

Synthesis and Characterization of the First Examples of Dicationic Dihydrogen Complexes of Iron and Ruthenium with the PF₃ Ligand

H. V. Nanishankar,^[a] Munirathinam Nethaji,^[a] and Balaji R. Jagirdar*^[a]

Keywords: Dihydrogen complexes / H–H activation / Hydride ligands / Iron / Phosphane ligands / Ruthenium

New dicationic dihydrogen complexes of the type *trans*-[M(η^2 -H₂)(PF₃)(diphosphane)₂]²⁺ [M = Ru, diphosphane = dppm (Ph₂PCH₂PPh₂); M = Fe, Ru, diphosphane = dppe (Ph₂PCH₂CH₂PPh₂)] have been prepared from the precursor hydrides *trans*-[M(H)(PF₃)(diphosphane)₂]⁺ upon reaction with HOTf. In the case of dppm, in addition to the *trans*-dihydrogen complex *cis*-[Ru(η^2 -H₂)(PF₃)(dppm)₂]²⁺ was also obtained in the protonation reaction. The intact nature of the H–H bond in these derivatives has been established using the spin–lattice relaxation time measurements (short *T*₁ values) and the large *J*_{H,D} coupling constant of the H–D isotopomers. The H–H bond lengths and the stabilities of the di-

hydrogen complexes are discussed in terms of the π -acidity of the PF₃ ligand and compared with other systems possessing *trans* CO and CNH ligands. The *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ complex was found to be remarkably stable with respect to the loss of bound H₂ for a period of about 16 h. The H–D isotopomer of this complex exhibits small temperature variations in the *J*_{H,D} coupling constant. The X-ray crystal structure of *trans*-[Ru(H)(PF₃)(dppm)₂][BF₄] has been determined.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The heterolytic activation of molecular hydrogen by transition metal centers to give a proton and a metal hydride is one of the most intriguing reactions of dihydrogen complexes. Highly electrophilic metal centers have been found to greatly promote heterolysis of dihydrogen.^[1,2] This activation pathway leads to interesting reactivity, including catalysis and selective proton transfer to an ancillary ligand.^[3,4] The ligand *trans* to the η^2 -H₂ moiety has a significant role in dictating the properties of the dihydrogen complex, including the heterolytic cleavage of the bound dihydrogen.

We have been interested in preparing systems that are capable of activating H₂ in a heterolytic fashion. Toward this goal, we have reported certain dicationic dihydrogen complexes of iron and ruthenium bearing *trans*-phosphite, phosphane,^[5–7] and nitrile^[8] ligands that were found to be quite acidic. Numerous examples of highly acidic η^2 -H₂ complexes have been reported in the literature.^[9–14] Rocchini et al.^[12] have reported two highly acidic dihydrogen complexes *trans*-[M(η^2 -H₂)(CO)(dppp)₂]²⁺ [M = Ru, Os; dppp = 1,3-bis(diphenylphosphanyl)propane]. The ruthenium derivative was found to be stable only at low temperatures whereas the osmium complex is stable even at room temperature. The strong π -accepting tendency of the

CO ligand *trans* to the H₂ imparts the high acidity to the dihydrogen ligand. Morris and co-workers have reported an iron dihydrogen complex *trans*-[Fe(η^2 -H₂)(CO)(dppe)₂]²⁺ that was found to be quite acidic.^[14] In addition to this species, they also prepared a highly acidic dicationic dihydrogen complex, *trans*-[Ru(η^2 -H₂)(CNH)(dppe)₂]²⁺ that was found to be stable with respect to the loss of protons or H₂ under strongly acidic conditions (excess triflic acid).^[13] A ligand that has similar π acidity to both CO and CNH is PF₃. Dihydrogen complexes with the PF₃ ligand are limited to only one example, the rhenium complex *fac*-[Re(H₂)(PPh₃)(PF₃)(dien)]⁺.^[15,16] As yet there are no reports in the literature of dicationic dihydrogen complexes of transition metals with the PF₃ ligand. Therefore, in continuation of our investigations on the heterolytic activation of molecular hydrogen we report here the first examples of dicationic dihydrogen complexes of iron and ruthenium with a *trans*-PF₃ ligand *trans*-[M(η^2 -H₂)(PF₃)(diphosphane)₂]²⁺ (M = Fe, diphosphane = dppe; M = Ru, diphosphane = dppm, dppe).

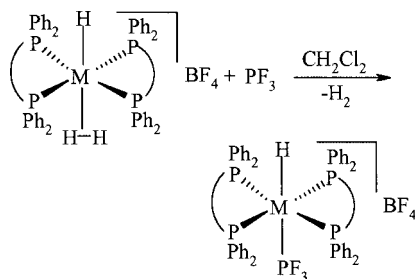
Results and Discussion

Preparation and Properties of the Hydride Complexes

The new hydride complexes *trans*-[M(H)(PF₃)(diphosphane)₂][BF₄] (M = Fe, diphosphane = dppe **1**; M = Ru, diphosphane = dppm **2**, dppe **3**) were prepared by substitution of the bound H₂ ligand in *trans*-[M(H)(η^2 -H₂)(diphosphane)₂][BF₄] with excess PF₃ gas [Equation (1)]. The

^[a] Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
Fax: (internat.) + 80-2360-0683
E-mail: jagirdar@ipc.iisc.ernet.in

products were obtained as colorless solids that were purified by crystallization from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture to give colorless crystals.



M	diphosphane	compd.
Fe	dppe	1
Ru	dppm	2
	dppe	3

The ^1H NMR spectra of the hydride complexes show a doublet of multiplets pattern for the hydride moiety due to coupling with the phosphorus (*trans* and *cis*) and fluorine nuclei. The $J_{\text{H,P}_{\text{trans}}}$ coupling constants were found to be 155.6 and 171.9 Hz whereas the $J_{\text{H,P}_{\text{cis}}}$ coupling constants were found to be 21.0 and 19.1 Hz for **2** and **3**, respectively. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectra gave a quadruplet in the hydride region due to H, F coupling, with $J_{\text{H,F}}$ equal to 33.1 and 34.4 Hz for **2** and **3**, respectively. In the case of **1**, a multiplet at $\delta = -7.06$ ppm in the ^1H NMR spectrum with an average $J_{\text{H,P}}$ coupling constant ($J_{\text{H,P}_{\text{trans}}}$ and $J_{\text{H,P}_{\text{cis}}}$) of 50.0 Hz was observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of one doublet for the dppe P nuclei coupled to the PF_3 ligand and a quadruplet of quintets for the PF_3 moiety coupled to three fluorine and the four dppe P nuclei. The $J_{\text{P,F}}$ coupling constant was found to be in the range 1267.0–1307.9 Hz, which is typical for compounds having direct P–F bonds.^[17–20] The ^{19}F NMR spectra of the hydride complexes consist of a doublet of doublets for the PF_3 ligand and a broad singlet for the BF_4^- counterion. The

NMR spectroscopic data for these complexes are summarized in Table 1. In order to get an insight into the structural aspects, we carried out an X-ray crystallographic study of **2**.

