equivalent reflections averaged (unit weights). [g] $R(F^2) = \sum|F_o^2 - (k^2F_c^2)|/\sum|F_o^2|$; $R_w(F^2) = [\sum w(F_o^2 - (k^2F_c^2)^2)/\sum wF_o^4]^{1/2}$. [h] $R(F)$, $R(F^2)$, and $R_w(F^2)$ for all neutron data were 0.177, 0.194, and 0.152, respectively. The goodness of fit (GOF) was 1.02. A least-squares calculation using all nonzero F_{obs} X-ray data gave $R(wR)$ = 0.0710 (0.0457) with GOF = 1.48.

Neutron Diffraction. The specimen was mounted on an aluminum pin oriented approximately along the crystallographic (1$\bar{1}$0) direction. The

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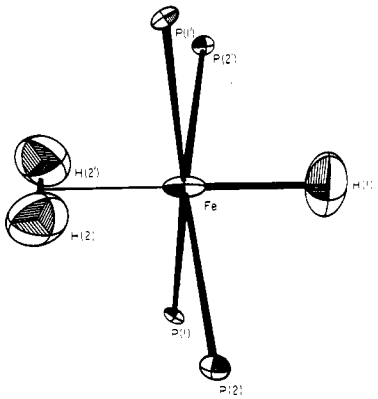

Figure 1. Octahedral coordination at iron; the ellipsoids are drawn to include 50% probability density[12c] (neutron results).

sample was sealed under a helium atmosphere in an aluminum container and placed in a closed-cycle helium refrigerator[13] mounted on a four-circle diffractometer[14,15] at the Brookhaven High Flux Beam Reactor. A beryllium (002) single-crystal monochromator was used to select a neutron beam of wavelength 1.0459 (4) Å based on KBr (a_0 = 6.6000 Å at T = 298 K).[16] The sample temperature was maintained at 20.0 (5) K[17] during the experiment, and unit cell dimensions were determined by least-squares fit of the averaged 2θ values of 16 Friedel pairs ($47° < 2\theta < 56°$).

Three-dimensional intensity data were obtained over one quadrant of reciprocal space with $2\theta \leq 112°$ by means of $\theta/2\theta$ step scans. Integrated intensities were obtained with the first and last tenth of each scan taken as background. Lorentz factors and absorption corrections (μ = 2.181 cm^{-1}, range of $e^{-\mu t}$ = 0.708–0.855) calculated by means of an analytical procedure[18] were applied, followed by averaging over the $2/m$ Laue symmetry, to yield squared structure factors, F_o^2, for 10157 unique reflections. Further details are given in Table I.

Initial coordinates for all but the iron-coordinated hydrogen atoms were taken from the X-ray results, and after a few cycles of differential synthesis refinement,[19] difference scattering density maps revealed the positions of the hydride and dihydrogen atoms. Least-squares refinements were carried out by a full-matrix procedure,[20] minimizing $\sum w(F_o^2 - (k^2F_c^2))^2$ using all unique data. The final model included positional and anisotropic thermal parameters for all 78 atoms, the scale factor k, and a parameter for an isotropic-type I extinction correction[21,22] with Lorentzian mosaic, for a total of 692 variable parameters. Extinction proved to be minimal, with no reflection affected by more than 5% in F_o^2.

Neutron scattering lengths ($\times 10^{-12}$ cm) were taken to be b_{Fe} = 0.954, b_P = 0.5130, b_C = 0.6648, b_B = 0.5350, and b_H = −0.3741.[23] The refinement was terminated when the maximum Δ/σ for positional and thermal parameters was less than 0.009. A difference map computed at this stage was essentially featureless, with the highest positive residual peak being approximately 3% the height of a carbon peak and the highest negative residual peak being approximately 8% the height of a hydrogen peak. A summary of the experimental conditions for both the X-ray and neutron experiments is included in Table I, while positional and thermal parameters for all atoms from the neutron experiment are given in Tables I and II of the supplementary material and corresponding values for the X-ray experiment are available as Table III of the supplementary material.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in the $[Fe(\eta^2\text{-}H_2)(H)(dppe)_2]^+$ Cation

