

Trans → Cis Isomerization of $trans\text{-}[(dppm)_2Ru(H)(L)][BF_4]$ ($L = P(OR)_3$) Complexes: Preparation of $cis\text{-}[(dppm)_2Ru(\eta^2-H_2)(L)][BF_4]_2^\dagger$

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A series of new dicationic dihydrogen complexes of ruthenium of the type $cis\text{-}[(dppm)_2Ru(\eta^2-H_2)(L)][BF_4]_2$ ($dppm = Ph_2PCH_2PPh_2$; $L = P(OMe)_3$, $P(OEt)_3$, $PF(O^iPr)_2$) have been prepared by protonating the precursor hydride complexes $cis\text{-}[(dppm)_2Ru(H)(L)][BF_4]$ ($L = P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$) using $HBF_4 \cdot Et_2O$. The $cis\text{-}[(dppm)_2Ru(H)(L)][BF_4]$ complexes were obtained from the trans hydrides via an isomerization reaction that is acid-accelerated. This isomerization reaction gives mixtures of cis and trans hydride complexes, the ratios of which depend on the cone angles of the phosphite ligands: the greater the cone angle, the greater is the amount of the cis isomer. The η^2-H_2 ligand in the dihydrogen complexes is labile, and the loss of H_2 was found to be reversible. The protonation reactions of the starting hydrides with trans PMe_3 or PMe_2Ph yield mixtures of the cis and the trans hydride complexes; further addition of the acid, however, give $trans\text{-}[(dppm)_2Ru(BF_4)Cl]$. The roles of the bite angles of the dppm ligand as well as the steric and the electronic properties of the monodentate phosphorus ligands in this series of complexes are discussed. X-ray crystal structures of $trans\text{-}[(dppm)_2Ru(H)(P(OMe)_3)][BF_4]$, $cis\text{-}[(dppm)_2Ru(H)(P(OMe)_3)][BF_4]$, and $cis\text{-}[(dppm)_2Ru(H)(P(O^iPr)_3)][BF_4]$ complexes have been determined.

Introduction

The nature of the ancillary ligand environment in a dihydrogen complex can have a profound effect on the structure and reactivity of the dihydrogen ligand. A thorough understanding of the structure and reactivity of the dihydrogen complexes is required for the rational design of new homogeneous metal catalysts. Transition metal complexes containing phosphorus coligands allow for a very systematic study because both electronic and steric properties of the phosphorus ligands could be varied systematically.¹ We have previously shown how the cone angles and the π -acceptor properties of certain phosphorus ligands influence the structure and reactivity of $trans\text{-}[(dppe)_2Ru(\eta^2-H_2)(L)][BF_4]_2$ complexes ($dppe = Ph_2PCH_2CH_2PPh_2$; $L = phosphite$).² Morris et al. studied the effect of changing the R substituents

in chelating phosphine ligands of $trans\text{-}[(R_2PCH_2CH_2PR_2)_2M(\eta^2-H_2)(L)]^+$ complexes.^{3,4} They also used different phosphines ($dppm$, $dppe$, $dppp$ [$Ph_2P(CH_2)_3PPh_2$], and $depe$ [$Et_2P(CH_2)_2PEt_2$]) in a series of dihydrogen complexes of the type $trans\text{-}[(P-P)_2Ru(\eta^2-H_2)(CN)]^+$ and $trans\text{-}[(P-P)_2Ru(\eta^2-H_2)(CNH)]^{2+}$ and found that these coligands influence their stability and reactivity.⁵ Several others have carried out variations in the cis ligands of $[(L)_4Ru(\eta^2-H_2)(H)]^+$ complexes to study their influence on the properties of these complexes.⁶

In 1994, Morokuma et al.⁷ reported theoretical studies on the nature of the $[(P-P)_2Ru^+H_3]^\dagger$ fragment ($[(P-P)_2Ru^+H_3]^\dagger = [(P-P)_2Ru(H)(\eta^2-H_2)]^+$; $P-P = dppb$, $diop$, $dpmb$, $dppe$) and concluded that with an increasing bite angle of the

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diphosphine the complexes change from trans hydrido dihydrogen to trihydride and to cis hydrido dihydrogen complexes. Chaudret et al.⁸ recently reported the preparation of [(diphos)₂Ru(H)(η^2 -H₂)]⁺ (diphos = thixantphos, sixantphos; both have xanthene-like backbones; bite angles, β_n = 103.1 and 102.5°, respectively) in which the hydride and the dihydrogen ligands were found to be in cis conformation, in agreement with Morokuma's prediction. These results show that the tuning of one steric parameter (in this case, the bite angles of the diphosphine ligands) bears a remarkable influence on the electronic properties of these complexes. To date, such studies dealing with the effect of geometrical changes on the nature and reactivity of the hydrogen complexes are very few.

