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Influence of the Cone Angles and the π-Acceptor Properties of Phosphorus-Containing Ligands in the Chemistry of Dihydrogen Complexes of Ruthenium

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A series of new dicationic dihydrogen complexes of ruthenium of the type *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$) have been prepared by protonating the precursor hydride complexes *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] using HBF$_4$·Et$_2$O. The precursor hydride complexes have been obtained from *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$, P(OEt)$_3$, P(O^{i}Pr)$_3$) via the substitution of a −OR group on the trans phosphorus ligand with a fluoride in the presence of HBF$_4$·Et$_2$O. Coupling of the dihydrogen ligand with the trans phosphorus moiety has been observed. In addition to the complexes bearing trans phosphite groups, the precursor hydrides containing trans phosphine ligands, viz., PMe$_3$ and PMe$_2$Ph, have also been prepared and characterized. It was found that the binding ability of the trans phosphorus ligand in both the hydride and dihydrogen complexes decreases with an increase in the steric congestion of the trans phosphorus moiety. This indicates that the stability of this series of complexes depends on the cone angles of the trans phosphorus ligand. The protonation reactions of the hydride precursors *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$, P(OEt)$_3$, P(O^{i}Pr)$_3$) (under certain experimental conditions in the case of P(O^{i}Pr)$_3$) result in mixtures of the new hydride complexes *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$) and the *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ derivatives. There is a strong dependence on the quantity of the acid used for the isolation of either the new hydrides or the corresponding dihydrogen complexes. Both dihydrogen and the new hydride complexes have been isolated and characterized. On the other hand, the protonation reactions of the starting hydrides that have *trans*-PMe$_3$, PMe$_2$Ph, or P(O^{i}R)$_3$ (under certain experimental conditions) ligands gave a hydride dihydrogen complex, the structure formulation of which could not be established with certainty. The roles of the steric as well as the π-accepting properties of the trans phosphorus ligands in this series of complexes are discussed. X-ray crystal structures of *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$], *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$], and *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OEt)$_2$)][BF$_4$]$_2$ have been determined. *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$) undergoes substitution of the trans phosphorus ligand with H$_2$ to give *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$] reversibly under very mild conditions.

Introduction

The activation of molecular hydrogen by transition-metal complexes is the central theme in catalytic hydrogenation reactions.[1] There have been numerous reports on the nature of the interaction of H$_2$ with a metal center: that is, either as η^2-H$_2$ ("side-on") or as the oxidatively added species, the dihydride. It has been found earlier that the nature of the metal center and the ancillary ligands play very important roles in dictating the equilibrium between these two species.[2,3] The homolytic activation of dihydrogen generates a dihydride, whereas heterolysis provides a metal hydride and a proton equivalent.

Transition-metal centers that are quite electrophilic in nature have been found to greatly promote the activation of dihydrogen toward heterolytic cleavage.[2c,d,4]

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Lau and co-workers[5a] reported dicationic dihydrogen complexes of ruthenium bearing triazacyclononane, trimethyltriazacyclononane, and hydrotris(pyrazolyl)borate as ancillary ligands. They found the dicationic species to be more acidic than the monocationic hydrotris(pyrazolyl)borate and cyclopentadienyl counterparts. A highly acidic and stable dicationic dihydrogen complex, *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(CNH)]^{2+}$, was recently reported by Morris et al.[5b] They found that this complex was only stable with respect to the loss of protons or H_2 under strongly acidic conditions (excess triflic acid). However, it should not be implied that the dicationic dihydrogen complexes would be stronger acids than the monocationic derivatives. Harman and Taube[6] found the dicationic osmium complex $[Os(H_2)(NH_3)_5]^{2+}$ to be a weak acid that was stable toward moderately strong bases such as NaOMe. Recently, Kubas and co-workers[7] reported a highly electrophilic rhenium monocationic species, $[Re(CO)_4(PR_3)]^+$, that was found to bring about activation of H_2 heterolytically. Their aim was to synthesize certain cationic systems that are extremely electrophilic, containing mainly π-acceptor ligands that enhance σ-donation from H_2 to the metal at the cost of back-donation, thus enhancing the tendency of H_2 to undergo heterolysis.

The coordination of molecular hydrogen to a metal center has been achieved in the presence of a large number of different coligands, e.g., phosphines, carbonyls, tris(pyrazolyl)borate, and mixed-ligand systems such as cyclopentadienyl and carbonyl or phosphine and phosphine and nitrogen or oxygen donors, etc. Amendola et al.[8] reported the synthesis of molecular hydrogen complexes of the type $[MH(\eta^2\text{-}H_2)P_4]^+$ of the iron triad containing monodentate phosphite ligands. Bianchini and co-workers[9,10] reported cationic rhodium and cobalt complexes, $[(PP)_3Rh(H_2)]^+$ and $[(PP)_3Co(H_2)]^+$ ($(PP)_3 = P(CH_2CH_2PPh_2)_3$), respectively. Both of these species were formulated as complexes having intact H−H bonds. However, Heinekey et al.[11] showed that in both the complexes the H_2 ligand was in fact oxidatively added rather than being intact. As yet, there are no reports in the literature on dicationic dihydrogen complexes of transition metals where the ancillary ligands are exclusively phosphorus-based ones.

The objective of this work is the synthesis of isostructural dihydrogen complexes of ruthenium consisting of only phosphorus-based ligands of the type *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(P)][BF_4]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$; P = phosphite, phosphine), to study how sensitive the properties of the dihydrogen complexes would be to the changes in the steric as well as the π-accepting abilities of the phosphorus ligand that is trans to the dihydrogen moiety. In addition, we intend to build systems that are capable of activating H_2 in a heterolytic fashion. Since phosphines and especially phosphites are good π-acceptors, one could achieve high electrophilicity on the metal center by having such phosphorus ligands trans to the η^2-H_2 ligand. In the current work, we have attempted to employ certain phosphites, $P(OMe)_3$ (cone angle $\theta = 107°$), $P(OEt)_3$ ($\theta = 109°$), and $P(O^iPr)_3$ ($\theta = 130°$), and phosphines, PMe_3 ($\theta = 118°$), PMe_2Ph ($\theta = 122°$), PBu_3 ($\theta = 132°$), PPh_3 ($\theta = 145°$), and PCy_3 ($\theta = 170°$),[12] as the trans ligands. However, it was found that the starting hydride complexes *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$), in the presence of $HBF_4{\cdot}Et_2O$, undergo substitution of an −OR group of the phosphite ligand with F^- (from the BF_4^- anion) to provide a series of new hydride derivatives with a trans fluorophosphite ligand of the type $PF(OR)_2$. During the preparation of this manuscript, Kubo et al.[13] reported the preparation of certain iron−fluorophosphorane complexes. The fluorophosphorane moiety was formed via a nucleophilic attack of F^- toward a trivalent phosphorus atom that is coordinated to the metal center. It has been reported earlier that a bound dihydrogen ligand often lacks observable coupling to adjacent bound phosphines.[2c,d] During this study we have observed substantial coupling of the dihydrogen ligand with the trans phosphorus which ranges from 49 to 51 Hz.[14] The trans phosphorus ligand in *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ (L = PMe_3, PMe_2Ph, or $P(O^iPr)_3$) undergoes substitution with molecular hydrogen to give *trans*-$[(dppe)_2Ru(H)(\eta^2\text{-}H_2)][BF_4]$ in a reversible fashion under very mild conditions.

Experimental Section

General Procedures. All reactions were carried out under N_2 or Ar at room temperature using standard Schlenk[15] and inert-atmosphere techniques unless otherwise specified. Solvents for the reactions that involved the synthesis of dihydrogen complexes were thoroughly saturated with either Ar or H_2 just before use.

The ^1H and ^{31}P NMR spectral data were obtained using an AMX Bruker 400 MHz instrument. All shifts are reported on the δ scale. 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).[16] The observed and the calcu-

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Table 1. ^1H NMR Spectral Data (δ) of *trans*-[$(dppe)_2Ru(H)(L)][BF_4]$ Complexes in CD_2Cl_2

L (compd no.)	δ(Ru−H)	$J(H,P_{trans})$, Hz	$J(H,P_{cis})$, Hz	δ(CH_2-CH_2)	δ(L)	δ(Ph)
$P(OMe)_3$ (**1**)	−9.27 (d qnt, 1H)	120	20.4	2.67 (m, 4H) 2.23 (m, 4H)	2.76 (d, 9H)	6.71−7.29 (m, 40H)
$P(OEt)_3$ (**2**)	−9.63 (d qnt,1H)	120	20.4	2.62 (m, 4H) 2.23 (m, 4H)	2.99 (q, 6H) 0.73 (t, 9H)	6.95−7.39 (m, 40H)
$P(O^iPr)_3$ (**3**)	−11.07 (d qnt, 1H)	120	22.4	2.72 (m, 4H) 2.47 (m, 4H)	4.13 (m, 3 H) 0.84 (d, 18H)	6.67−7.49 (m, 40H)
PMe_3 (**4**)	−10.81 (d qnt, 1H)	60	20.7	2.55 (m, 4H) 2.24 (m, 4H)	0.34 (d, 9H)	6.86−7.63 (m, 40H)
PMe_2Ph (**5**)	−11.86 (d qnt, 1H)	64	21.6	2.40 (m, 4H) 2.11 (m, 4H)	0.58 (d, 6H)	6.56−7.71 (m, 45H)