		1-BPh_4	
	1-BF_4[a]	X-ray	neutron
Fe–P(1) (axial)[a]	2.247 (3), 2.243 (3)	2.2576 (6)	2.252 (3)
Fe–P(2) (equatorial)[a]	2.235 (3), 2.231 (3)	2.240 (4)	2.234 (3)
Fe–H(1)	1.28 (8)	1.30 (3)	1.535 (12)
Fe–H(2)	1.53 (8), 1.55 (8)	1.67 (2)	1.616 (10)
H(2)–H(2')[b]	0.89 (11)	0.87 (3)	0.816 (16)
P(1)–C(1)	1.838 (9), 1.837 (10)	1.831 (3)	1.845 (4)
P(1)–C(111)	1.848 (10), 1.834 (9)	1.831 (3)	1.830 (4)
P(1)–C(121)	1.829 (9), 1.828 (10)	1.832 (2)	1.826 (4)
P(2)–C(2)	1.832 (10), 1.836 (10)	1.846 (3)	1.851 (4)
P(2)–C(211)	1.844 (8), 1.842 (9)	1.829 (2)	1.831 (4)
P(2)–C(221)	1.827 (10), 1.855 (10)	1.839 (2)	1.844 (4)
C(1)–C(2)	1.523 (14), 1.521 (13)	1.512 (4)	1.533 (4)
B–C(11)		1.640 (3)	1.640 (4)
B–C(21)		1.640 (3)	1.647 (4)
C–H(methylene)$_{av}$		0.941 [37][c]	1.097 (7)[d]
C–H(phenyl)$_{av}$		0.937 [37][c]	1.089 (9)[d]
C–C(phenyl)$_{av}$		1.378 [13][c]	1.397 (5)[d]
P(1)–Fe–P(1')	178.7 (1)	172.45 (4)	172.1 (2)
P(1)–Fe–P(2)	85.3 (1), 85.2 (1)	84.40 (2)	84.4 (1)
P(1)–Fe–P(2')	93.7 (1), 96.0 (1)	96.40 (2)	96.5 (1)
P(1)–Fe–H(1)	93 (3), 87 (3)	93.77 (2)	94.0 (1)
P(1)–Fe–H(2)	85 (3), 95 (3)	87.6 (10)	87.7 (4)
P(1)–Fe–H(2')	95 (3), 85 (3)	85.1 (10)	84.7 (4)
P(2)–Fe–P(2')	163.0 (1)	167.91 (4)	166.6 (2)
P(2)–Fe–H(1)	79 (3), 84 (3)	83.95 (2)	83.3 (1)
P(2)–Fe–H(2)	112 (3), 118 (3)	111.1 (7)	111.3 (3)
P(2)–Fe–H(2')	79 (3), 85 (3)	81.0 (7)	82.1 (3)
H(1)–Fe–H(2)	158 (4), 167 (4)	164.9 (7)	165.4 (3)
H(2)–Fe–H(2')	34 (4)	30.2 (10)	29.3 (5)
P(1)–C(1)–H(11)		104.8 (14)	107.1 (4)
P(2)–C(1)–H(12)		112.7 (14)	112.6 (4)
P(1)–C(1)–C(2)	106.4 (6), 105.7 (7)	107.4 (2)	106.2 (2)
P(2)–C(2)–H(21)		107.4 (14)	109.1 (4)
P(2)–C(2)–H(22)		110.2 (14)	110.3 (4)
P(2)–C(2)–C(1)	106.5 (7), 106.8 (6)	107.9 (2)	107.6 (2)
C(2)–C(1)–H(11)		110.4 (15)	110.7 (4)
C(2)–C(1)–H(12)		110.3 (14)	112.0 (4)
H(11)–C(1)–H(12)		111.0 (22)	108.1 (5)
C(1)–C(2)–H(21)		107.6 (13)	110.4 (4)
C(1)–C(2)–H(22)		112.7 (13)	112.4 (4)
H(21)–C(2)–H(22)		110.8 (17)	107.0 (5)
Fe–P(1)–C(1)	106.7 (3), 108.1 (3)	107.37 (10)	108.0 (2)
Fe–P(1)–C(111)	117.1 (3), 117.3 (3)	114.50 (9)	113.9 (2)
Fe–P(1)–C(121)	122.0 (3), 122.2 (3)	125.46 (8)	125.5 (2)
C(1)–P(1)–C(111)	104.4 (4), 102.3 (5)	103.6 (1)	103.6 (2)
C(1)–P(1)–C(121)	99.9 (4), 99.0 (4)	102.3 (1)	102.2 (2)
C(111)–P(1)–C(121)	104.2 (4), 104.7 (4)	101.2 (1)	101.1 (2)
Fe–P(2)–C(2)	108.4 (3), 107.4 (3)	109.90 (8)	110.1 (2)
Fe–P(2)–C(211)	120.5 (3), 120.7 (3)	117.34 (7)	117.2 (2)
Fe–P(2)–C(221)	120.2 (3), 120.1 (3)	121.77 (8)	121.8 (2)
C(2)–P(2)–C(211)	100.0 (4), 101.4 (4)	103.2 (1)	102.7 (2)
C(2)–P(2)–C(221)	102.0 (5), 100.1 (4)	99.5 (1)	100.4 (2)
C(211)–P(2)–C(221)	102.5 (4), 103.8 (4)	102.3 (1)	101.9 (2)
C(11)–B(1)–C(11')		115.2 (3)	
C(11)–B(1)–C(21)		110.53 (9)	
C(11)–B(1)–C(21')		102.9 (1)	
C(21)–B(1)–C(21')		115.3 (3)	