The chemical shifts of the ³¹P nuclei of the chelating phosphine rings experience large upfield shifts upon complexation with metal with increase in *n*.⁹ A steric effect was observed in the square planar–tetrahedral equilibrium of [Ph₂P(CH₂)_nPPh₂][NiX₂] complexes.¹⁰ Ruthenium complexes bearing the fragment [(dppm)₂Ru] have been the subject of current interest due to the ability of the dppm ligands to serve either as chelates or as monodentate ligands via binding through only one P atom to a metal or as bidentate ligands bridging two metal atoms.^{5,11,12}

The objective of this work is the synthesis of dihydrogen complexes of ruthenium bearing only phosphorus coligands of the type [(dppm)₂Ru(η^2 -H₂)(L)][BF₄]₂ (L = phosphite or phosphine); in addition, we wish to compare the present results with those of analogous dppe-containing derivatives that we reported earlier² to understand the effect of the smaller bite angle of the chelating phosphine ligands on the structure–reactivity behavior of these complexes. We also intend to prepare dihydrogen complexes that are capable of activating H₂ in a heterolytic manner; one could achieve this by having strong π -acceptor ligands trans to the η^2 -H₂ moiety.

In the current work, we have attempted to carry out protonation reactions of a series of hydride complexes *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (cone angle θ = 107°), P(OEt)₃ (θ = 109°), P(OⁱPr)₃ (θ = 130°), PMe₃ (θ = 118°), and PMe₂Ph (θ = 122°)) with HBF₄·Et₂O. We found that these hydrides, in the presence of ≤ 1 equiv of HBF₄·Et₂O, isomerize to give new hydride complexes *cis*-[(dppm)₂Ru(H)(L)][BF₄]. Further addition of acid to the *cis*-[(dppm)₂Ru(H)(L)][BF₄] complexes afforded the *cis*-[(dppm)₂Ru(η^2 -H₂)(L)][BF₄]₂ complexes. These are the first examples in this class of complexes wherein the H₂ ligand and a monodentate phosphorus ligand are in cis conformation.

Table 1. Numbering Scheme for the Complexes^a

L	compd. no.	compd. no.	compd. no.	compd. no.	compd. no.	compd. no.
H ₂	trans-1H					
P(OMe) ₃	trans-2H	cis-2H	trans-2H ₂	cis-2H ₂	trans-2HD	cis-2HD
P(OEt) ₃	trans-3H	cis-3H	trans-3H ₂	cis-3H ₂	trans-3HD	cis-3HD
P(O ⁱ Pr) ₃	trans-4H	cis-4H	trans-4H ₂ ^b	cis-4H ₂ ^b	trans-4HD ^b	cis-4HD ^b
PMe ₃	trans-5H	cis-5H	trans-5H ₂	cis-5H ₂		
PMe ₂ Ph	trans-6H	cis-6H	trans-6H ₂	cis-6H ₂		
CH ₃ CN	trans-7H					
Cl	trans-8H ^c		trans-8H ₂ ^d		trans-8HD ^d	

^a [M] = (dppm)₂M fragment. ^b L = PF(OⁱPr)₂. ^c Neutral. ^d +1.

Experimental Section

General Procedures. All reactions were carried out under N₂ or Ar atmosphere at room temperature using standard Schlenk^{13a,b} 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. CHCl₃ was purified using standard procedures.^{13c} Although sufficient measures were taken to ensure that the CHCl₃ solvent was free of acid and other impurities, it was found to have small amounts of acid impurities.^{13d}

The NMR spectra were obtained using an AMX Bruker 400 MHz spectrometer. 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.¹⁴ The ³¹P{¹H} NMR spectra were measured in CD₂Cl₂ relative to 85% H₃PO₄ (aqueous solution) as an external standard and ¹⁹F NMR spectra with respect to CFCl₃. Elemental analyses were carried out using a Heraeus CHNO Rapid elemental analyzer. Bis(diphenylphosphino)methane (dppm),¹⁵ *cis*-[(dppm)₂RuCl₂],¹⁶ and *cis/trans*-[(dppm)₂Ru(H)₂]¹⁷ were prepared by literature methods. The numbering scheme for the compounds reported in this work is summarized in Table 1.