Table 2. $^{31}P\{^1H\}$ NMR Spectral Data (δ) of *trans*-[$(dppe)_2Ru(H)(L)][BF_4]$ Complexes in CD_2Cl_2

	δ(P)		
compd no.	L	dppe	J(P,P), Hz
1	133 (qnt, 1P)	61.89 (d, 4P)	32.2
2	132.23 (qnt, 1P)	61.25 (d, 4P)	32.4
3	127.7 (qnt, 1P)	59.99 (d, 4P)	32.4
4	−37.75 (qnt, 1P)	60.11 (d, 4P)	21.4
5	−25.75 (qnt, 1P)	58.63 (d, 4P)	17.5

lated T_1 data for the complexes are summarized in Table 7. All ^{31}P NMR spectra were proton-decoupled, unless otherwise stated. ^{31}P NMR chemical shifts have been measured relative to 85% H_3PO_4 in CD_2Cl_2. ^{19}F NMR spectra were recorded with respect to $CFCl_3$ in CD_2Cl_2. Elemental analyses were carried out at the National Chemical Laboratory, Pune, India. 1,2-Bis(diphenylphosphino)ethane[17] (dppe) and *trans*-[$(dppe)_2Ru(H)(\eta^2-H_2)][BF_4]$[18] were prepared according to literature procedures.

Preparation of *trans*-[$(dppe)_2Ru(H)(P(OMe)_3)][BF_4]$ (1). *trans*-[$(dppe)_2Ru(H)(\eta^2-H_2)][BF_4]$ (0.25 g, 0.25 mmol) was dissolved in 7 mL of CH_2Cl_2 under 1 atm of H_2. Then $P(OMe)_3$ (0.09 mL, 0.5 mmol) was added dropwise using a syringe over a period of 1 min with stirring. The reaction mixture turned color from bright orange to pale yellow soon after the addition was over. This solution was stirred at room temperature overnight under a hydrogen atmosphere, after which time it was filtered through a Celite pad on a filter frit under an atmosphere of nitrogen. The volume of the filtrate was reduced to ca. 1 mL. Addition of excess diethyl ether caused the precipitation of a colorless solid that was washed with diethyl ether (10 × 5 mL) and dried in vacuo. Yield: 0.29 g, 81%. Anal. Calcd for $C_{55}H_{58}BF_4RuP_5\cdot CH_2Cl_2$: C, 56.29; H, 5.06. Found: C, 56.88; H, 5.41. The NMR spectral data are summarized in Tables 1 and 2.

Preparation of *trans*-[$(dppe)_2Ru(H)(P(OEt)_3)][BF_4]$ (2). This complex was prepared using a procedure similar to the one that was employed for **1**. The yield of the colorless product obtained was 82%. Anal. Calcd for $C_{58}H_{64}BF_4RuP_5$: C, 60.47; H, 5.6. Found: C, 59.96; H, 5.72. The NMR spectral data are summarized in Tables 1 and 2.

Preparation of *trans*-[$(dppe)_2Ru(H)(P(O^iPr)_3)][BF_4]$ (3). A procedure similar to the one that was used for **1** was employed for the preparation of compound **3**, except that after the reaction mixture was stirred for a period of 30 min under a hydrogen atmosphere, nitrogen was introduced and the stirring was continued overnight. A cream-colored product was obtained upon workup of the reaction mixture. Yield: 80%. The product always contained certain impurities, and purification procedures resulted in partial decomposition of the product. Anal. Calcd for $C_{61}H_{70}BF_4RuP_5\cdot CH_2Cl_2$: C, 58.22; H, 5.67. Found: C, 59.28; H, 5.82. The NMR spectral data are summarized in Tables 1 and 2.

Preparation of *trans*-[$(dppe)_2Ru(H)(PMe_3)][BF_4]$ (4). This complex was prepared in the same manner as for complex **1**, except that the workup procedure was carried out exclusively under an atmosphere of H_2. Upon workup, a cream-colored product was obtained, which was crystallized from a $CH_2Cl_2-Et_2O$ mixture. Yield: 85%. Anal. Calcd for $C_{55}H_{58}BF_4P_5Ru\cdot 0.5CH_2Cl_2$: C, 60.36; H, 5.38. Found: C, 60.53; H, 5.15. The NMR spectral data are summarized in Tables 1 and 2.

Preparation of *trans*-[$(dppe)_2Ru(H)(PMe_2Ph)][BF_4]$ (5). This complex was also prepared using a procedure similar to the one employed for the preparation of **4**. A cream-colored product resulted upon workup of the reaction mixture. Yield: 80%. Anal. Calcd for $C_{60}H_{60}BF_4P_5Ru\cdot 3CH_2Cl_2$: C, 54.83; H, 4.82. Found: C, 55.32; H, 4.40. The NMR spectral data are summarized in Tables 1 and 2.

Attempt To Prepare *trans*-[$(dppe)_2Ru(H)(PBu_3)][BF_4]$. A procedure similar to that employed for the preparation of **1** was used for the synthesis of this complex. Upon workup of the reaction mixture, a yellow powder resulted whose spectroscopic properties were similar to the compound of the formula *trans*-[$(dppe)_2Ru(H)Cl$] (**6**) reported earlier.[19]

Attempts To Prepare *trans*-[$(dppe)_2Ru(H)(PPh_3)][BF_4]$ and *trans*-[$(dppe)_2Ru(H)(PCy_3)][BF_4]$. A 5 mm NMR tube was charged with 20 mg (0.02 mmol) of *trans*-[$(dppe)_2Ru(H)(\eta^2-H_2)][BF_4]$, which was dissolved in 0.7 mL of CD_2Cl_2 under 1 atm of argon. The tube was maintained under argon pressure, using an inlet needle through a septum. Then 1 equiv (0.02 mmol) of PPh_3/PCy_3 was added to the tube by briefly removing the septum under argon pressure. The tube was then capped and the ^1H NMR spectrum recorded. No change from the starting spectrum took place. The tube was then shaken continuously, and at regular intervals of time, ^1H NMR spectra were recorded. Substitution of the dihydrogen ligand with the phosphine did not take place even after 48 h at room temperature.

Protonation Reaction of *trans*-[$(dppe)_2Ru(H)(L)][BF_4]$ (L = $P(OEt)_3$). A 20 mg portion (0.017 mmol) of *trans*-[$(dppe)_2Ru(H)(P(OEt)_3)][BF_4]$ was dissolved in 0.7 mL of CD_2Cl_2 in a 5 mm NMR tube that was capped with a septum. The resulting solution was subjected to three cycles of freeze−pump−thaw degassing. One atmosphere of argon gas was then introduced into the tube. Two equivalents (0.03 mmol) of 54% $HBF_4\cdot Et_2O$ was added to this solution and the ^1H NMR spectrum recorded. Thereafter, the concentration of the acid added was increased in increments of 2 equiv each time. The new hydride complex *trans*-[$(dppe)_2Ru(H)(L')][BF_4]$ (L′ = $PF(OEt)_2$) was observed soon after 2 equiv of the acid was added. In the presence of excess acid, the dihydrogen complex *trans*-[$(dppe)_2Ru(\eta^2-H_2)(L')][BF_4]_2$ was obtained. Complete conversion of the hydride complex to the dihydrogen complex took place after the addition of ca. 30 equiv of the acid.

Preparation of *trans*-[$(dppe)_2Ru(H)(L')][BF_4]$ (L′ = $PF(OMe)_2$ (7), $PF(OEt)_2$ (8)). Similar procedures were employed for the preparation of both these complexes. As a

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Table 3. ^{1}H NMR Spectral Data (δ) of *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] Complexes in CD$_2$Cl$_2$

L′ (compd no.)	δ(Ru−H)	J(H,P$_{trans}$),Hz	J(H,P$_{cis}$), Hz	J(H,F), Hz	δ(CH$_2$CH$_2$)	δ(L′)	δ(Ph)
PF(OMe)$_2$ (**7**)	−8.3 (d sex, 1H)	136.0	20	24	2.63 (m, 4H) 2.25 (m, 4H)	2.79 (d, 6H)	6.66−7.22 (m, 40H)
PF(OEt)$_2$ (**8**)	−8.24 (d sex, 1H)	136.0	20.6	24	2.62 (m, 4H) 2.25 (m, 4H)	3.17 (m, 4H) 0.54 (t, 6H)	6.70−7.28 (m, 40H)
PF(O^{i}Pr)$_2$ (**9**)	−8.78 (d sex, 1H)	132.0	21.2	21.5	2.66 (m, 4H) 2.30 (m, 4H)	4.02 (m, 2H) 0.78 (d, 12H)	6.79−7.25 (m, 40H)

Table 4. ^{31}P{^{1}H} and ^{19}F NMR Spectral Data (δ) of *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] Complexes in CD$_2$Cl$_2$

	δ(P)			δ(F)		
compd no.	dppe	L′	J(P,P), Hz	BF$_4$	L′	J(P,F), Hz
7	62.28 (d, 4P)	134.22 (d qnt, 1P)	32.9	−33.85 (s, 4F)	71.70 (d, 1F)	1158.2
8	61.86 (d, 4P)	134.75 (d qnt, 1P)	32.4	−33.97 (s, 4F)	76.08 (d, 1F)	1142
9	61.42 (d, 4P)	134.85 (d qnt, 1P)	32.2	−31.41 (s, 4F)	86.78 (d, 1F)	1140.3

Table 5. ^{1}H NMR Spectral Data (δ) of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ Complexes in CD$_2$Cl$_2$

L′ (compd no.)	δ(Ru(η^2-H$_2$))	J(H,P$_{trans}$), Hz	δ(CH$_2$CH$_2$)	δ(L′)	δ(Ph)
PF(OMe)$_2$ (**10**)[a]	−5.12 (d, 2H)	50.4	3.04 (m, 4H) 2.75 (m, 4H)	3.23 (d, 6H)	6.27−7.31 (m, 40H)
PF(OEt)$_2$ (**11**)	−5.24 (d, 2H)	50.9	3.07 (m, 4H) 2.79 (m, 4H)	3.64 (m, 4H) 0.76 (t, 6H)	6.7−7.74 (m, 40H)
PF(O^{i}Pr)$_2$ (**12**)	−5.63 (d, 2H)	49.5	2.84 (m, 4H) 3.13 (m, 4H)	4.41 (m, 2H) 0.94 (d, 12H)	6.78−7.45 (m, 40H)

[a] From ref 14f.