[a] Reference 4. Coordinates for this compound are available on the Cambridge Crystallographic Database as refcode DECXOY. In comparing equivalent distances and angles in the BF_4^- salt with those in the present structure, note that the following atom correspondences have been made: P(2), P(3) ≡ $P(1)_{axial}$; P(1), P(4) ≡ $P(2)_{equatorial}$; H(1), H(2) ≡ H(2); and H(3) ≡ H(1), where the BF_4^- atom notation is given first. [b] Atoms related by the 2-fold axis are primed. [c] Root-mean-square error in square brackets. [d] Standard deviations of mean values are given as the larger of the individual esd's or $\sigma(x_{av}) = [\sum_{i=1}^{n}(x_i - x_{av})^2/n(n-1))]^{1/2}$, where x_{av} is the mean value and x_i are individual values.

Results and Discussion

The iron dihydrogen complex was prepared by protonation of the dihydride complex with $HBF_4 \cdot Et_2O$ to give 1-BF_4 (eq 1) and

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(14) McMullan, R. K.; (and, in part) Andrews, L. C.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. NEXDAS, Neutron and X-ray Data Acquisition System. Unpublished work.
(15) Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398.
(16) Donnay, J. D. H., Ondik, H. M., Eds., *Crystal Data Determinative Tables*, 3rd ed.; U.S. Department of Commerce and Joint Committee on Powder Diffraction Standards: Washington, DC, 1973; Vol. 2, p C-164.
(17) Temperature readings were calibrated with reference to a magnetic phase transition in FeF_2 at T_N = 78.38 (1) K (Hutchings, M. T.; Schulhof, M. P.; Guggenheim, H. J. *Phys. Rev. B* **1975**, *5*, 154). With an FeF_2 crystal mounted in the same fashion as the sample employed in the present study, the platinum resistance thermometer used to monitor the temperature indicated T_N = 76.1 K. Thus, 2 K was added to the recorded values.
(18) (a) DeMeulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014. (b) Templeton, L. K.; Templeton, D. H. American Crystallographic Association Meeting, Storrs, CT, Abstract E10, 1973.
(19) McMullan, R. K. DIFSYN. Unpublished work.
(20) Lundgren, J.-O. Crystallographic Computer Programs. Report UUIC-B13-4-05; Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982.
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(22) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A.* **1975**, *A31*, 417.
(23) Koester, L.; Rauch, M.; Herkens, M.; Schröder, K. K.F.A. Report Jül-1755, 1981.