Structure of *trans*-[Ru(H)(PF₃)(dppm)₂][BF₄] (**2**)

The ORTEP diagram of the *trans*-[Ru(H)(PF₃)(dppm)₂]⁺ cation is shown in Figure 1. In addition to a discrete BF_4^- counterion, two molecules of H_2O were also found (the source of these water molecules could be the solvent used for crystallization because strict measures were not taken to exclude the moisture). The structure is a highly distorted square pyramid defined by the four nearly coplanar dppm phosphorus atoms, with the PF_3 group almost perpendicular to this plane. The hydride ligand that occupies the sixth coordination site on the metal was not located, although its presence was confirmed by ^1H NMR spectroscopy. The Ru–P(dppm) bond lengths vary from 2.3302(18) to

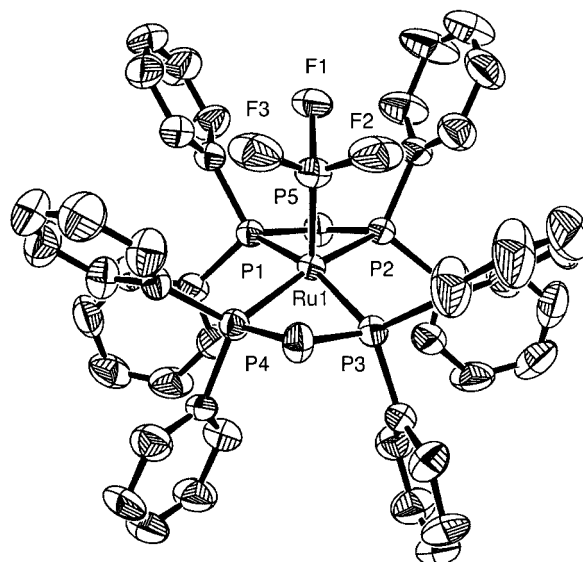


Figure 1. ORTEP view of the *trans*-[(dppm)₂Ru(H)(PF₃)]⁺ (**2**) cation at the 50% probability level

Table 1. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and ^{19}F NMR spectral data (δ) for *trans*-[M(H)(PF₃)(diphosphane)₂][BF₄] complexes in CD_2Cl_2

Fragment		1	2	3
^1H	$\delta(\text{M}-\text{H})$	−7.06 (m, 1 H)	−2.95 (dm, 1 H)	−6.73 (dm, 1 H)
	$J_{\text{H,P}_{\text{trans}}}(\text{Hz})$	50.0 ^[a]	155.6	171.9
	$J_{\text{H,P}_{\text{cis}}}(\text{Hz})$		21.0	19.1
	$J_{\text{H,F}}(\text{Hz})$	20.2	33.1	34.4
	$\delta(\text{CH}_2)$	2.30 (m, 4 H)	4.64 (m, 2 H)	2.29 (m, 4 H)
		2.60 (m, 4 H)	4.97 (m, 2 H)	2.61 (m, 4 H)
^{31}P	$\delta(\text{Ph})$	6.60–8.20 (m, 40 H)	7.11–7.57 (m, 40 H)	6.66–7.30 (m, 40 H)
	$\delta(\text{diphosphane})$	77.9 (d, 4 P)	−3.8 (d, 4 P)	57.7 (d, 4 P)
	$J_{\text{P,P}}(\text{Hz})$	44.2	32.1	29.2
	$\delta(\text{PF}_3)$	149.0 (q quint, 1 P)	132.9 (q quint, 1 P)	126.8 (q quint, 1 P)
	$J_{\text{P,F}}(\text{Hz})$	1267.0	1307.9	1304.6
^{19}F	$\delta(\text{PF}_3)$	−12.13 (dd)	−19.00 (dd)	−18.20 (dd)
	$\delta(\text{BF}_4)$	−159.28 (br)	−161.18 (br)	−166.07 (br)

^[a] Average; no separate $J_{\text{H,P}_{\text{trans}}}$ and $J_{\text{H,P}_{\text{cis}}}$ couplings seen.

2.352(2) Å whereas the Ru–P(PF₃) distance was found to be 2.206(2) Å. The bond lengths of certain analogous ruthenium derivatives fall in the following order: 2.3153(17) Å {Ru–P(OMe)₃ in *trans*-[Ru(H){P(OMe)₃}(dppm)₂][BF₄]}^[7] > 2.264(2) Å {Ru–P(OMe)₂ in *trans*-[Ru(H){P(OMe)₂}(dppe)₂][BF₄]}^[5] > 2.206(2) Å {Ru–PF₃ in *trans*-[Ru(H)(PF₃)(dppm)₂][BF₄]}]. This order is a combined effect of the progressive increase in the π -accepting ability as well as the decrease in the steric crowding due to the reduction in the cone angles^[21,22] of the *trans*-phosphorus ligands. The dppm bite angles P(1)–Ru(1)–P(2) and P(3)–Ru(1)–P(4) are 71.87(6)° and 70.48(5)°, respectively. The P(1)–C(25)–P(2) and P(3)–C(50)–P(4) bond angles are 96.6(3)° and 94.4(3)°, respectively, falling at the lower end of the range of P–C–P angles (92–133°) that the dppm ligand exhibits in its complexes. The crystallographic data are given in the Exp. Sect. and selected bond lengths and angles are summarized in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for *trans*-[Ru(H)(PF₃)(dppm)₂][BF₄] (**2**)

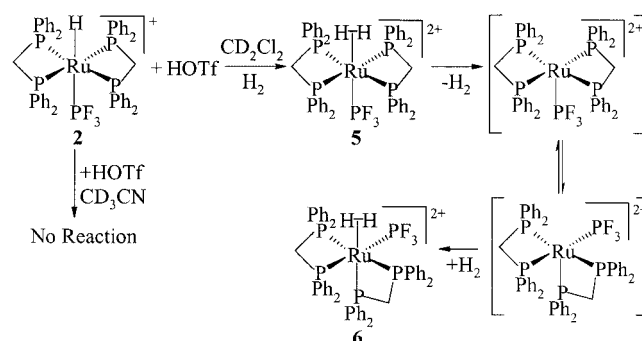
Ru(1)–P(1)	2.3302(18)
Ru(1)–P(2)	2.3481(17)
Ru(1)–P(3)	2.352(2)
Ru(1)–P(4)	2.3437(18)
Ru(1)–P(5)	2.206(2)
P(5)–F(1)	1.554(4)
P(5)–F(2)	1.552(5)
P(5)–F(3)	1.549(5)
P(1)–Ru(1)–P(2)	71.87(6)
P(3)–Ru(1)–P(4)	70.48(5)
P(1)–Ru(1)–P(3)	165.15(6)
P(2)–Ru(1)–P(4)	168.11(6)
P(1)–Ru(1)–P(5)	100.70(7)
P(2)–Ru(1)–P(5)	96.78(7)
P(3)–Ru(1)–P(5)	93.78(7)
P(4)–Ru(1)–P(5)	95.05(7)

Protonation Reactions of *trans*-[Fe(H)(PF₃)(dppe)₂][BF₄] and *trans*-[Ru(H)(PF₃)(dppm)₂][BF₄].