Table 6. ^{31}P{^{1}H} and ^{19}F NMR Spectral Data (δ) of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ Complexes in CD$_2$Cl$_2$

	δ(P)			δ(F)		
compd no.	L′	dppe	J(P,P), Hz	L′	J(P,F), Hz	BF$_4$
10[a]	125.29 (d qnt, 1P)	48.56 (d, 4P)	43.3	73.97 (d, 1F)	1158.2	−29.67 (br s, 8F)
11	124.94 (d qnt, 1P)	48.04 (d, 4P)	42.8	79.36 (d, 1F)	1148.4	−28.91 (br s, 8F)
12	123.14 (d qnt, 1P)	47.54 (d, 4P)	42.4	91.24 (d, 1F)	1153.3	−27.17 (br s, 8F)

[a] From ref 14f.

representative example, the preparation of *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] will be described here. *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (0.2 g, 1.8 mmol) was dissolved in CH$_2$Cl$_2$ (6 mL) under 1 atm of argon. To this solution was added 5 equiv (9 mmol) of 54% HBF$_4$·Et$_2$O dropwise using a syringe. The addition of HBF$_4$·Et$_2$O led to a color change of the solution from colorless to yellow. The reaction mixture was stirred for a period of 4 h, after which time nitrogen was introduced. The solution was stirred under these conditions overnight. The yellow solution was then filtered through a Celite pad on a filter frit, and the filtrate was concentrated to ca. 1 mL. Addition of excess diethyl ether caused the precipitation of a pale yellow solid that was washed several times with diethyl ether to remove the excess HBF$_4$·Et$_2$O, and the product was dried in vacuo. The sample was crystallized from a CH$_2$Cl$_2$ solution via slow diffusion of Et$_2$O at room temperature for several days. Yield: 81%. Anal. Calcd for C$_{54}$H$_{55}$BF$_5$O$_2$P$_5$Ru·0.5CH$_2$Cl$_2$ (**7**): C, 57.4; H, 4.95. Found: C, 57.63; H, 5.12. Calcd for C$_{56}$H$_{59}$BF$_5$O$_2$P$_5$Ru·0.5CH$_2$Cl$_2$ (**8**): C, 58.08; H, 5.18. Found: C, 57.35; H, 4.80.

The NMR spectral data of these two derivatives are summarized in Tables 3 and 4.

Preparation of *trans*-[(dppe)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$] (9). To a solution of *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$] (0.2 g, 0.2 mmol) in CH$_2$Cl$_2$ (6 mL) under 1 atm of H$_2$ were added excesses of both 54% HBF$_4$·Et$_2$O and P(O^{i}Pr)$_3$. The reaction mixture was then stirred under an atmosphere of H$_2$ for a period of 12 h, after which time nitrogen was introduced for the workup procedure. *trans*-[(dppe)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$] (**9**) was obtained as a cream-colored product in a yield of 82%, which was crystallized from a CH$_2$Cl$_2$ solution via slow diffusion of Et$_2$O at room temperature over a period of several days. Anal. Calcd for C$_{58}$H$_{63}$BF$_5$O$_2$P$_5$Ru·0.5CH$_2$Cl$_2$: C, 58.72; H, 5.39. Found: C, 59.08; H, 5.99. The NMR spectral data of this complex are given in Tables 3 and 4.

Preparation of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$ (10), PF(OEt)$_2$ (11), PF(O^{i}Pr)$_2$ (12)). Similar procedures were employed for the preparation of all of these complexes. A 20 mg portion of *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] was dissolved in 0.7 mL of CD$_2$Cl$_2$ in a 5 mm NMR tube provided with a septum. It was then subjected to three freeze−pump−thaw cycles, after which argon gas was introduced. Then ca. 10 equiv of 54% HBF$_4$·Et$_2$O was added. The dihydrogen complexes formed were characterized using NMR spectroscopy. The NMR spectral data are summarized in Tables 5 and 6.

The same reactions were carried out on a preparative scale in order to attempt the isolation of the dihydrogen complexes. As a representative example, the isolation of the PF(OEt)$_2$ complex will be described. Upon addition of a large excess (ca. 40 equiv) of 54% HBF$_4$·Et$_2$O to a solution of *trans*-[(dppe)$_2$Ru(H)(PF(OEt)$_2$)][BF$_4$] (0.15 g, 0.13 mmol) in CH$_2$Cl$_2$ under 1 atm of argon, a reddish orange solution resulted. The product was allowed to crystallize from the reaction mixture by slow diffusion of diethyl ether at room temperature over a period of several days. Red crystals were obtained that were handled under an atmosphere of argon and were found to be extremely sensitive with respect to loss of H$_2$.

Note: In the preparation of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$, a very large excess of the protonating agent was used.

Protonation Reactions of *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$). A 5 mm NMR tube was charged with 20 mg of *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$], which was dissolved in 0.7 mL of CD$_2$Cl$_2$. The resulting solution was subjected to three cycles of freeze−pump−thaw degassing. One atmosphere of argon gas was then introduced into the tube. About 1 equiv of 54% HBF$_4$·Et$_2$O was added to this solution, and the ^{1}H NMR spectrum was recorded, which gave an

Table 7. Observed and Calculated Spin−Lattice Relaxation Times (T_1, ms; 400 MHz) of the Dihydrogen Ligand in the Complexes *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$ (10), PF(OEt)$_2$ (11), PF(O^{i}Pr)$_2$ (12)) in CD$_2$Cl$_2$[a]

	T_1(**10**)[b]		T_1(**11**)		T_1(**12**)	
T, K	obsd	calcd	obsd	calcd	obsd	calcd
305					19.19	18.86
302					18.61	18.52
298	18.04	18	18.33	18.31	17.60	18.12
283	17.32	17.12	17.75	17.44	*17.03*	*17.20*
268	*16.6*	*16.94*	*16.74*	*17.25*	17.89	17.35
253	18.04	17.68	18.47	17.98	19.05	18.95
243	18.76	18.88	19.05	19.17	21.36	21.20
233	20.92	20.88	21.36	21.15	24.53	24.89
223	24.53	24.04	24.10	24.27	30.88	30.75
213	28.86	28.91	30.30	29.08	42.13	39.97
203	36.07	36.39	35.35	36.43		

[a] Italicized data indicate T_1 minima. [b] From ref 14f.

indication of the formation of a hydride dihydrogen complex (**13**).[20] Upon further addition of HBF$_4$·Et$_2$O in increments of 1 equiv each time, the ^{1}H NMR spectrum indicated the presence of another dihydrogen complex; the structure formulations of these two species could not be established with certainty. Formation of the dihydrogen complex *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$) was not observed.

Observation of the H−D Isotopomers of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$ (14), PF(OEt)$_2$ (15), PF(O^{i}Pr)$_2$ (16)). D$_2$ gas was purged through a solution containing a mixture of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (major) and *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$]$_2$ in CD$_2$Cl$_2$ in a 5 mm NMR tube for ca. 10 min. The H−D isotopomer formed was observed by ^{1}H NMR spectroscopy. The *J*(H,D) values obtained for the complexes **14**−**16** are respectively 29, 28, and 27 Hz.

X-ray Structure Determination of *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (1) and *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] (7). High-quality crystals of the complexes **1** and **7** were chosen after examination under an optical microscope and coated with epoxy before mounting. X-ray diffraction intensities were measured by ω scans using a Siemens three-circle diffractometer attached to a CCD area detector and a graphite monochromator for the Mo Kα radiation (50 kV, 40 mA). The crystal of **7** was cooled to 130 K on the diffractometer using a stream of cold nitrogen gas from a vertical nozzle, and this temperature was maintained throughout the data collection. In the case of **1**, the data collection was carried out at room temperature. The unit cell parameters and the orientation matrix of the crystal were initially determined using ca. 60 reflections from 25 frames collected over a small ω scan of 7.5° sliced at 0.3° interval. A hemisphere of reciprocal space was then collected using the SMART software[21] with 2θ setting of the detector at 28°. Data reduction was performed using the SAINT program,[21] and the orientation matrix along with the detector and the cell parameters were refined for every 40 frames on all the measured reflections. The crystal data parameters are listed in Table 8. An empirical absorption correction based on symmetry-equivalent reflections was applied using the SADABS program,[22] taking the merged reflection file obtained from SAINT as the input. The correct Laue group of the crystal was chosen for the absorption correction. The R_{int} values before and after the absorption corrections were 0.1312 and 0.0597 and 0.1143 and 0.1096 for the complexes **1** and **7**, respectively.