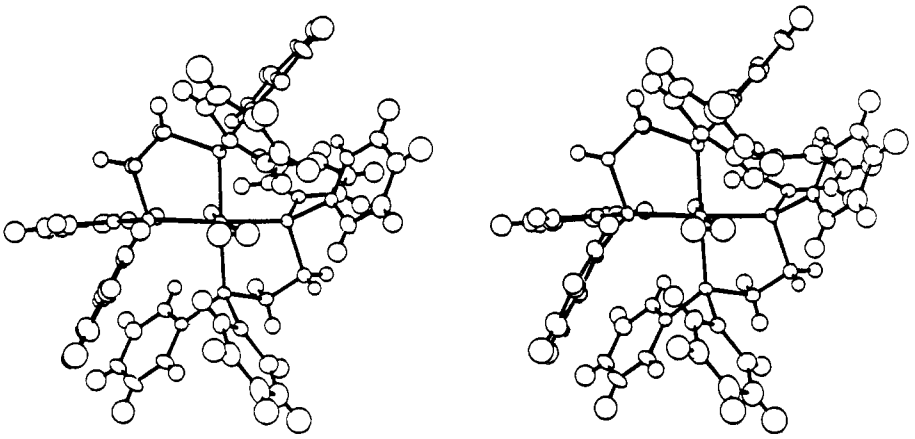

Figure 2. ORTEP stereoscopic view of the cation from the X-ray diffraction study, showing the overall environment of the η^2-H_2 ligand. All thermal ellipsoids have been drawn at the 30% probability level.

then counterion exchange with $NaBPh_4$ in CH_2Cl_2/MeOH to give **1**-BPh_4 (eq 2). The Fe atom in **1**-BF_4 has a distorted octahedral

$$FeH_2(dppe)_2 + HBF_4 \rightarrow [Fe(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4 \quad (1)$$

$$[Fe(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4 + NaBPh_4 \rightarrow [Fe(\eta^2\text{-}H_2)(H)(dppe)_2]BPh_4 + NaBF_4 \quad (2)$$

geometry with the η^2-H_2 ligand trans to the terminal hydride ligand.[4] The η^2-dihydrogen ligand was found by X-ray diffraction to be symmetrically coordinated with Fe–H distances of 1.53 (8) and 1.55 (8) Å and an H–H separation of 0.89 (11) Å. A significant distortion from octahedral geometry is manifested in the trans P–Fe–P angle of 163.0 (1)°, which is coplanar with the H_2 ligand. The NMR and some chemical properties of **1**-BF_4 have been described elsewhere.[4,6] The ^1H NMR spectra recorded below 250 K (200 MHz) are consistent with the solid-state structure with a broad resonance at −8.0 ppm due to the rapidly relaxing protons of the H_2 ligand (T_1^{min} = 8.5 ms) and a sharp quintet at −12.9 ppm (J_{PH} = 47 Hz) due to the terminal hydride (T_1^{min} = 120 ms) trans to the H_2 ligand. Above 250 K, these resonances coalesce because of exchange of H atoms between the terminal hydride and dihydrogen ligands. **1**-BPh_4 gives identical ^1H NMR spectra apart from the BPh_4^- multiplets at 7.5 and 6.8 ppm.

Initial X-ray work on **1**-BPh_4 did not unambiguously locate the η^2-H_2 and hydride ligands. Final proof of the structure came from a neutron diffraction study of **1**-BPh_4 at 20 K. Views of the coordination about iron, showing atomic nomenclature, are given in Figures 1 and 2. A list of selected interatomic distances and bond angles is presented in Table II. As was found for **1**-BF_4, the compound contains an η^2-H_2 ligand that is symmetrically side-on bonded to the iron and trans to the terminal hydride such that the Fe has a distorted octahedral configuration. Both the cation and anion in **1**-BPh_4 have crystallographically imposed 2-fold symmetry, with the 2-fold axis passing through the hydride and the iron atom and bisecting the H–H bond in the cation. Least-squares refinement of the occupancies of the hydride, H(1), and hydrogen atom, H(2), in the dihydrogen ligand using the neutron data gave values of 1.060 (28) and 0.952 (18), respectively.[24] The η^2-dihydrogen ligand shows Fe–H(2) distances of 1.616 (10) Å, and it is oriented such that the H–H bond lies in the plane formed by H(1), P(2), and P(2′).[25] The dihedral angle between this plane and that formed by H(1), H(2), and H(2′) is 0.3 (14)°. This orientation of the H_2 ligand, also observed for $W(CO)_3(P(i\text{-}Pr)_3)_2(\eta^2\text{-}H_2)$[3,8] and **1**-$BF_4$,[4] may be favored because of enhanced $d_\pi(Fe) \rightarrow \sigma^*(H)$ bonding[26] or more likely for the present symmetrical binding site, the minimizing of nonbonding repulsions between the $\sigma(H_2)$ and $d_{xy}(Fe)$ pairs of electrons as identified for the related olefin complex $Cr(CO)_5(\eta^2\text{-}C_2H_4)$.[27] Measurement of the barrier to rotation of the H_2 in **1**-BF_4 by inelastic neutron scattering reveals a small barrier and a splitting of absorption bands due to quantum mechanical tunneling of H atoms.[28] Some molecular mechanics calculations suggest that steric as well as electronic factors contribute to this barrier.[29]