The protonation of the hydrides with HOTf in CD₃CN or with HBF₄·Et₂O in CD₂Cl₂ did not afford the dihydrogen complexes; even with large excesses of the acid, no reaction took place. These experiments indicate that the p*K*_a of the protonating agent must be less than –2.4 in order to obtain the dihydrogen complexes since the p*K*_a of HOTf in CH₃CN is 2.6^[23] and that of HBF₄·Et₂O is –2.4.^[24] When the hydrides were protonated with excess triflic acid under H₂ atmosphere in CD₂Cl₂ at room temperature, the corresponding dihydrogen complexes *trans*-[Fe(η²-H₂)(PF₃)(dppe)₂]²⁺ (**4**) and *trans*-[Ru(η²-H₂)(PF₃)(dppm)₂]²⁺ (**5**) were presumably formed, although we found that they lose the H₂ ligand quite rapidly thus precluding the NMR spectroscopic characterization of these complexes. The singlet at δ = 4.6 ppm in the ¹H NMR spectrum due to free H₂ grew in intensity in these experiments. In the case of protonation of **1**, the resulting mixture gave NMR

signals that were extensively broadened upon loss of H₂ due to the generation of some Fe^{III} species, amongst others. In an attempt to observe the dihydrogen complexes spectroscopically, the addition of the protonating agent was done at liquid N₂ temperature and then the mixture was slowly warmed up to 0 °C; the NMR spectral studies were also carried out at this temperature. Under these conditions, we observed signals corresponding to the dihydrogen complexes only in the case of **2**.

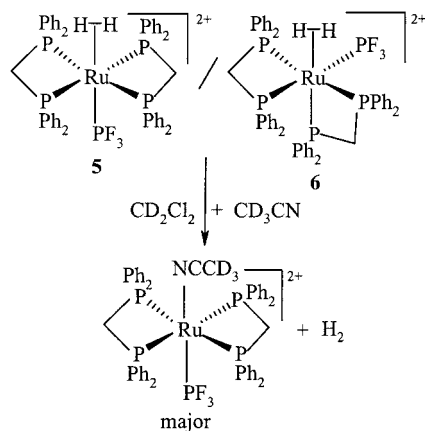
The protonation of **2** with HOTf under an atmosphere of H₂ resulted in a mixture of *trans*-[Ru(η²-H₂)(PF₃)(dppm)₂]²⁺ (**5**) and *cis*-[Ru(η²-H₂)(PF₃)(dppm)₂]²⁺ (**6**) in a ratio of 1:3. We have previously observed a similar behavior in certain analogous ruthenium complexes with *trans* phosphite ligands.^[7] The complexes of the type *trans*-[Ru(H)[P(OR)₃](dppm)₂][BF₄] isomerize under thermal conditions (in the presence of small amounts of acid impurities in the solvent) to give a mixture of the *trans* and the *cis* hydride phosphite derivatives. We traced the origin of this isomerization to the lability of the *trans* phosphite ligand. The addition of acid accelerated the isomerization reaction in those derivatives resulting in the corresponding *trans* and *cis* dihydrogen complexes *trans/cis*-[Ru(η²-H₂)[P(OR)₃](dppm)₂][BF₄]₂.^[7] The mechanism of the isomerization in the current work, however, seems to be different. The PF₃ ligand was not found to be labile; refluxing solutions containing the starting *trans* hydride complexes did not give any isomerized species, thus suggesting that the isomerization occurs only upon addition of the acid. We monitored the loss of the bound H₂ ligand and found that it was faster in the case of **5** than **6**. A plausible mechanism could involve the loss of H₂ ligand from the *trans* dihydrogen complex, rearrangement of the five-coordinate species, followed by the re-binding of the H₂ *cis* to the PF₃ moiety. When the protonation was carried out under an Ar atmosphere, we found no evidence of isomerization except for the loss of H₂ ligand from **5**; a singlet at δ = 4.6 ppm due to free H₂ was observed in the ¹H NMR spectrum in this case. This suggests that the isomerization is effected upon loss of H₂ from the *trans* dihydrogen complex followed by the re-binding of H₂ *cis* to PF₃ only when there is excess H₂. The mechanism is illustrated in Scheme 1.



Scheme 1

Another possible mechanism for the isomerization could involve the protonation of one of the dpmm P atoms, opening up of the chelate arms to give $\text{Ru}-(\eta^1\text{-dpmmH}^+)$, followed by the isomerization. The dpmmH^+ could then protonate the hydride ligand and close its arm. The $\text{p}K_{\text{a}1}$ of dpmmH^+ has been reported to be 3.81.^[25] The protonated dpmm P ($[\text{Ph}_2\text{PCH}_2\text{PPh}_2]^+$) undergoes a dramatic downfield shift with respect to the bound dpmm P chemical shifts in the ^{31}P NMR spectroscopy, as has been observed by Rotting and Angelici earlier.^[26] We did not find any evidence for a dangling dpmmH^+ in our ^{31}P NMR spectral studies. In addition, since the $\text{p}K_{\text{a}}$ of the protonating agent needs to be lower than -2.4 in order to obtain the dihydrogen complexes, we can rule out this mechanism.

The protonation of **2** in CD_2Cl_2 followed by the addition of CD_3CN gave $\text{trans}-[\text{Ru}(\text{CD}_3\text{CN})(\text{PF}_3)(\text{dpmm})_2]^{2+}$ (major product)^[27] and the precursor hydride **2** (minor product). The observation of a small amount of the precursor hydride could be due to a part of **2** remaining unchanged under these conditions. These results are summarized in Scheme 2.



Scheme 2

$\text{trans}-[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dpmm})_2]^{2+}$ (**5**) gives a broad doublet at $\delta = -1.75$ ppm in the ^1H NMR spectrum for the bound H_2 ligand coupled to the $\text{trans}\text{-PF}_3$ ligand

($J_{\text{H}_2, \text{P}_{\text{trans}}} = 56.4$ Hz). We have observed such strong couplings in the past.^[5–7] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a single signal for all the four dpmm phosphorus atoms indicating that they are coplanar. On the other hand, $\text{cis}-[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**6**) shows a broad singlet at $\delta = -4.86$ ppm for the bound H_2 ligand in the ^1H NMR spectrum and two multiplets for the dpmm P atoms in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The NMR spectroscopic data for these derivatives are summarized in Table 3.

Protonation Reaction of $\text{trans}-[\text{Ru}(\text{H})(\text{PF}_3)(\text{dppe})_2][\text{BF}_4]$

The protonation of **3** was attempted with various protonating agents such as HCl , HBr , HI , CF_3COOH , and $\text{HBF}_4\cdot\text{Et}_2\text{O}$; once again, the behavior of this hydride was similar to that of **1** and **2**. The dihydrogen complex $\text{trans}-[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**7**) was obtained upon protonation with excess triflic acid. Titration of the hydride complex with triflic acid revealed that it requires 50 equivalents of the acid for the complete conversion of the hydride to the dihydrogen complex. This suggests that the $\text{p}K_{\text{a}}$ of **7** must be much less than -5 since the aqueous $\text{p}K_{\text{a}}$ of HOTf has been estimated to be about -5 .^[12]

Basallote and co-workers^[28] obtained similar results in the protonation of CpRuHL complexes ($\text{L} = \text{dpmm}$, dppe , 2PPh_3) with various acids. They suggested that the lack of formation of the dihydrogen complexes in the presence of a large excess of HCl , HBr , or CF_3COOH was unlikely to be due to kinetic reasons because they observed protonation of certain other metal hydrides with these acids to be usually faster than with $\text{HBF}_4\cdot\text{Et}_2\text{O}$. The failure of the protonation was related to the thermodynamics of the process. There have been other reports in the literature of the formation of dihydrogen complexes upon protonation of the hydrides with both strong and weak acids.^[29,30] The fact that protonation of our hydride complexes failed with all acids except HOTf , and that the complete conversion of the hydrides to the corresponding $\eta^2\text{-H}_2$ derivatives requires large excesses of the acid (HOTf), indicates that our dihydrogen complexes are extremely strong acids, being roughly similar to HOTf .^[31] It is intriguing to note that **7** was found to be stable at room temperature under H_2 atmosphere for about