Table 8. Crystallographic Data for *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (1) and *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] (7)

	1	7
formula	$C_{56}H_{59}BCl_2F_4O_5P_5Ru$	$C_{54.40}H_{54}BF_5O_{2.40}P_5Ru$
fw	1225.66	1107.91
cryst syst	orthorhombic	monoclinic
space group	*Fdd*2 (No. 43)	*P*2$_1$/*n* (No. 14)
a, Å	36.134(7)	12.4134(1)
b, Å	52.258(14)	23.4229(1)
c, Å	12.951(2)	19.0126(3)
α, deg	90	90
β, deg	90	106.384(1)
γ, deg	90	90
V, Å^3	24455.8(89)	5303.58(10)
Z	16	4
D_{calcd}, g/cm^3	1.332	1.388
T, K	298	130
λ, Å	0.710 73	0.710 73
μ, mm^{-1}	0.530	0.505
R^a	0.0625	0.0654
$R_w{}^a$	0.1592	0.1416

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

The phase problem was solved by the Patterson method, and the non-hydrogen atoms were refined anisotropically, by means of full-matrix least-squares procedures using the SHELXTL program.[23] Hydrogen atoms other than those on ruthenium were fixed and were refined isotropically.

X-ray Structure Determination of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OEt)$_2$)][BF$_4$]$_2$ (11). We experienced certain difficulties in this case during data collection and analysis. The main problem was that the crystals had cracks in them and were found to be quite unstable with respect to decomposition. Therefore, it was necessary to coat them with polyacrylate adhesive before mounting. A small portion possibly devoid of cracks was cut from a crystal and mounted on a glass fiber. The data were collected at 130 K in order to bring down any thermal disorder in the BF$_4^-$ counterion. Although the hydrogen atoms could not be located, the presence of two BF$_4^-$ anions indicates that the complex is a dicationic dihydrogen complex. Some residual density (peak, 2.172 e Å^{-3}; hole, −1.282 e Å^{-3}) near BF$_4^-$ exists which could not be identified with certainty. The crystal data parameters, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for this complex have been deposited in the Supporting Information.

Results and Discussion

Synthesis and Characterization of the New Ruthenium Hydride Complexes. The new ruthenium hydride complexes *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$, P(OEt)$_3$, P(O^{i}Pr)$_3$, PMe$_3$, PMe$_2$Ph) were prepared from *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$] by substituting the dihydrogen ligand with a phosphite or the phosphine ligand, analogous to the preparation of *trans*-[(dppe)$_2$Os(H)(CH$_3$CN)][BF$_4$] reported by Schlaf et al.[24] (eq 1). All the reactions provide the products in good yields. The products are all colorless to pink solids. The compounds have been purified by crystallization from CH$_2$Cl$_2$−Et$_2$O solutions in the presence of a small excess of the appropriate phosphite or phosphine in the crystallization solution. We have observed that the phos-

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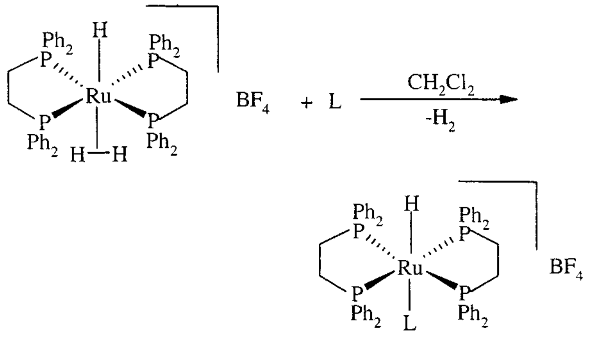
[20] ^{1}H NMR spectral data (CD$_2$Cl$_2$) for (**13**): δ −10.26 (q, 1H, Ru−*H*, *J*(H,P$_{cis}$) = 18 Hz), −4.90 (br s, 2H, η^2-*H*$_2$), 2.32 (m, 4H, C*H*$_2$CH$_2$), 2.83 (m, 4H, CH$_2$C*H*$_2$), 6.46−7.77 (m, 40H, P*Ph*$_2$). (a) T_1 (400 MHz, CD$_2$Cl$_2$, 298 K): hydride, 310 ms; dihydrogen ligand, 27 ms. (b) T_1(min) (240 K): dihydrogen ligand, 18.04 ms; *J*(H,D) = 27 Hz.

[21] Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

[22] Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, Germany, 1993.

[23] SHELXTL (SGI version); Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

[24] Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270.



(1)

L = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**), $P(O^iPr)_3$ (**3**), PMe_3 (**4**), PMe_2Ph (**5**)

phite or the phosphine ligand in the hydride phosphite/phosphine complex to be quite labile, and in the absence of an excess phosphite or phosphine in the crystallization mixture, the hydride complex undergoes loss of the phosphorus ligand, yielding intractable products.

In the preparation of the triisopropyl phosphite hydride complex we always obtained mixtures of *trans*-$[(dppe)_2Ru(H)(P(O^iPr)_3)][BF_4]$ and *trans*-$[(dppe)_2Ru(H)(PF(O^iPr)_2)][BF_4]$ (mechanism of the formation of this compound is elucidated in the later sections). When appropriate reaction conditions are employed, either one of the products can be obtained exclusively, as mentioned in the Experimental Section.

The ^1H NMR spectra of the complexes show doublet of quintets for the hydride ligand, confirming the coupling of the hydride with trans phosphorus (phosphite or phosphine) and the cis phosphorus (dppe) ligands. Whereas the trans coupling with the phosphorus has been found to be on the order of 120 Hz for the complexes containing phosphite ligands, the $J(H,P_{trans})$ values are considerably reduced, 60 and 64 Hz in the cases of PMe_3 and PMe_2Ph hydride complexes, respectively. Phosphites, in general, have been found to exhibit larger couplings to other nuclei than phosphines in metal complexes.[25] This has been attributed to an increase in the "s" character of the bonding orbitals in phosphite complexes compared to that in phosphines. On the other hand, the $J(H,P)$ values for the cis phosphorus atoms range from 20 to 22 Hz. The $^{31}P\{^1H\}$ NMR spectra consist of only one doublet ($J(P,P)$ ranging from 17 to 32 Hz) for the dppe phosphorus nuclei, indicating all four phosphorus nuclei to be equivalent and split by the phosphite/phosphine ligand, and a quintet corresponding to the phosphite or the phosphine ligand coupled to the four dppe phosphorus nuclei.

We have found that the phosphorus ligand in the case of *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ (L = PMe_3, PMe_2Ph, $P(O^iPr)_3$, PBu_3) (cone angles of 118, 122, 130, and 132°, respectively), is relatively loosely bound in comparison to the complexes where L = $P(OMe)_3$, $P(OEt)_3$ (cone angles of 107 and 109°, respectively). In fact, the *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ (L = PMe_3, PMe_2Ph, $P(O^iPr)_3$) complexes undergo substitution of the phosphine/phosphite ligand with molecular hydrogen under very mild conditions (see the following sections). We were unable to isolate the PBu_3 hydride derivative. The phosphine in this case is quite labile toward substitution. A complex of the formula *trans*-$[(dppe)_2Ru(H)Cl]$ that has been previously reported[19] only was obtained in an attempt to isolate the PBu_3 hydride. The solvent CH_2Cl_2 is the source of the chloride in this case. However, attempts to prepare the PPh_3 and PCy_3 hydride derivatives failed and the starting hydride−dihydrogen complex only was left behind. This is due to the greater steric crowding (cone angles of 145 and 170°, respectively) in the resulting complexes. Therefore, we sought to examine the crystal structure of one of the hydride complexes, *trans*-$[(dppe)_2Ru(H)(P(OMe)_3)][BF_4]$, in order to obtain some insight regarding the cavity formed by the sterically encumbered $[(dppe)_2Ru(H)]^+$ fragment which eventually will help us in choosing the appropriate ligands for the preparation of the dihydrogen complexes with desired properties.

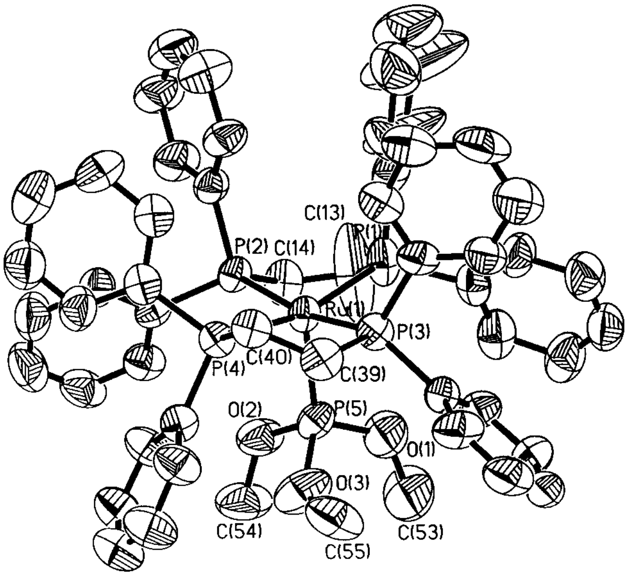


Figure 1. ORTEP view of the *trans*-$[(dppe)_2Ru(H)(P(OMe)_3)]^+$ (**1**) cation at the 50% probability level.