The H–H separation of 0.816 (16) Å may be compared to those of 0.75 (16) (X-ray) and 0.82 (1) Å (neutron) found in the complex $W(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$,[3,8] 0.80 (6) Å (X-ray) in (P-N)$(\eta^2\text{-}H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(H)(PPh_3)_2$, P-N = $Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)P(i\text{-}Pr)_2\text{-}1,2)(\eta^3\text{-}C_5H_5)$,[30] and 0.74 Å for free H_2. These solid-state H_2 bond lengths do not explain why the tungsten complex has a more labile H_2 ligand than the iron complex in solution and possibly a shorter H–H bond as judged by the differences in minimum T_1 values (8.5 ± 1 ms at 200 MHz for the Fe complex and ≤4 ms at 250 MHz for the W complex). The greater lability of the H_2 in the tungsten complex would argue for a weaker interaction of the H_2 ligand with the metal for W over Fe. The W–H distances of 1.89 (1) Å are longer than the Fe–H distances to the H_2 ligand of 1.616 (10) Å, but it is difficult to compensate in a meaningful way for the larger covalent radius of tungsten and find evidence for weaker W–H bonding. The differences in T_1 values may not be significant because of the uncertainties in their measurements and difficulties in their interpretation. In fact, the spectroscopic data available so far are reasonably consistent with the similar H–H distances found for the Fe and W complexes considering that the minimum T_1 values for both are at the low end of the range of values reported so far for dihydrogen complexes (ca. 3 to >50 ms at 200 MHz) and the $^1J(H,D)$ coupling constants of 32 ± 1 Hz for *trans*-$[Fe(HD)(D)(dppe)_2]BF_4$[5] compared to 34 Hz for $W(HD)(CO)_3(P(i\text{-}Pr)_3)_2$ are at the high end of the range of such values (ca. 18–34 Hz).

The well-defined H–H distance of complex **1** has allowed the Morris group to calibrate H–H distances obtained by the T_1 NMR method for complexes in solution.[5,6] The distance of 0.816 (16) Å for **1** supports the method of treatment of the T_1 data, which assumes that the H_2 ligand is spinning (or tunneling quantum mechanically) very rapidly in the plane perpendicular to the Fe–H_2 bond. The use of Woessner's spectral density function to account for this internal motion of the H_2 gives an H–H distance of 0.86 (2) Å, which is in good agreement with the 20 K neutron and 298 K X-ray results, whereas if no spinning is assumed, then the

(24) The corresponding refinement of the population parameters of these positions using the X-ray data, however, tended to indicate that the H(1) site was overpopulated and the H(2) site was underpopulated, although these values were significantly correlated with the temperature factors of the two atoms.

(25) Primed atoms are related to unprimed atoms by the 2-fold axis.

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distance calculated is too long (1.09 Å).[7]

The terminal hydride–iron distance (H(1)–Fe) of 1.535 (12) Å is shorter than the distances to the dihydrogen ligand (H(2)–Fe = H(2′)–Fe = 1.616 (10) Å). This is the first experimental demonstration of this expected difference in metal bonding to hydride and H_2 although it should be noted that, when the effects of thermal motion on these bonds were examined by use of the program THMA11,[31] one calculation gave corrected Fe–H(1) and Fe–H(2) distances of 1.570 and 1.560 Å, respectively. The sum of the corrections to these bonds (+0.035 and −0.056 Å, respectively) involve contributions due to rigid body motion and also a riding correction according to the model given by Busing and Levy.[32] However, the most significant term for these bonds involving hydrogen is the anharmonic correction that arises out of situations where the forces between pairs of atoms are not adequately described by squared terms of the expansion of the crystal potential so that higher order (cubic, quartic) terms in the potential are required.[33] For H(1) on the 2-fold axis, however, this correction is effectively zero, while for H(2) it amounts to −0.075 Å.[34]