Table 3. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and ^{19}F NMR spectral data (δ) for $[\text{M}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{diphosphane})_2]^{2+}$ complexes in CD_2Cl_2

	Fragment	5	6	7
^1H	$\delta(\text{Ru}-\text{H}_2)$	-1.75 (br. d, 2 H)	-4.86 (br. s, 2 H)	-4.33 (br. d, 2 H)
	$J_{\text{H,P}_{\text{trans}}}$ (Hz)	56.4		63.0
	$\delta(\text{CH}_2)$	4.86 (m, 2 H) 5.08 (m, 2 H)	5.93 (m, 4 H)	2.83 (m, 4 H) 3.00 (m, 4 H)
	$\delta(\text{Ph})$	6.35–7.76 (m, 40 H)	6.35–7.76 (m, 40 H)	6.24–7.82 (m, 40 H)
^{31}P	$\delta(\text{diphosphane})$	-15.6 (d, 4 P)	-13.9 (m, 2 P) -16.2 (m, 2 P)	49.3 (d, 4 P)
	$J_{\text{P,P}}$ (Hz)	40.0	45.0	29.2
	$\delta(\text{PF}_3)$	134.4 (q quint, 1 P)	130.8 (m, 1 P)	127.4 (q quint, 1 P)
	$J(\text{P,F})$ (Hz)	1261.5	1286.0	1262.5
^{19}F	$\delta(\text{PF}_3)$	-16.20 (d)	-20.80 (d)	-5.50 (d)
	$\delta(\text{OTf})$	-90.54 (br)	-91.10 (br)	-91.71 (br)
	$\delta(\text{BF}_4)$	-160.14 (br)	-144.25 (br)	-144.77 (br)

16 h after which time it begins to decompose. We found evidence for some dppeH^+ in the ^{31}P NMR spectrum (singlet at $\delta = 10.0$ ppm).^[14] We attempted to isolate **7** by precipitation with Et_2O ; our attempts, however, failed, and only the starting hydride complex **3** was recovered. In this case, the dihydrogen complex **7** protonates the Et_2O to give Et_2OH^+ .

The NMR spectral features of **7** (Table 3) are quite similar to those of **5**; the $J_{\text{H}_2, \text{P}_{\text{trans}}}$ coupling constant of 63.0 Hz is even larger than the values (49–51 Hz) we found earlier in the cases of $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{P})(\text{diphosphane})_2]^{2+}$ complexes [diphosphane = dppe, $\text{P} = \text{PF}(\text{OR})_2$; diphosphane = dppm, $\text{P} = \text{P}(\text{OR})_3$, $\text{PF}(\text{OR})_2$].^[5–7] This stronger coupling could be due to the presence of the more electronegative F substituents in the PF_3 complex, which results in an enormous enhancement of the “s” character of the bonding orbitals in comparison to the $\text{PF}(\text{OR})_2$ complexes if it is assumed that the coupling is dominated by the Fermi contact term.^[32] No observable $\text{H}_2\text{—F}$ couplings were observed. In an attempt to look for $\text{H}_2\text{—F}$ couplings in the ^1H NMR spectrum, we decoupled all the P nuclei and obtained a broad singlet, indicating that the $J_{\text{H}_2, \text{F}}$ coupling constant is smaller than the line-width of the signal.

Rate Constant for the Decomposition of $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**7**)

We studied the kinetics of the decomposition of **7** by monitoring the decrease in the integrals of the dihydrogen complex for the $\eta^2\text{-H}_2$ ligand in the ^1H NMR spectrum and the dppe phosphorus in the $^{31}\text{P}\{\text{gated } ^1\text{H}\}$ NMR spectrum. From the kinetics data, the pseudo-first-order rate constant was found to be $4 \times 10^{-5} \text{ s}^{-1}$ with a half-life of about 4.45 h. The residual material in the NMR tube after 16 h consisted of dppeH^+ (ca. 46%), $\text{trans-}[\text{RuCl}(\text{PF}_3)(\text{dppe})_2]^+$ (**8**; ca. 36%), and $\text{trans-}[\text{Ru}(\text{OTf})(\text{PF}_3)(\text{dppe})_2]^+$ (**9**; <5%) along with certain other unidentifiable Ru^{III} species. The source of the chloride in **8** is the solvent, CD_2Cl_2 .

Variable Temperature Spin–Lattice Relaxation Time Measurements.

The variable temperature spin–lattice relaxation times (T_1) for the $\eta^2\text{-H}_2$ moiety were determined; the data are summarized in Table 4. T_1 minima of 10.1, 7.2, and 13.0 ms (at 400 MHz and 273 K) were obtained for **5**, **6**, and **7**, respectively. The H–H distances for the slow- and fast-rotation regimes thus calculated^[33] from the T_1 minima are tabulated in Table 5.

HD Isotopomers

In an attempt to prepare the HD isotopomers of **5**, **6**, and **7**, we purged the respective CD_2Cl_2 solutions containing the H_2 complexes with HD gas (generated from NaH and D_2O). Despite purging with HD for a considerable period of time, no observable HD isotopomer was obtained. Therefore, we reacted the starting hydride complexes **2** and **3** with excess $\text{F}_3\text{CSO}_3\text{D}$ in CD_2Cl_2 to obtain the $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppm})_2]^{2+}$ **5-D₁**, $\text{cis-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)-$

Table 4. Variable-temperature spin–lattice relaxation times (T_1 , ms; 400 MHz) of the dihydrogen ligand in $[\text{M}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{diphosphane})_2]^{2+}$ complexes in CD_2Cl_2 ^[a]

T (K)	T_1 (5)	T_1 (6)	T_1 (7)
298			18.0
284			17.3
283	12.3	8.7	
273	<i>10.1</i>	7.2	<i>13.0</i>
263	10.8	7.5	
258			15.9
243	11.5	8.7	20.2
233	13.0	8.7	
228			28.9
223	14.4	10.8	
200	18.7	14.4	

^[a] Italicized data indicate T_1 minima.

Table 5. d_{HH} values from T_1 (min) (400 MHz) for $[\text{M}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{diphosphane})_2]^{2+}$ complexes in CD_2Cl_2

	T_1 min	d_{HH} (slow) Å	d_{HH} (fast) Å
5	10.1	0.99	0.79
6	7.2	0.94	0.79
7	13.0	1.03	0.81

$(\text{dppm})_2]^{2+}$ **6-D₁**, and $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppe})_2]^{2+}$ **7-D₁** derivatives, respectively. The ^1H NMR spectrum of the hydride region of **5-D₁** and **7-D₁** is expected to show a doublet of 1:1:1 triplets pattern: the doublet due to the coupling of H with the *trans* phosphorus, and 1:1:1 triplet from the coupling of the proton with deuterium. Figure 2a displays this pattern in the case of **7-D₁**. An overlap of the signals is the cause of the poor resolution of the six lines. Upon decoupling the phosphorus atoms, the ^1H NMR spectrum shows an approximate 1:1:1 triplet pattern due to