Structure of *trans*-$[(dppe)_2Ru(H)(P(OMe)_3)][BF_4]$ (1). The structure of the cation is shown in Figure 1. It consists of a square pyramid defined by the four dppe phosphorus atoms and the $P(OMe)_3$ moiety with certain deviations from an ideal square-pyramidal geometry. In addition to a discrete BF_4^- counterion a molecule of CH_2Cl_2 and two water molecules (this compound was found to be stable toward air and moisture; therefore, adequate precautions were not taken to exclude moisture from the solvent, which could be the source of water molecules) are also present. The hydride ligand that completes the sixth coordination site on the ruthenium center was not located; however, ^1H NMR spectroscopy provides evidence of its presence. The four phosphorus atoms of the dppe ligand define a square plane with a small mean deviation of 0.02°. The ruthenium atom is slightly displaced from this plane by 0.241 Å and is closer to the phosphite phosphorus atom. The dppe bite angles P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are 78.07(7) and 84.59(7)°, respectively. The Ru−P (of dppe) bond distances vary between 2.351(2) and 2.381(2) Å, and the Ru−P distance (of $P(OMe)_3$) is 2.337(2) Å. The

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[25] (a) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spectroscopy of the Non-Metallic Elements*; Wiley: Chichester, U.K., 1996; pp 895−981, and references therein. For comparative phosphite−X and phosphine−X couplings in transition metal complexes, see: (b) George, T. A.; Sterner, C. D. *Inorg. Chem.* **1976**, *15*, 165. (c) Garrou, P. E.; Hartwell, G. E. *Inorg. Chem.* **1976**, *15*, 646. (d) Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 3574. (e) Guesmi, S.; Taylor, N. J.; Dixneuf, P. H.; Carty, A. J. *Organometallics* **1986**, *5*, 1964.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (1)

Ru(1)−P(5)	2.337(2)	P(5)−O(1)	1.577(7)
Ru(1)−P(4)	2.351(2)	P(5)−O(2)	1.606(7)
Ru(1)−P(3)	2.370(2)	P(5)−O(3)	1.629(8)
Ru(1)−P(2)	2.374(2)	O(1)−C(53)	1.454(13)
Ru(1)−P(1)	2.381(2)	O(2)−C(54)	1.416(10)
		O(3)−C(55)	1.373(13)
P(5)−Ru(1)−P(4)	97.50(7)	P(3)−Ru(1)−P(1)	98.31(8)
P(5)−Ru(1)−P(3)	97.38(9)	P(2)−Ru(1)−P(1)	78.07(7)
P(4)−Ru(1)−P(3)	84.59(7)	O(1)−P(5)−O(2)	105.9(4)
P(5)−Ru(1)−P(2)	93.41(8)	O(1)−P(5)−O(3)	102.0(4)
P(4)−Ru(1)−P(2)	96.55(7)	O(2)−P(5)−O(3)	92.3(4)
P(3)−Ru(1)−P(2)	168.91(8)	O(1)−P(5)−Ru(1)	114.7(3)
P(5)−Ru(1)−P(1)	95.37(9)	O(2)−P(5)−Ru(1)	113.5(2)
P(4)−Ru(1)−P(1)	166.33(8)	O(3)−P(5)−Ru(1)	125.1(3)

phosphorus−oxygen bond distances of the phosphite moiety fall in the range 1.577(7)−1.629(8) Å. The phosphite ligand is not perfectly perpendicular to the square plane defined by the four dppe phosphorus atoms; it is somewhat tilted toward P(2). However, the tilt is not really very appreciable. There are large deviations from an idealized tetrahedral geometry around the phosphite P atom. The selected bond lengths and angles have been summarized in Table 9.

Protonation Reaction of the Hydride Complex *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = P(OEt)$_3$). The protonation reaction of the hydride complex was carried out in CD$_2$Cl$_2$ using excess HBF$_4$·Et$_2$O under 1 atm of either dihydrogen or argon. The ^{1}H NMR spectrum of the hydride region showed two sets of signals consisting of a doublet of sextets (that are further split; see text later) and a broad doublet corresponding to a mixture of two products in major amounts. In accordance with the variable-temperature T_1 relaxation times (400 MHz; 9 equiv of HBF$_4$ added: see Table 7 for the T_1 data), the doublet of sextets has been assigned to a new hydride complex (the T_1 data for the PF(OR)$_2$ hydrides has been deposited in the Supporting Information), whereas the broad doublet has been assigned to the dihydrogen complex. A titration with an increasing number of equivalents of HBF$_4$·Et$_2$O was carried out. Initially with 2 equiv of the acid, only the new hydride (doublet of sextets centered at −8.24 ppm) was obtained (Figure 2). However, a small amount of the dihydrogen complex (a broad doublet centered at −5.20 ppm) begins to emerge with an increase in the concentration of the acid. In the presence of a large excess of HBF$_4$·Et$_2$O, the major product is the dihydrogen complex. Another new overlapping doublet of quintets centered at −9.39 ppm that is further split (J = 68.1 Hz) arises upon addition of 2 equiv of the acid to the starting hydride complex. The concentration of this species is small. From the coupling constants it is clear that a phosphine P atom is trans to the hydride, indicating an isomerized hydride derivative in the presence of 2 equiv of the acid. The origin of the isomerization reaction is not clear. This hydride complex upon protonation gives rise to the corresponding minor isomer of the dihydrogen complex (−6.0 ppm, br d).

The protonation reaction of *trans*-[(dppe)$_2$Ru(H)-(P(OEt)$_3$)][BF$_4$] was carried out on a preparative scale with 2 equiv of HBF$_4$·Et$_2$O, and the major new hydride complex was isolated as pale yellow crystals. The ^{1}H NMR spectrum of this species showed a doublet of sextets pattern in the hydride region (centered at −8.24 ppm) that is further split. The separation between these two sextets corresponds to 136 Hz. The ^{1}H{^{31}P} NMR spectrum gave a doublet centered at −8.24 ppm. A doublet of quintets centered at 134.75 ppm was obtained in the ^{31}P{^{1}H} NMR spectrum corresponding to the phosphite phosphorus, in addition to the doublet centered at 61.86 ppm for the dppe phosphorus. The separation between the two quintets is equal to 1142 Hz. We found that J(P,F) falls in the range of 900−1300 Hz for compounds having a direct P−F bond.[26] The new hydride complex, thus, can be formulated as having a fluoride on the phosphite: that is, *trans*-[(dppe)$_2$Ru(H)-(L′)][BF$_4$], where L′ = PF(OEt)$_2$. This formulation seemed quite reasonable, and the coupling constants are as follows: $^2J(\mathrm{H,P_{trans}}) = 136$ Hz, $^2J(\mathrm{H,P_{cis}}) = 20$ Hz, $^1J(\mathrm{P,F}) = 1142$ Hz, and $^3J(\mathrm{H,F}) = 24$ Hz. Using an NMR simulation program,[27] the hydride region was simulated, which matched the observed spectrum. The coupling of the hydride with the fluorine is shown in Figure 3. To prove this structure formulation, we sought to obtain the X-ray crystal structure of one of these complexes. And indeed, X-ray crystallography revealed without any ambiguity that the new hydride complex was *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$], where L′ = PF(OMe)$_2$.

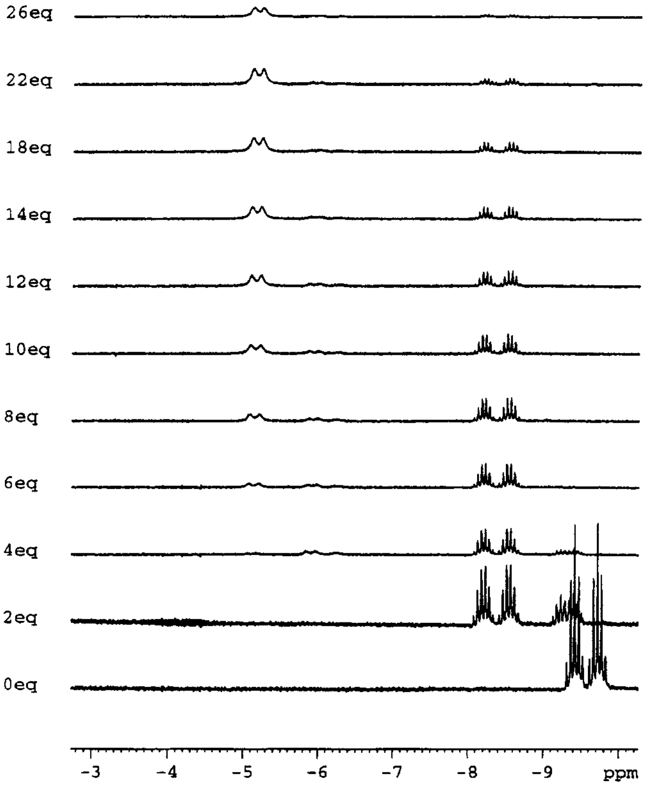

Figure 2. Protonation reaction of *trans*-[(dppe)$_2$Ru(H)-(P(OEt)$_3$)][BF$_4$] (**2**) in CD$_2$Cl$_2$ showing the hydride region of the ^{1}H NMR spectrum. The number of equivalents of HBF$_4$·Et$_2$O added with respect to the starting hydride complex is indicated on the left of each spectrum.