Preparation of *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (*trans*-2H), P(OEt)₃ (*trans*-3H), P(OⁱPr)₃ (*trans*-4H), PMe₃ (*trans*-5H), PMe₂Ph (*trans*-6H), CH₃CN (*trans*-7H)). All of these compounds were prepared using similar procedures. The preparation of *trans*-2H only is described here: To a CH₂Cl₂ (10 mL) solution of *cis/trans*-[(dppm)₂RuH₂] (0.200 g, 0.2 mmol) was added 1 equiv (32 μ L) of 54% HBF₄·Et₂O. To this solution containing the *trans*-[(dppm)₂Ru(η^2 -H₂)(H)][BF₄] (*trans*-1H) complex was added P(OMe)₃ (0.04 mL, 0.3 mmol) dropwise. The reaction mixture was stirred for only 1 min after which time N₂ was introduced and the volume increased to ca. 30 mL by adding CH₂Cl₂. Addition of excess petroleum ether caused the precipitation of a cream colored product

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Table 2. ¹H NMR Spectral Data (δ) for trans-[(dppm)₂Ru(H)(L)][BF₄] Complexes in CD₂Cl₂

compd no.	δ(Ru–H)	<i>J</i> (H, <i>P</i> _{trans}), Hz	<i>J</i> (H, <i>P</i> _{cis}), Hz	δ(CH ₂)	δ(L)	<i>J</i> (H,E), Hz	δ(Ph)
trans-2H	–5.31 (d qnt, 1H)	106.8	21.0	4.90 (m, 2H) 4.46 (m, 2H)	2.60 (d, 9H)	12.0 ^a	6.96–7.69 (m, 40H)
trans-3H	–5.51 (d qnt, 1H)	104.1	21.0	4.81 (m, 2H) 4.53 (m, 2H)	3.00 (q, 6H) 0.40 (t, 9H)	8.0 ^b	6.84–7.40 (m, 40H)
trans-4H	–6.53 (d qnt, 1H)	105.0	21.5	4.69 (m, 2H) 4.12 (m, 2H)	4.26 (m, 3H) 0.54 (d, 18H)	8.0 ^b	6.81–7.51 (m, 40H)
trans-5H	–6.20 (d qnt, 1H)	50.0	21.0	4.80 (m, 2H) 4.58 (m, 2H)	0.43 (d, 9H)	8.0 ^b	6.94–7.48 (m, 40H)
trans-6H	–6.39 (d qnt, 1H)	52.0	21.0	4.73 (m, 2H) 4.50 (m, 2H)	0.62 (d, 6H)	8.0 ^b	6.55–7.39 (m, 45H)
trans-7H	–11.93 (qnt, 1H)		19.0	4.40 (m, 2H) 4.91 (m, 2H)	1.13 (s, 3H)		7.04–7.35 (m, 40H)

^a E = P, ^b E = H.**Table 3.** ³¹P{¹H} NMR Spectral Data (δ) for trans-[(dppm)₂Ru(H)(L)][BF₄] Complexes in CD₂Cl₂

compd no.	P(L)	P(dppm)	<i>J</i> (P,P), Hz
trans-2H	136.6 (qnt, 1P)	–1.2 (d, 4P)	33.2
trans-3H	135.9 (qnt, 1P)	–1.3 (d, 4P)	33.3
trans-4H	133.3 (qnt, 1P)	–3.5 (d, 4P)	32.7
trans-5H	–30.8 (qnt, 1P)	–2.9 (d, 4P)	23.8
trans-6H	–15.8 (qnt, 1P)	–3.5 (d, 4P)	23.8
trans-7H		–1.4 (s, 4P)	