The X-ray study of **1**-BPh_4 at 298 K provided very similar bond distances and angles to those from the neutron study, apart from the Fe–H(1) and all the C–H distances which were underestimated as expected (Table II). The H(2)–H(2′) and Fe–H(2) distances are comparable to those of the neutron study given the large standard deviations.

Corresponding distances for the X-ray structures of **1**-BF_4 and **1**-BPh_4 are very similar (Table II), although the latter structure is more symmetrical with closely equivalent trans P–Fe–P angles [Δ(P(1)FeP(1′)–P(2)FeP(2′)) = 15.7° in **1**-BF_4 versus 4.5° in **1**-BPh_4]. An effect of the difference in the P–Fe–P angle is that for **1**-BPh_4 the phosphorus atoms P(2) and P(2′) have moved toward the H_2 ligand compared to the **1**-BF_4 structure. Although the esd's for the Fe–H distances are large, it is possible that the Fe–η^2-H_2 coordination in **1**-BPh_4 (Fe–H = 1.616 (10) Å) has been weakened by this change relative to that in **1**-BF_4 (Fe–H = 1.54 (8) Å) and hence the H_2 may be freer to rotate. Perhaps this explains why distinct H atom positions for the H_2 ligand were located for **1**-BF_4 but not for **1**-BPh_4 by our X-ray study at room temperature. In **1**-BPh_4 at 20 K, the shortest intramolecular H···H contacts in the cation involving H(1) and H(2) are to *o*-phenyl hydrogens: H(1)···H(222) = 1.986 and H(2)···H(112) = 2.066 Å. A series of calculations using the room-temperature X-ray data and rotating the H_2 axis about the 2-fold axis through Fe and H(1) indicates that rotation of the dihydrogen by ca. 60° away from its present observed position would place the atom H(2) close to the minimum contact distance (1.92 Å) with respect to atom H(112) on the *o*-phenyl of P(1) [cf. its observed X-ray distance of 2.122 Å].

The trans P–Fe–P angles in **1**-BPh_4 (166.6 (2)°, 172.1 (2)°) are much closer to 180° than the corresponding P–Re–P angles in the pentagonal bipyramidal trihydrides $ReH_3(dppe)_2$ (167.4 (5)° and 151.5 (5)°) and $ReH_3(dppe)(PPh_3)_2$ (159.1° and 126.9°), which are isoelectronic in terms of valence electrons with complex **1** but which likely do not contain H–H bonds.[2,35]

There are no unusual intermolecular contacts, the shortest such distance being between cation and anion, H(223)···H(161), at 2.32 Å. The BPh_4^- anion is significantly distorted from tetrahedral geometry with two contracted C–B–C bond angles [102.9 (1)°] and four expanded angles [average 113°]. Similarly, the B–C–C bond angles are all greater than 120° [121.4–124.2 (3)°].

Additional structures with reliable H–H bonding distances are badly needed to understand the variations possible in these distances and how these variations correlate with quantities such as ^1J(H,D) and T_1 and chemical properties such as the rate of intermolecular exchange of H_2, the rate of the intramolecular H atom exchange process, and the acidity of the H_2 ligand.

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Registry No. **1**-BF_4, 109750-49-4; **1**-BPh_4, 113088-85-0; $FeH_2(dppe)_2$, 47898-23-7.

Supplementary Material Available: Figure 3 showing the stereoscopic view of the packing in a unit cell of **1**-BPh_4 from the results of the neutron study at 20 K, Table I listing the final neutron atomic coordinates and equivalent isotropic thermal parameters, Table II listing the anisotropic thermal parameters, and Table III listing the positional and thermal parameters for the room-temperature X-ray experiment (8 pages); tables of calculated and observed structure factors (74 pages). Ordering information is given on any current masthead page.

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