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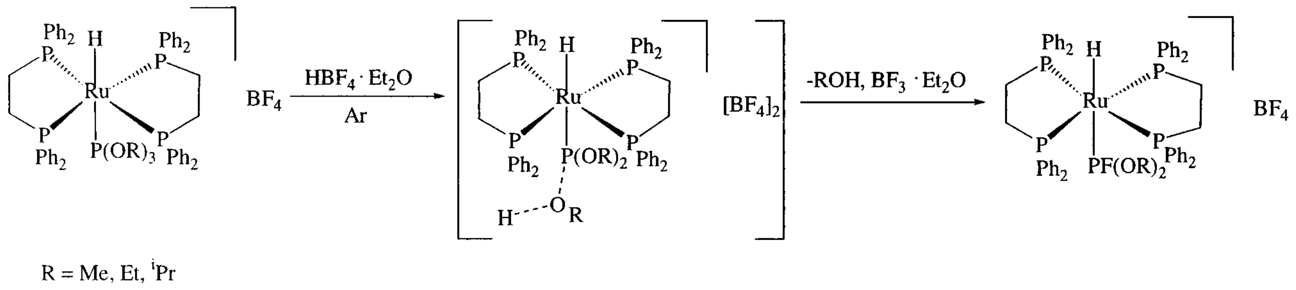
(26) (a) Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1972**, *11*, 1858. (b) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5271. (c) Nixon, J. F. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 363. (d) Bystrov, V. F.; Neimysheva, A. A.; Stepanyants, A. U.; Knunyants, I. L. *Dokl. Akad. Nauk SSSR* **1964**, *156*, 637; *Chem. Abstr.* **1964**, *61*, 6548c.

(27) Bruker WIN-DAISY 4.05 version.

Scheme 1



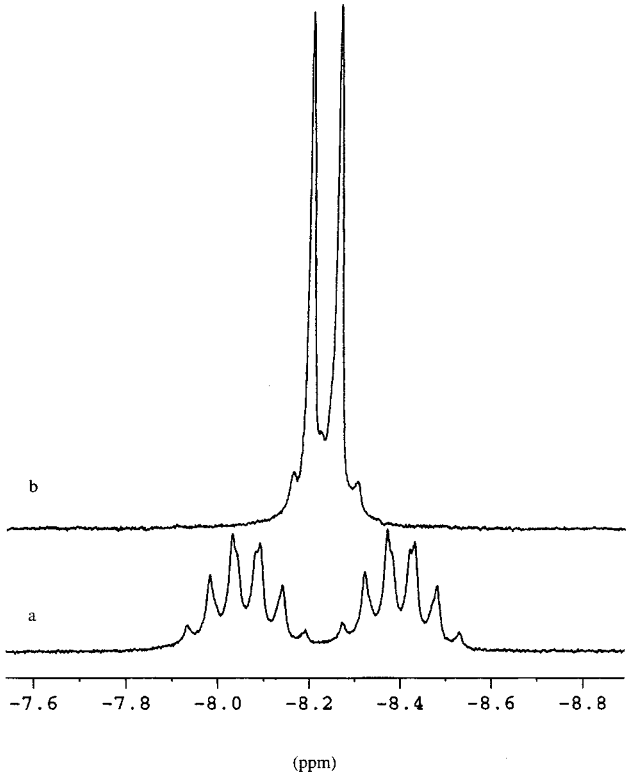


Figure 3. (a) ^1H NMR spectrum of the hydride region of *trans*-[(dppe)$_2$Ru(H)(PF(OEt)$_2$)][BF$_4$] (**8**) in CD_2Cl_2. (b) $^1H\{^{31}P\}$ NMR spectrum showing J(H,F).

A mechanism involving the reduction of the cone angle of the trans phosphorus ligand induced by the reaction with $HBF_4{\cdot}Et_2O$ seems reasonable. During the reaction, the $-$OR group on the phosphite phosphorus is likely to get protonated followed by the elimination of ROH. Consequently, one of the BF_4^- counterions provides the F^- for the phosphite (Scheme 1).

We have carried out a reaction of *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$], L = P(OR)$_3$ with 1 equiv of $DBF_4{\cdot}Et_2O$ under an atmosphere of Ar in CD_2Cl_2 in a 5 mm NMR tube. One could expect either isotope scrambling in the hydride complex to yield a deuteride derivative or the formation of ROD. We have not been able to observe either of these species using NMR spectroscopy. However, X-ray crystallographic studies of *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] revealed a molecule of MeOH (see description of the structure). A blank experiment was also carried out by the addition of $HBF_4{\cdot}Et_2O$ to a solution of P(OR)$_3$ in CH_2Cl_2, and then ^{19}F NMR was recorded. A small amount of the substituted product PF(OR)$_2$ was obtained, as indicated in the ^{19}F NMR spectrum.

Table 10. Comparison of the Cone Angles (deg) of the Trans Phosphorus Ligands

ligand	cone angle (θ)[a]	ligand	cone angle (θ)[b]
PF_3	104		
$P(OMe)_3$	107	$PF(OMe)_2$	106
$P(OEt)_3$	109	$PF(OEt)_2$	107
PMe_3	118		
PMe_2Ph	122		
$P(O^iPr)_3$	130	$PF(O^iPr)_2$	121
PBu_3	132		
PPh_3	145		
PCy_3	170		

[a] Entries in these columns have been taken from ref 12. [b] Entries in these columns have been computed.[31]

PF(OR)$_2$ compounds have been prepared earlier[28] by treating PCl(OR)$_2$ with a fluorinating agent such as SbF_3. Recently, Pregosin and co-workers[29] found that the P$-$C bond undergoes cleavage that is HBF_4 induced in certain chiral ruthenium MeO$-$Biphep (MeO$-$Biphep = 6,6′-dimethoxybiphenyl-2,2′-diylbis(diarylphosphine)) complexes. The P$-$C bond breaking process has been shown to involve a monofluorophosphine intermediate possessing a P$-$F bond, the source of the fluoride being BF_4^- anion. It has been earlier reported[30] that the transition-metal complex L_nMX (X = halide) reacts with trialkyl phosphite, P(OR)$_3$, resulting in the cationic phosphite intermediate [L_nM(P(OR)$_3$)]X. The halide X^- then readily attacks an α-carbon atom in the OR group of the phosphite to give the phosphonate complex [L_nM(P(O)(OR)$_2$)] and RX in an Arbuzov-like dealkylation reaction. This has been observed by Kubo et al.[13] in the reaction of their iron phosphite complex with F^-, wherein the F^- attacks the methyl carbon of the phosphite ligand and not the phosphorus atom, resulting in a phosphonate complex. No phosphonate derivative has been obtained in our case.

The cone angles θ for the resulting fluorophosphite ligands can be easily computed using the θ value of PF_3, which is 104° as a base value.[31] These angles have been summarized in Table 10.

Structure of *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] (7). An ORTEP diagram of the [(dppe)$_2$Ru(H)(PF(OMe)$_2$)] cation is shown in Figure 4. The molecular structure consists of discrete [(dppe)$_2$Ru(H)(PF(OMe)$_2$)]$^+$ and the [BF$_4$]$^-$ counterion together with one molecule of CH_3OH. The [BF$_4$]$^-$ counterion as well as CH_3OH are

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[31] $\theta(PF(OR)_2) = {}^1/_3[\theta(PF_3)] + {}^2/_3[\theta(P(OR)_3)]$.[12]

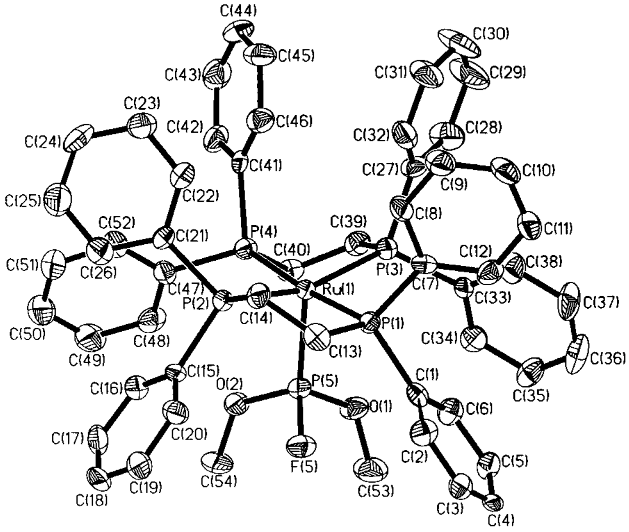


Figure 4. ORTEP view of the *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)]$^+$ (**7**) cation at the 50% probability level.