that was washed several times with more petroleum ether and then dried in vacuo. Yield: 0.200 g, 81%. Anal. Calcd for C₅₃H₅₄BF₄O₃P₅Ru·CH₂Cl₂: C, 55.59; H, 4.83. Found: C, 56.09; H, 5.13. Yield of trans-3H: 80%. Anal. Calcd for C₅₆H₆₀BF₄O₃P₅Ru·0.5CH₂Cl₂: C, 58.19; H, 5.27. Found: C, 58.25; H, 5.43. Yield of trans-4H: 85%. This product contained certain impurities, and purification procedures resulted in its partial decomposition. Anal. Calcd for C₅₉H₆₆BF₄O₃P₅Ru·0.5CH₂Cl₂: C, 59.14; H, 5.59. Found: C, 59.91; H, 5.57. Yield of trans-5H: 84%. Anal. Calcd for C₅₃H₅₄BF₄P₅Ru: C, 61.58; H, 5.27. Found: C, 61.24; H, 5.12. Yield of trans-6H: 78%. Anal. Calcd for C₅₈H₅₆BF₄P₅Ru·CH₂Cl₂: C, 60.02; H, 4.95. Found: C, 60.49; H, 4.89. Yield of trans-7H: 84%. Anal. Calcd for C₅₂H₄₈BF₄NP₄Ru: C, 62.54; H, 4.84. Found: C, 62.18; H, 4.99. The presence or absence of solvent molecules in the samples was ascertained by recording their ¹H NMR spectra in CDCl₃ and measuring the integrals for the CH₂–Cl₂ (δ 5.3) of solvation (if present) with respect to the dppm–CH₂ signal. The integrals reproduced fairly well for multiple samples of the same compound. The NMR data are summarized in Tables 2 and 3. Characterization data for trans-[(dppm)₂Ru(η²-H₂)(H)][BF₄] (trans-1H) are as follows. ¹H NMR (CD₂Cl₂): δ –6.63 (qnt, 1H, Ru–H, *J*(H,*P*_{cis}) = 18.7 Hz); –2.34 (br s, 2H, η²-H₂), 4.10 (m, 2H, PCH₂P), 4.54 (m, 2H, PCH₂P), 6.28–7.79 (m, 40H, PPh₂). ³¹P NMR (CD₂Cl₂): δ –0.03 (s, 4P, Ph₂PCH₂PPh₂). *T*₁ (400 MHz, CD₂Cl₂, 298 K): η²-H₂ ligand, 17.3 ms; *J*(H,D) = 29 Hz, *d*_{HH} = 0.94 Å; hydride ligand, 216 ms.

Isomerization of trans-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (trans-2H), P(OEt)₃ (trans-3H), P(OⁱPr)₃ (trans-4H), PMe₃ (trans-5H), PMe₃Ph (trans-6H)). **Method A.** A CHCl₃ solution (30 mL) of trans-2H (0.150 g, 0.13 mmol) was refluxed for 20 h and then cooled to room temperature, filtered, and concentrated. Addition of Et₂O (2 mL) and excess petroleum ether caused the precipitation of a mixture of trans-2H and cis-[(dppm)₂Ru(H)-(P(OMe)₃)] [BF₄] (cis-2H) complexes. ¹H NMR spectroscopy evidenced the presence of the trans and the cis isomers in a ratio of 19:81. The product was washed with Et₂O and petroleum ether and then dried in vacuo. Yield: 0.090 g. It was crystallized from a CH₂Cl₂ solution containing a few drops of toluene and P(OMe)₃ via diffusion of petroleum ether over a period of several days at room temperature. The cis isomer (pale orange crystals) could be

manually separated from the trans isomer (colorless crystals). The isomerizations of trans-3H, trans-4H, trans-5H, and trans-6H were also carried out using this method. ¹H NMR of the products in CD₂Cl₂: (a) L = P(OEt)₃, mixture of trans- and cis-[(dppm)₂Ru(H)-(P(OEt)₃)] [BF₄] (trans- and cis-3H) complexes in a ratio of 3 and 97%; (b) L = P(OⁱPr)₃, the cis isomer, 100%; cis-4H complex crystallized from a CH₂Cl₂ solution via diffusion of petroleum ether; (c) L = PMe₃, ratio of trans to cis, 42 to 58%; (d) L = PMe₃Ph, 41% trans to 59% cis. The NMR data for these compounds are summarized in Tables 4 and 5.

Method B. To a CHCl₃ solution (7 mL) of trans-2H (0.100 g, 0.09 mmol) under H₂ atmosphere was added 1 equiv (13 μL) of HBF₄·Et₂O. This solution was stirred for 1 min, and Et₂O (2 mL) and excess petroleum ether were added. The precipitated product was washed with Et₂O and petroleum ether and dried in vacuo. ¹H NMR spectrum indicated the presence of trans-2H (minor) and cis-2H (major) complexes.