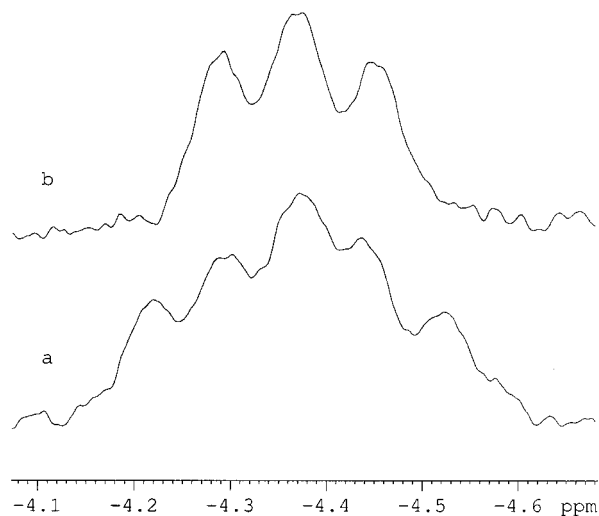


Figure 2. (a) ^1H NMR spectrum of $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**7-D₁**); (b) $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**7-D₁**)

H–D coupling (Figure 2b). The complex **6-D₁** exhibits only a 1:1:1 triplet pattern due to the presence of a *trans* phosphane that is not as strong an acceptor as PF₃. The $J_{\text{H,D}}$ coupling constants were found to be 27.0, 28.0, and 30.0 Hz at 273 K for **5-D₁**, **6-D₁**, and **7-D₁**, respectively. The H–H distances calculated from the H–D coupling constant^[34,35] are 0.97, 0.96, and 0.92 Å for **5-D₁**, **6-D₁**, and **7-D₁**, respectively. In addition, we carried out variable temperature $J_{\text{H,D}}$ measurements for **7-D₁**; the data are summarized in Table 6 and show an interesting temperature dependence.

Table 6. Temperature dependence of $J_{\text{H,D}}$ for *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ in CD₂Cl₂

<i>T</i> (K)	$J_{\text{H,D}}$	d_{HH} (Å)
298	29.8	0.922
273	30.0	0.919
258	30.4	0.912
243	31.0	0.902
228	31.4	0.895
213	32.0	0.885

There have been a few reports on the unusual temperature dependence of $J_{\text{H,D}}$ coupling in the case of elongated dihydrogen complexes, for example [RuCp*(H···D)-(dpmp)]⁺,^[36] *trans*-[Os(H)(H···D)(dppe)₂]⁺,^[37] *trans*-[Os(Cl)(H···D)(dppe)₂]⁺,^[36] and [RuCp/Cp*(H···D/T)-(PP)]⁺.^[38] Based on the theoretical studies by Gelabert et al.,^[39] it was interpreted that the varying thermal population of the vibrational excited states of the M–H₂ unit results in the unusual temperature dependence of $J_{\text{H,D}}$ of the elongated dihydrogen complexes. The data presented in Table 6 show that the variations in $J_{\text{H,D}}$ with temperature are small and close to the error in the determination of the H–D coupling constant.

H–H Distances and the Stabilities of the Dihydrogen Complexes

The H–H distances obtained from the $T_1(\text{min})$ data fall in the range 1.03–0.75 Å (see Table 5) for the slow- and the fast-rotation regimes. A correlation between the H–H distances calculated from $J_{\text{H,D}}$ and $T_1(\text{min})$ and $\Delta G^\ddagger$ for the loss of the H₂ ligand from the metal center has been reported by Gusev et al.^[40] The d_{HH} values calculated from $J_{\text{H,D}}$ in the current work are of the order of 0.92–0.97 Å (273 K) which are intermediate between the values of 1.03 and 0.75 Å obtained using the slow- and the fast-spinning approximations of H₂. Morris and Wittebort^[33] have suggested that H–H distances obtained from $J_{\text{H,D}}$ that are intermediate between those derived from the $T_1(\text{min})$ data indicate that librational motion significantly influences the H₂ relaxation process. In addition to these complexes, several examples have been reported earlier where such a situation has been observed.^[33]

The effect of the ligand *trans* to H₂ on the properties of the dihydrogen complex, for example d_{HH} and stability, can be interpreted in terms of the σ donation (η^2 -H₂ → empty metal d orbital) and the back-donation (filled metal d orbital → σ^* orbital of η^2 -H₂) components. Woska et al.^[41] have determined the stereoelectronic parameters of a series of phosphorus ligands and concluded that PF₃ is the weakest σ donor and the strongest π acid. Thus, the *trans*-PF₃ ligand exerts a high *trans* influence due to its strong π -acidity; in addition, it is also expected to stabilize the metal d orbitals resulting in reduced overlap with the antibonding orbitals of the H₂. Consequently, a strengthening of the H–H bond and a weakening of the M–H₂ interaction occurs giving rise to dihydrogen complexes with short d_{HH} values. The dihydrogen complexes **5**, **6**, and **7** show H–H distances of 0.97, 0.96, and 0.92 Å, respectively, at 273 K. These distances, rather surprisingly, are not appreciably short. We have also measured the $J_{\text{H,D}}$ coupling constant of **7-d₁** at various temperatures and obtained a d_{HH} of 0.88 Å at 213 K. This distance is similar to the H–H distance found in the case of *trans*-[Ru(η^2 -H₂)(CO)(dpmp)₂]²⁺ (0.85 Å) reported by Rocchini et al.^[12] and *trans*-[Ru(η^2 -H₂)(CNH)(dpmp)₂]²⁺ (0.88 Å) reported by Morris and co-workers.^[13] Both of these compounds are unstable with respect to the loss of H₂. Since **7** loses H₂ as noted earlier, we attempted to determine the equilibrium constant for the substitution of the bound H₂ with CH₃CN as this could provide insight into the relative M–H₂ bond strength for the complexes prepared in this study. However, we found that CH₃CN substitutes H₂ completely even under stoichiometric conditions (1:1 molar ratio, complex:CH₃CN) thus precluding the measurement of the equilibrium constant. We earlier found that the H₂ ligand in complexes of the type *trans*-[Ru(η^2 -H₂)[P(OR)₃](dpmp)₂]²⁺ and *cis*-[Ru(η^2 -H₂)[PF(OR)₂](dpmp)₂]²⁺ is labile; however, upon loss of the H₂ ligand (typically loss of H₂ starts to occur after 24–36 h), the dihydrogen complex could be recovered by purging the solutions containing the five-coordinate species with H₂ gas.^[7] Considering the greater π -acidity of the PF₃ ligand in comparison to P(OR)₃ or PF(OR)₂, it is not surprising to find that **7** is stable only for about 16 h before it starts to decompose. Thus, the π -acidities of the CO, CNH, and PF₃ ligands account for the trend in the stability of the M–H₂ bond for the above three complexes, which increases in the order CO ≤ CNH < PF₃. We found that the protonation of **1** with HOTf resulted in extensive broadening of the ¹H NMR signals due to the presence of Fe^{III} species that are generated quite rapidly from a highly unstable iron dihydrogen complex. We believe that the origin of the Fe^{III} species is a dihydrogen complex since, upon its (Fe^{III} species) generation, a singlet at δ = 4.6 ppm was observed, indicating the evolution of H₂. This observation further supports the earlier suggestion that the M–H₂ interaction becomes stronger on going down the group, as has been found earlier.^[12,42] We speculate that a compound of formula *trans*-[Os(η^2 -H₂)(PF₃)(diphosphane)₂]²⁺, if realized, could be isolable. Efforts toward this goal are in progress in our laboratories.