Table 11. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] (7)

Ru(1)−P(5)	2.264(2)	P(5)−O(2)	1.567(6)
Ru(1)−P(2)	2.341(2)	P(5)−O(1)	1.568(6)
Ru(1)−P(4)	2.364(2)	P(5)−F(5)	1.595(5)
Ru(1)−P(1)	2.367(2)	O(2)−C(54)	1.438(9)
Ru(1)−P(3)	2.388(2)	O(1)−C(53)	1.439(9)
P(5)−Ru(1)−P(2)	97.05(8)	P(4)−Ru(1)−P(3)	78.87(8)
P(5)−Ru(1)−P(4)	90.40(8)	P(1)−Ru(1)−P(3)	98.15(8)
P(2)−Ru(1)−P(4)	97.55(8)	O(2)−P(5)−O(1)	106.1(3)
P(5)−Ru(1)−P(1)	93.80(8)	O(2)−P(5)−F(5)	99.3(3)
P(2)−Ru(1)−P(1)	84.30(8)	O(1)−P(5)−F(5)	99.7(3)
P(4)−Ru(1)−P(1)	175.18(8)	O(2)−P(5)−Ru(1)	115.7(2)
P(5)−Ru(1)−P(3)	98.41(8)	O(1)−P(5)−Ru(1)	116.5(2)
P(2)−Ru(1)−P(3)	164.14(8)	F(5)−P(5)−Ru(1)	117.1(2)

not shown in the figure. The hydride hydrogen could not be located. The cation can be described as a distorted octahedron. The four phosphorus atoms of the dppe ligand deviate from a square plane with a mean deviation of 0.12°. P(1) and P(4) are below this square plane and are relatively closer to the PF(OMe)$_2$ phosphorus atom, whereas P(2) and P(3) are above the plane and pushed away slightly from the phosphite phosphorus atom. The ruthenium atom sits approximately in the center of the square plane and is displaced by 0.203 Å toward the PF(OMe)$_2$ moiety. The Ru−P (of dppe) bond distances fall in the range 2.341(2)−2.388(2) Å. The dppe bite angles P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are respectively 84.30(8) and 78.87(8)°. The significant feature is the tightening of the fluorophosphite P(5)−Ru(1) bond, which is 2.264(2) Å relative to the Ru(1)−P (of dppe) bond distances. This distance is also shorter compared to the Ru−P (of P(OMe)$_3$) distance of 2.337(2) Å in the case of *trans*-[(dppe)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$]. This reduction of the bond distance reflects a combined effect of the decrease in the steric crowding: that is, the reduction of the cone angle as well as the better π-accepting nature of the PF(OMe)$_2$ ligand. Appreciable reduction in the P−O bond distances has also been observed. The P−F bond distance has been found to be 1.595(5) Å. Pertinent bond distances and the angles are collected in Table 11.

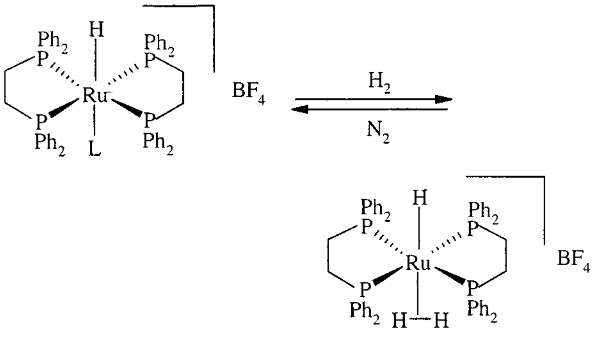
Protonation Reactions of *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$] (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$). The dihydrogen complexes *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OR)$_2$) were obtained upon further addition of HBF$_4$·Et$_2$O to the new hydride complexes *trans*-[(dppe)$_2$Ru(H)(L′)][BF$_4$]. Protonation was complete upon addition of ca. 30 equiv of the acid. The ^{1}H NMR spectrum of the dihydrogen complex shows a broad doublet in the hydride region corresponding to the coupling of the dihydrogen with the trans phosphorus (^2J(H,P$_{trans}$) = 49−51 Hz). This has been proved beyond doubt by carrying out selective decoupling experiments in both ^{1}H and ^{31}P NMR spectroscopy.[14f] Such a large coupling of dihydrogen ligand with a heteronucleus is unprecedented, although coupling constants on the order of 32 Hz or less have been reported earlier.[14a−e] Since the line broadening of the dihydrogen ligand is more than the ^3J(H,F) value, coupling with the fluorine of the phosphite was not observed. The dihydrogen complex has been isolated in the case of L′ = PF(OEt)$_2$, and the X-ray crystal structure has been determined.

Structure of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OEt)$_2$)][BF$_4$]$_2$ (11). Due to the difficulties experienced during both data collection as well as analysis as described in the Experimental Section, it was not possible to solve the structure of **11** satisfactorily. However, the presence of two BF$_4^-$ counterions indicates the dicationic nature of this species. Evidence for the existence of a dihydrogen ligand with an intact H−H bond was obtained from NMR spectroscopy. The important parameter that is useful in the context of the coupling of the dihydrogen ligand with the trans phosphorus ligand is the Ru−P (of phosphite) bond distance in this complex. The Ru−P (of phosphite) bond length was found to be 2.173(4) Å, which is much shorter than that in the P(OMe)$_3$ hydride complex (2.337(2) Å) and the hydride PF(OMe)$_2$ derivative (2.263(2) Å).

Protonation Reactions of the Hydride Complexes *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$). The protonation reactions of these complexes have been carried out exclusively under an atmosphere of Ar in a similar manner as in the cases of the trimethyl phosphite and triethyl phosphite hydrides. Upon protonation with HBF$_4$·Et$_2$O, a hydride dihydrogen complex whose formulation is unclear resulted in each case. NMR spectroscopy of this species evidenced the absence of the trans phosphorus ligand originally present in the starting hydride complex. This species is moderately stable and can be observed in the presence of a slight excess of acid. We have found the hydride dihydrogen complex that finally results has spectroscopic properties which are different from another hydride dihydrogen complex, *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$], reported earlier.[18] Currently, we are attempting to decipher the nature of this complex.

Attempts to prepare *trans*-[(dppe)$_2$Ru(H)(PBu$_3$)][BF$_4$] from *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$] and PBu$_3$ in CH$_2$Cl$_2$ provided the previously reported *trans*-[(dppe)$_2$Ru(H)Cl].[19] The reaction pathway leading to the chloride complex is unclear at this time; however, it perhaps goes through an intermediate phosphine complex that is highly sterically congested. The phosphine complex and the 5-coordinate species [(dppe)$_2$Ru(H)] are at equilibrium that is shifted far to the side of the 5-coordinate complex at room temperature. As a result of the instability of this 17-electron complex (5-coordinate species), it abstracts a chloride from the solvent, CH_2Cl_2.

Labilities of the Phosphorus Ligands in *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$). The trans phosphorus ligands in *trans*-[(dppe)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$, PMe$_2$Ph, P(O^{i}Pr)$_3$) were found to be quite labile with respect to substitution. When these hydride complexes were dissolved in solvents that were presaturated with H_2, the phosphorus ligand underwent substitution with H_2 in a facile manner at room temperature to yield *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][BF$_4$], reported by Morris and co-workers.[18] This reaction was found to be reversible, as shown in eq 2. Currently we are studying the kinetics of this reaction and its scope in catalysis.



(2)

L = PMe$_3$ (**4**), PMe$_2$Ph (**5**), P(O^{i}Pr)$_3$ (**3**)

^{1}H NMR T_1 Measurements. The variable-temperature spin–lattice relaxation times (T_1) for the η^2-H$_2$ and the hydride hydrogen signals were determined. Table 7 lists the measured and calculated T_1 values for the dihydrogen ligand as a function of temperature.[32] The T_1 minima (400 MHz) for *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$) are respectively 16.6 ms at 268 K, 16.74 ms at 268 K, and 17.03 ms at 283 K. These values have been obtained directly from the experiments and also by fitting the equations that describe the dominant dipolar relaxation mechanism to the variable-temperature T_1 data as described earlier.[33] The H–H distances can be calculated from the T_1 minima values after appropriate corrections[34] have been made for the relaxation contributions from other nuclei in the vicinity. Thus, the H–H distances are 1.08 and 0.86 Å, 1.08 and 0.86 Å, and 1.09 and 0.87 Å, respectively, for slow and fast rotation regimes for *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ complexes (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$).

H–D Isotopomers. The partial incorporation of deuterium into an H_2 ligand of dihydrogen complexes has been achieved by exposing the complex to deuterium gas. Albeniz et al.[35] proposed that isotopic scrambling occurs due to a combination of the lability and the acidity of the H_2 ligand. The η^2-HD isotopomers of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$) have been obtained by purging CD_2Cl_2 solutions containing the dihydrogen complex with D_2 gas for ca. 5–10 min at a steady rate. The η^2-HD ligand has been observed in the ^{1}H NMR spectrum without nullifying the η^2-H$_2$ signal in the cases of PF(OMe)$_2$ and PF(OEt)$_2$ complexes and in the case of PF(O^{i}Pr)$_2$ derivative by nullifying the residual signal of the η^2-H$_2$ species by an inversion recovery pulse sequence using the relationship $T_1 = \tau_{null}/\ln 2$ and the known T_1 value of the dihydrogen complex at room temperature.[33,36,37] The η^2-HD isotopomer shows a doublet of triplets pattern: the doublet is due to the coupling of H with trans phosphorus, and triplets (1:1:1) arise from the coupling of the proton with deuterium. Figure 5 displays this pattern in the case of *trans*-[(dppe)$_2$Ru(η^2-HD)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$. There is an overlap of signals, as a result of which all of the six lines are not well-resolved. The H–H distances have been calculated from these coupling constants using an empirical equation derived from a database of J(H,D) and H–H distances for dihydrogen complexes as reported earlier.[2d,38,39] The J(H,D) values for *trans*-[(dppe)$_2$Ru(η^2-HD)(L′)][BF$_4$]$_2$ (L′ = PF(OMe)$_2$, PF(OEt)$_2$, PF(O^{i}Pr)$_2$) are respectively 29, 28, and 27 Hz, and the corresponding H–H distances calculated from these coupling constants are 0.94, 0.95, and 0.97 Å.

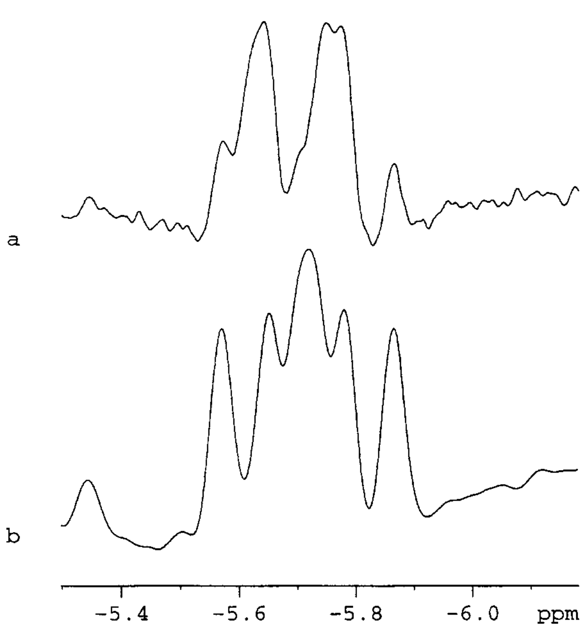


Figure 5. (a) ^{1}H NMR spectrum (hydride region) of *trans*-[(dppe)$_2$Ru(η^2-HD)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (400 MHz, 298 K) in CD_2Cl_2. (b) Spectrum where the resonance due to the η^2-H$_2$ ligand has been nullified.

Comments on H,D Coupling Constants and H–H Distances. Craw et al.[40] carried out a quantum chemi-

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[32] Temperature-dependent correlation time $\tau = \tau_0 e^{E_a/RT}$. Parameters used for the calculated T_1 values: (a) *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ (**9**), $\tau_0 = 1.78 \times 10^{-11}$ s; $E_a = 2.41$ kcal mol^{-1}; (b) *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OEt)$_2$)][BF$_4$]$_2$ (**10**), $\tau_0 = 1.88 \times 10^{-11}$ s; $E_a = 2.38$ kcal mol^{-1}; (c) *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (**11**), $\tau_0 = 7.40 \times 10^{-12}$ s; $E_a = 2.94$ kcal mol^{-1}.

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cal study on a series of osmium dihydrogen complexes and brought out a qualitative model in which a linear correlation between the observed J(H,D) coupling constants and the effective spectrochemical parameter $f^*(L^z)$[41,42] was established. One perhaps could extend this model qualitatively to ruthenium derivatives as well to find the correlation. They found that in an idealized octahedral environment, a large ligand field parameter $f^*(L^z)$ brings about a large splitting $\Delta(L^z)$ of the osmium $t_{2g}(\pi)$ and $e_g^*(\sigma)$ levels. The stabilization of the t_{2g} orbitals reduces the π-donor ability of the metal. As a consequence, back-bonding into the σ^* orbital of the η^2-H_2 ligand gets reduced, resulting in a shorter H−H bond or a larger J(H,D) coupling constant. Therefore, the J(H,D) coupling constant can be expected to be large for stronger field ligands such as halophosphites ($f^*(L^z) > 2$) compared to the phosphites ($f^*(L^z) \cong 2$) or phosphines ($f^*(L^z) \cong 1.25$).[43] Although we do not have the data for a direct comparison of the J(H,D) coupling constants in these three kinds of derivatives, we can expect the trend to be in the order $PF(OR)_2 > P(OR)_3 > PR_3$, corresponding to a decrease in the π-acidity[44] and to increasing steric bulk[45] of the trans phosphorus ligand in that order. The suggested correlation by Craw et al.[40] that a dihydrogen complex with a ligand that has a large spectrochemical constant would be quite unstable does not seem to be in accord with our observation in the case of the complexes reported here. Our dihydrogen complexes are quite stable at room temperature.

Morris and co-workers earlier found that their complexes *trans*-$[(dppe)_2Fe(\eta^2\text{-}H_2)(CN)][OTf]_2$[46] and *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(CNH)][OTf]_2$[5b] were quite stable with respect to loss of H_2. This was unexpected on the basis of the report by Craw et al.[40] They explained this behavior as an increase in Lewis acidity of the metal centers and a σ-donation from η^2-H_2 to the metal rather than π-back-bonding from the metal to the antibonding orbital of H_2. These complexes are most relevant to the current work because of the similarities in behavior of our derivatives with those of Morris' with respect to loss of H_2 and the H−H distances determined by NMR methods.

An additional point to discuss here is the H−H distance derived from the T_1(min) data. The complexes described here show distances of 1.08 and 0.86 or 0.87 Å for the slow- and the fast-spinning regimes, respectively, for H−H. Gusev et al.[47] reported a correlation of the H−H distances calculated from J(H,D) and T_1(min) and $\Delta G^{\ddagger}$ for the loss of H_2 ligand from the metal center. The H−H distances obtained from J(H,D) in our complexes are on the order of 0.94−0.97 Å. These distances are intermediate between 1.08 and 0.86 Å, obtained using the slow- and the fast-spinning approximations of H_2. In the case of a family of complexes of the type $[(PP)_2Ru(H)(H_2)]^+$ reported by Morris and co-workers[18,33] the H−H distances obtained from the H−D coupling constants are consistent with the fast-spinning result calculated from the T_1(min) data. Our complexes differ from those of Morris' in this aspect. Morris and Wittebort[48] suggested that the H−H distances calculated from J(H,D) that fall between those derived from the T_1(min) data indicates that librational motion significantly influences the relaxation process. There are many examples reported in the literature where such a situation has been observed.[48]

One exciting challenge would be to attempt the synthesis of a complex having PF_3 trans to the dihydrogen ligand and study its properties. In addition, it would be interesting to compare the properties of such a complex with those of *trans*-$[(dppp)_2Ru(\eta^2\text{-}H_2)(CO)]^{2+}$.[4a] Efforts toward this goal are in progress in our laboratories.

Conclusions

The protonation reactions of the hydride complexes of the type *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ ($L = P(OR)_3$) with $HBF_4 \cdot Et_2O$ result in new hydride derivatives, *trans*-$[(dppe)_2Ru(H)(L')][BF_4]$ ($L' = PF(OR)_2$). The driving force for such reactivity seems to be the cone angle reduction induced by the reaction of $HBF_4 \cdot Et_2O$, thereby minimizing the steric crowding around the ruthenium center. Protonation of these hydride derivatives gives the corresponding dihydrogen complexes. Substantial coupling of the dihydrogen with the trans phosphorus moiety on the order of 49−51 Hz has been observed. This could be due to the bond shrinkage of the Ru−P (of the trans phosphorus ligand) bond that in turn brings the trans phosphorus ligand in greater proximity to the dihydrogen moiety, as evidenced by X-ray crystallographic studies. The Ru−P (of the trans phosphite ligand) distances successively decrease from the hydride $P(OMe)_3$ complex (2.337(2) Å) to the hydride $PF(OMe)_2$ derivative (2.264(2) Å) to the $PF(OEt)_2$ dihydrogen complex (2.167(4) Å).

The lability of the phosphorus ligand in the cases of *trans*-$[(dppe)_2Ru(H)(L)][BF_4]$ (L = phosphine, $P(O^iPr)_3$) has been exploited to carry out reversible binding of H_2 via substitution of the phosphorus ligand under very mild conditions. In addition, this lability opens the possibility of catalytic activity for these derivatives, which is under study in our laboratories. From this study it can be concluded that the properties of the dihydrogen complexes bearing only phosphorus coligands can be fine-tuned by an interplay of the cone angles (steric crowding around the metal center) and the π-accepting ability of the trans phosphorus ligands.

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analysis data. We also thank Prof. C. N. R. Rao (JNCASR) for allowing us to use the X-ray diffractometer facility.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**, **7**, and **11**, variable-temperature spin−lattice relaxation times of the hydride ligand in **7**, a figure showing the observed and simulated ^{1}H NMR spectra of the hydride region of **8**, an ORTEP diagram of **11**, and a figure showing the T_1 (400 MHz) plot for a mixture of **8** and **11** at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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