Conclusion

The complexes *trans*-[Ru(η^2 -H₂)(PF₃)(dppm)₂]²⁺ (**5**), *cis*-[Ru(η^2 -H₂)(PF₃)(dppm)₂]²⁺ (**6**), and *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (**7**) are formulated as dihydrogen complexes based on their short *T*₁ values and the observation of substantial H–D coupling in the corresponding HD isotopomers. *trans*-[Ru(η^2 -HD)(PF₃)(dppe)₂]²⁺ shows a temperature-dependent *J*_{H,D} coupling, although this effect is only small. All of these derivatives, including *trans*-[Fe(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (**4**), are unstable at room temperature. The dihydrogen complexes are formed only upon addition of excess HOTf to the precursor hydrides and they protonate Et₂O in solution, indicating the high acidities of these derivatives.

Experimental Section

General Remarks: All reactions were carried out under N₂ at room temperature using standard Schlenk^[43,44] and inert atmosphere techniques unless otherwise noted. Solvents used for the preparation of dihydrogen complexes were thoroughly saturated with either H₂ or Ar just before use. The ¹H, ³¹P, and ¹⁹F NMR spectroscopic data were obtained using AMX Bruker 400 MHz or Avance Bruker 400 MHz instruments. The shift of the residual protons of the deuterated solvent was used as an internal reference. Variable-temperature proton *T*₁ measurements were carried out at 400 MHz using the inversion recovery method (180°-τ-90° pulse sequence at each temperature)^[45] and the data are summarized in Table 4; the *d*_{HH} values obtained from the *T*₁ minima are given in Table 5. All ³¹P NMR spectra were proton decoupled, unless otherwise specified. ³¹P NMR chemical shifts were measured relative to 85% H₃PO₄ (as an aqueous solution, external reference) in CD₂Cl₂. ¹⁹F NMR spectra were recorded with respect to CFCl₃ (external reference) in CD₂Cl₂. Satisfactory elemental analysis data for the samples could not be obtained because of the formation of non-combustible metal fluorides during combustion. The mass spectral studies of the compounds were carried out using a Micromass Q-TOF instrument. 1,2-Bis(diphenylphosphanyl)ethane^[46] (dppe), bis(diphenylphosphanyl)methane^[47] (dppm), *trans*-[Fe(H)(η^2 -H₂)(dppe)₂][BF₄], *trans*-[Ru(H)(η^2 -H₂)(dppe)₂][BF₄],^[48] *trans*-[Ru(H)(η^2 -H₂)(dppm)₂][BF₄],^[17] and PF₃^[49] were prepared according to literature procedures.

Preparation of *trans*-[Fe(H)(PF₃)(dppe)₂][BF₄] (1**):** *trans*-[Fe(H)(η^2 -H₂)(dppe)₂][BF₄] (0.100 g, 0.1 mmol) was dissolved in CH₂Cl₂ (8 mL) under an atmosphere of H₂. PF₃ gas was then purged through this solution at a steady rate for about 10 min after which time it was stirred for 2 h. Concentration of the reaction mixture to about 2 mL and addition of Et₂O (20 mL) caused the complete precipitation of a cream-colored product of **1**. The product was dried in vacuo and recrystallized from a CH₂Cl₂ solution by slow diffusion of Et₂O over a period of several days. Yield 0.082 g (75%). ES-MS: *m/z* = 941 [*M*⁺ – BF₄], 853 [*M*⁺ – PF₃ + BF₄]. The NMR spectroscopic data of **1** are summarized in Table 1.

Preparation of *trans*-[Ru(H)(PF₃)(diphosphane)₂][BF₄] (diphosphane = dppm **2, dppe **3**):** These compounds were prepared in a similar manner to that of **1** starting from *trans*-[Ru(H)(η^2 -H₂)(diphosphane)₂][BF₄]. Yields of **2** and **3** were 0.075 g (69%) and 0.080 g (73%), respectively. ES-MS of **2**: *m/z* = 871 [*M*⁺ – PF₃ +

BF₄]. ES-MS of **3**: *m/z* = 897 [*M*⁺ – PF₃ + HBF₄]. The NMR spectroscopic data of **2** and **3** are given in Table 1.

Attempt to Prepare *trans*-[Fe(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (4**):** A sample of *trans*-[Fe(H)(PF₃)(dppe)₂][BF₄] (15 mg) was placed in a 5 mm NMR tube capped with a septum. The tube was then evacuated and filled with H₂ in three cycles. The hydride complex was then dissolved in 0.6 mL of CD₂Cl₂ and the solution was frozen in a liquid-nitrogen bath. About 20 μ L (16 equiv.) of triflic acid (HOTf) was added and the tube was warmed up to 273 K slowly. It was then transferred to the NMR probe precooled to 273 K. ¹H NMR spectroscopy revealed a decrease in the intensity of the hydride resonances, whereas the ³¹P{¹H} NMR spectrum showed the appearance of an intense signal at δ = 10.0 ppm due to dppeH⁺. At the same time, the lock signal deteriorated, signaling the formation of some Fe^{III} species. No evidence of the formation of a dihydrogen complex was apparent, although the singlet at δ = 4.6 ppm due to free H₂ increased in intensity. Upon addition of a further 10 μ L (8 equiv.) of HOTf, the lock signal deteriorated further and all the ¹H NMR signals broadened. The intensity of the dppeH⁺ in the ³¹P NMR spectrum increased significantly.

Preparation of *trans*- and *cis*-[Ru(η^2 -H₂)(PF₃)(dppm)₂]²⁺ (5** and **6**):** The preparation of these two complexes was carried out as described above. Upon addition of 30 μ L (60 equiv.) of HOTf the tube was warmed up to 273 K and then transferred to the NMR probe precooled to 273 K. The dihydrogen complexes formed were observed by NMR spectroscopy. The NMR spectroscopic data of **5** and **6** are summarized in Table 3.

Preparation of *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (7**):** The dihydrogen complex **7** was prepared as described above starting from *trans*-[Ru(H)(PF₃)(dppe)₂][BF₄], except that the protonation was carried out at room temperature and a large excess of HOTf (100 μ L, 80 equiv.) was used. The resulting solution was analyzed by NMR spectroscopy. The NMR spectroscopic data of **7** are summarized in Table 3.

Attempted Protonation of *trans*-[Ru(H)(PF₃)(dppe)₂][BF₄] with HCl/HBr/HI/CF₃CO₂H: The protonation of *trans*-[Ru(H)(PF₃)(dppe)₂][BF₄] was attempted with various other acids such as HCl, HBr, HI, and CF₃CO₂H in addition to HOTf as described above. The corresponding dihydrogen complex *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (**7**) was obtained only in the case of HOTf, whereas only the starting hydride was recovered with the other acids. The addition of a large excess of acid (HCl, HBr, HI, and CF₃CO₂H) also did not afford the corresponding dihydrogen complex.

Attempt to Isolate *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (7**):** The dihydrogen complex **7** was prepared as described above. NMR spectroscopy revealed the complete conversion of the starting hydride into the dihydrogen complex. In an attempt to isolate it, excess Et₂O was added to the reaction mixture to precipitate the colorless dihydrogen complex. The supernatant solution was carefully removed with a syringe and the precipitate was washed a few times with Et₂O and then dried under a stream of H₂ gas. The NMR spectrum revealed the presence of only the starting hydride complex *trans*-[Ru(H)(PF₃)(dppe)₂][BF₄] and no other species, suggesting that complete deprotonation had taken place upon addition of Et₂O. The dihydrogen complex was found to be stable with respect to deprotonation only in the presence of a large excess of acid.

Measurement of the Rate Constant for the Decomposition of *trans*-[Ru(η^2 -H₂)(PF₃)(dppe)₂]²⁺ (7**):** A sample of *trans*-[Ru(H)(PF₃)(dppe)₂][BF₄] (6 mg) was placed in a 5 mm NMR tube

capped with a septum. The tube was evacuated and filled with dihydrogen gas in three cycles. The hydride complex was then dissolved in CD_2Cl_2 (0.6 mL). Excess HOTf (15 μL , 30 equiv.) was added and the tube was transferred immediately to the NMR probe. The ^1H and the $^{31}\text{P}\{\text{gated } ^1\text{H}\}$ NMR spectra were recorded at intervals of 30 min. The rate constant for the decomposition of $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ was determined from the integrals of the $\eta^2\text{-H}_2$ signal with respect to the residual CDHCl_2 resonance ($\delta = 5.32$ ppm) in the ^1H NMR spectra and those of the dppe P signal with respect to externally added $[\text{Ph}_3\text{PH}][\text{OTf}]$ ($\delta = 7.11$ ppm) in the $^{31}\text{P}\{\text{gated } ^1\text{H}\}$ NMR spectra. After about 16 h, the NMR spectra showed the formation of dppeH^+ (ca. 40%), $\text{trans-}[\text{Ru}(\text{Cl})(\text{PF}_3)(\text{dppe})_2]^+$ (**8**; ca. 36%), and $\text{trans-}[\text{Ru}(\text{OTf})(\text{PF}_3)(\text{dppe})_2]^+$ (**9**; <5%).

8: ^1H NMR (CD_2Cl_2): $\delta = 3.01$ (m, 4 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 6.81–7.91 (m, 40 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) ppm. ^{19}F NMR (CD_2Cl_2): $\delta = -18.57$ (d, PF_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 64.3$ (d, $J_{\text{P,P}} = 41.0$ Hz, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 127.9 (q quint, $J_{\text{P,F}} = 1308.0$ Hz, PF_3) ppm.

9: ^1H NMR (CD_2Cl_2): $\delta = 2.94$ (m, 2 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 3.13 (m, 2 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 6.81–7.91 (m, 40 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) ppm. ^{19}F NMR (CD_2Cl_2): $\delta = -21.81$ (d, PF_3), -75.70 (br. s, OTf – coordinated) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 46.6$ (d, $J_{\text{P,P}} = 41.3$ Hz, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 132.1 (q quint, $J_{\text{P,F}} = 1312.0$ Hz, PF_3) ppm.

Attempt to Determine the Equilibrium Constant for the Substitution of $\eta^2\text{-H}_2$ with CH_3CN in $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$: The dihydrogen complex $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ was prepared starting from $\text{trans-}[\text{Ru}(\text{H})(\text{PF}_3)(\text{dppe})_2][\text{BF}_4]$ (20 mg) and HOTf (50 μL , 30 equiv.) as described above. After ensuring that the starting hydride complex had been completely converted into the dihydrogen complex, the solution was frozen in a liquid-nitrogen bath. Then, CH_3CN (1 μL , 1 equiv.) was added and the NMR tube was slowly warmed up to 253 K. It was then transferred to the NMR probe precooled to 253 K. NMR spectroscopy revealed the complete disappearance of the resonances due to the dihydrogen complex and the appearance of signals due to the nitrile complex $\text{trans-}[\text{Ru}(\text{CH}_3\text{CN})(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**10**) thus precluding the measurement of the equilibrium constant for the substitution of the coordinated H_2 ligand with CH_3CN .

10: ^1H NMR (CD_2Cl_2): $\delta = 1.45$ (s, 3 H, CH_3CN), 3.05 (m, 4 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 6.91–7.91 (m, 40 H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) ppm. ^{19}F NMR (CD_2Cl_2): $\delta = -13.51$ (d, PF_3), -91.03 (br. s, OTf), -144.62 (br. s, BF_4) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 38.2$ (d, $J_{\text{P,P}} = 42.5$ Hz, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 132.8 (q quint, $J_{\text{P,F}} = 1258.0$ Hz, PF_3) ppm.

Observation of the HD Isotopomers, $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppm})_2]^{2+}$ (5-D₁**), $\text{cis-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppm})_2]^{2+}$ (**6-D₁**), and $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{PF}_3)(\text{dppe})_2]^{2+}$ (**7-D₁**):** The HD isotopomers were prepared using similar procedures as the corresponding H_2 complexes except that appropriate quantities of DOTf were used. The HD isotopomers formed were observed by NMR spectroscopy. The temperature dependent $J_{\text{H,D}}$ data for $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{PF}_3)(\text{dppe})_2]^{2+}$ are summarized in Table 6.

X-ray Crystallographic Study: Colorless crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of $\text{trans-}[\text{Ru}(\text{H})(\text{PF}_3)(\text{dppm})_2][\text{BF}_4]$ (**2**) in an H-tube at room temperature. The unit-cell parameters and intensity data were collected on a Bruker SMART APEX CCD diffractometer equipped with a fine-focus Mo-K_α X-ray source. The SMART software was used for data acquisition and the SAINT software for data abstraction.^[50] Absorption corrections were made using the psi-scans method.^[51]

The structure was solved and refined using the SHELX program suite.^[52] The Ru atom position was located from the Patterson map and the non-hydrogen atoms were located from successive difference-Fourier maps and were refined anisotropically. All other hydrogen atoms were fixed in idealized positions and refined in a riding model. Additional details of data collection and structure refinements are listed in Table 7.

Table 7. Crystallographic data for $\text{trans-}[\text{Ru}(\text{H})(\text{PF}_3)(\text{dppm})_2][\text{BF}_4]$ (**2**)

Formula	$\text{C}_{50}\text{H}_{48}\text{BF}_7\text{O}_2\text{P}_5\text{Ru}$
Mol. wt.	1080.61
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	11.845(5)
b (Å)	16.252(6)
c (Å)	27.617(10)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å ³)	5316(3)
Z	4
D_{calcd} (g/cm ³)	1.350
T (K)	293(2)
λ (Å)	0.71073
μ (mm ⁻¹)	0.506
$R^{\text{[a]}}$	0.0607
$R_w^{\text{[b]}}$	0.1726

^[a] $R = (F_o - F_c)/F_o$. ^[b] $R_w = [w(F_o - F_c)^2/wF_o^2]^{1/2}$ [based on reflections with $I > 2\sigma(I)$].

CCDC-231476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support from the Council of Scientific and Industrial Research, India, is gratefully acknowledged. Acquisition of a 400 MHz NMR spectrometer was supported by the Department of Science and Technology, India, under the “FIST” program.

^[1] P. G. Jessop, R. H. Morris, *Coord. Chem. Rev.* **1992**, 121, 155–284.

^[2] D. M. Heinekey, W. J. Oldham Jr., *Chem. Rev.* **1993**, 93, 913–926.

^[3] P. G. Jessop, R. H. Morris, *Inorg. Chem.* **1993**, 32, 2236–2237.

^[4] M. Schlaf, R. H. Morris, *J. Chem. Soc., Chem. Commun.* **1995**, 625–626.

^[5] N. Mathew, B. R. Jagirdar, R. S. Gopalan, G. U. Kulkarni, *Organometallics* **2000**, 19, 4506–4517.

^[6] N. Mathew, B. R. Jagirdar, *Inorg. Chem.* **2000**, 39, 5404–5406.

^[7] N. Mathew, B. R. Jagirdar, A. Ranganathan, *Inorg. Chem.* **2003**, 42, 187–197.

^[8] K. K. Majumdar, H. V. Nanishankar, B. R. Jagirdar, *Eur. J. Inorg. Chem.* **2001**, 1847–1853.

^[9] M. S. Chinn, D. M. Heinekey, N. G. Payne, C. D. Sofield, *Organometallics* **1989**, 8, 1824–1826.

^[10] M. S. Keady, J. D. Koola, A. C. Ontko, R. K. Merwin, D. M. Roddick, *Organometallics* **1992**, 11, 3417–3421.

- [11] M. Schlaf, A. J. Lough, P. A. Maltby, R. H. Morris, *Organometallics* **1996**, *15*, 2270–2278.
- [12] E. Rocchini, A. Mezzetti, H. Rüegger, U. Burckhardt, V. Gramlich, A. Del Zotto, P. Martinuzzi, P. Rigo, *Inorg. Chem.* **1997**, *36*, 711–720.
- [13] T. P. Fong, C. E. Forde, A. J. Lough, R. H. Morris, P. Rigo, E. Rocchini, T. Stephan, *J. Chem. Soc., Dalton Trans.* **1999**, 4475–4486.
- [14] S. E. Landau, R. H. Morris, A. J. Lough, *Inorg. Chem.* **1999**, *38*, 6060–6068.
- [15] R. M. Chin, J. Barrera, R. H. Dubois, L. E. Helberg, M. Sabat, T. Y. Bartucz, A. J. Lough, R. H. Morris, W. D. Harman, *Inorg. Chem.* **1997**, *36*, 3553–3558.
- [16] The *mer* isomer of this complex was obtained in very small concentrations thus precluding its thorough characterization: R. H. Morris, *personal communication*.
- [17] R. Mathieu, R. Poilblanc, *Inorg. Chem.* **1972**, *11*, 1858–1861.
- [18] P. Meakin, E. L. Muetterties, J. P. Jesson, *J. Am. Chem. Soc.* **1972**, *94*, 5271–5285.
- [19] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 363–469.
- [20] V. F. Bystrov, A. A. Neimysheva, A. U. Stepanyants, I. L. Knu-nyants, *Dokl. Akad. Nauk. SSSR* **1964**, *156*, 637–640; *Chem. Abstr.* **1964**, *61*, 6548c.
- [21] Cone angles: 107° $[\text{P}(\text{OMe})_3] > 106^\circ$ $[\text{PF}(\text{OMe})_2] > 104^\circ$ (PF_3) .^[22]
- [22] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
- [23] T. Fujinaga, I. Sakamoto, *J. Electroanal. Chem.* **1977**, *85*, 185–201.
- [24] G. Perdoncin, G. Scorrano, *J. Am. Chem. Soc.* **1977**, *99*, 6983–6986.
- [25] S. J. Berners-Price, R. E. Norman, P. J. Sadler, *J. Inorg. Biochem.* **1987**, *31*, 197–209.
- [26] M. K. Rottink, R. J. Angelici, *Inorg. Chem.* **1993**, *32*, 2421–2425.
- [27] Characterization of *trans*- $[\text{Ru}(\text{NCCD}_3)(\text{PF}_3)(\text{dppm})_2]^{2+}$. ^1H NMR (CD_2Cl_2): $\delta = 4.91$ (m, 2 H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 5.08 (m, 2 H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 6.48–7.81 (m, 40 H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) ppm. ^{31}P NMR (CD_2Cl_2): $\delta = -13.9$ (d, $J_{\text{P,P}} = 34.4$ Hz, 4 P, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 135.1 (q quint, $J_{\text{P,F}} = 1303.0$ Hz, 1 P, PF_3).
- [28] M. G. Basallote, J. Durán, J. Fernández-Trujillo, M. A. Máñez, *Organometallics* **2000**, *19*, 695–698.
- [29] G. Jia, R. H. Morris, *J. Am. Chem. Soc.* **1991**, *113*, 875–883.
- [30] G. Jia, R. H. Morris, *Inorg. Chem.* **1990**, *29*, 581–582.
- [31] R. M. Bullock, J.-S. Song, D. J. Szalda, *Organometallics* **1996**, *15*, 2504–2516.
- [32] S. Berger, S. Braun, H. -O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, Wiley, Chichester, **1996**, pp. 895–981.
- [33] R. H. Morris, R. Wittebort, *J. Magn. Reson.* **1997**, *35*, 243–250 and references cited therein.
- [34] P. A. Maltby, M. Schlaf, M. Steinbeck, A. J. Lough, R. H. Morris, W. T. Klooster, T. F. Koetzle, R. C. Srivastava, *J. Am. Chem. Soc.* **1996**, *118*, 5396–5407.
- [35] $d_{\text{HH}} = -0.0167J_{\text{H,D}} + 1.42$.
- [36] W. T. Klooster, T. F. Koetzle, G. Jia, T. P. Fong, R. H. Morris, A. Albinati, *J. Am. Chem. Soc.* **1994**, *116*, 7677–7681.
- [37] K. A. Earl, G. Jia, P. A. Maltby, R. H. Morris, *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.
- [38] J. K. Law, H. Mellows, D. M. Heinekey, *J. Am. Chem. Soc.* **2002**, *124*, 1024–1030.
- [39] R. Gelabert, M. Moreno, J. M. Lluch, A. Lledós, *J. Am. Chem. Soc.* **1997**, *119*, 9840–9847.
- [40] D. G. Gusev, R. L. Kuhlman, K. B. Renkema, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1996**, *35*, 6775–6783.
- [41] D. Woska, A. Prock, W. P. Giering, *Organometallics* **2000**, *19*, 4629–4638.
- [42] E. P. Cappellani, S. D. Drouin, G. Jia, P. A. Maltby, R. H. Morris, C. T. Schweitzer, *J. Am. Chem. Soc.* **1994**, *116*, 3375–3388.
- [43] D. F. Shriver, M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley, New York, **1986**.
- [44] S. Herzog, J. Dehnert, K. Luhder, in *Techniques of Inorganic Chemistry* (Ed.: H. B. Johnassen), Interscience, New York, **1969**, vol. VII.
- [45] D. G. Hamilton, R. H. Crabtree, *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.
- [46] J. Chatt, F. A. Hart, *J. Chem. Soc.* **1960**, 1378–1389.
- [47] W. Hewertson, H. R. Watson, *J. Chem. Soc.* **1962**, 1490–1494.
- [48] M. T. Bautista, E. P. Cappellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella, J. Zubkowski, *J. Am. Chem. Soc.* **1991**, *113*, 4876–4887.
- [49] R. J. Clark, H. Belefant, S. M. Williamson, *Inorg. Synth.* **1990**, *28*, 310.
- [50] Bruker SMART and SAINT Versions 6.22a, BRUKER AXS Madison, Wisconsin, USA, **1999**.
- [51] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351–359.
- [52] G. M. Sheldrick, SHELXL-97 Program for the solution of crystal structures, University of Göttingen, Germany.

Received February 17, 2004

Early View Article

Published Online May 25, 2004