Protonation Reaction of trans-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (trans-2H), P(OEt)₃ (trans-3H)). A 12 mg portion of trans-[(dppm)₂Ru(H)(L)][BF₄] was dissolved in 0.9 mL of CD₂–Cl₂ in an NMR tube. This solution was freeze–pump–thaw degassed and then purged with H₂ gas for 5 min. Upon addition of 1 equiv of HBF₄·Et₂O (1.8 μL for L = P(OMe)₃; 1.4 μL for L = P(OEt)₃) the ¹H NMR spectrum evidenced the formation of the cis isomer, cis-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (cis-2H), P(OEt)₃ (cis-3H)). Thereafter, the acid was added in small increments. Addition of excess acid gave a mixture of trans- and cis-dihydrogen complexes [(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = P(OMe)₃ (trans-2H₂ and cis-2H₂); P(OEt)₃ (trans-3H₂ and cis-3H₂)), respectively. Characterization data for trans-2H₂ are as follows. ¹H NMR (CD₂–Cl₂): δ –3.07 (d, 2H, Ru–η²-H₂, *J*(H₂,*P*_{trans}) = 50 Hz). Signals due to other moieties could not be assigned with confidence. ³¹P-{¹H} NMR (CD₂Cl₂): δ 116.25 (qnt, 1P, P(OMe)₃, *J*(P,P) = 41.8 Hz), –10.01 (d, 4P, dppm). Characterization data for trans-3H₂ are as follows. ¹H NMR (CD₂Cl₂): δ –3.11 (br d, 2H, η²-H₂, *J*(H₂,*P*_{trans}) = 43 Hz). Signals due to other moieties could not be assigned definitively. ³¹P NMR (CD₂Cl₂): δ 114.5 (qnt, 1P, P(OEt)₃), *J*(P,P) = 40.2 Hz), –10.8 (d, 4P, Ph₂PCH₂PPh₂).

Protonation Reaction of trans-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OⁱPr)₃ (trans-4H)). The protonation of trans-4H was carried out in a manner similar to that of trans-2H. Upon addition of 1 equiv of 54% HBF₄·Et₂O new hydride complexes were formed, cis-[(dppm)₂Ru(H)(P(OⁱPr)₃)] [BF₄] (cis-4H) and trans-[(dppm)₂Ru(H)-(PF(OⁱPr)₂)] [BF₄]. When excess acid was added, trans-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (trans-4H₂) and cis-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (cis-4H₂), respectively, were obtained. Characterization data for trans-4H₂ are as follows. ¹H NMR (CD₂Cl₂, rt (room temperature)): δ –2.94 (br d, 2H, η²-H₂,

Table 4. ^1H NMR Spectral Data (δ) for *cis*-[(dppm) $_2$ Ru(H)(L)][BF $_4$] Complexes in CD $_2$ Cl $_2$

compd no.	$\delta(\text{Ru}-\text{H})^a$	$J(\text{H}, \text{P}_{\text{trans}})$, Hz	$J(\text{H}, \text{P}_{\text{cis-av}})$, Hz	$\delta(\text{L})$	$J(\text{H}, \text{E})$, Hz	$\delta(\text{CH}_2)$	$\delta(\text{Ph})$
<i>cis</i> -2H	−8.51 (1H)	68.0	8.5	3.07 (d, 9H)	20 ^b	5.95 (m, 4H)	6.57–7.81 (m, 40H)
<i>cis</i> -3H	−8.49 (1H)	68.0	10.2	3.43 (m, 6H) 0.68 (t, 9H)	8 ^c	5.90 (m, 4H)	6.63–7.70 (m, 40H)
<i>cis</i> -4H	−8.52 (1H)	80.4	9.0	4.27 (m, 3H) 0.8 (dd, 18H)	32 ^b 8 ^c	5.62 (m, 4H)	6.40–7.90 (m, 40H)
<i>cis</i> -5H	−8.73 (1H)	82.0	9.5	0.76 (d, 9H)	4 ^c	5.95 (m, 4H)	6.73–7.79 (m, 40H)
<i>cis</i> -6H	−8.35 (1H)	92.4	15.0	1.00 (d, 6H)	4 ^c	5.74 (m, 4H)	6.42–7.80 (m, 45H)

^a XABCDM spin system. ^b E = P. ^c E = H.**Table 5.** ^{31}P NMR Spectral Data^a (δ) for *cis*-[(dppm) $_2$ Ru(H)(L)][BF $_4$] Complexes in CD $_2$ Cl $_2$

compd no.	$\delta(\text{P}_\text{M})$ ($J(\text{P}_\text{M}, \text{P}_\text{B})$; $J(\text{P}_\text{M}, \text{P}_{\text{av}(\text{A}, \text{C}, \text{D})})$, Hz))	$\delta(\text{P}_\text{D})$ ($J(\text{P}_\text{D}, \text{P}_\text{C})$; $J(\text{P}_\text{D}, \text{P}_{\text{av}(\text{A}, \text{B}, \text{M})})$, Hz))	$\delta(\text{P}_\text{C})$ ($J(\text{P}_\text{C}, \text{P}_{\text{av}(\text{A}, \text{B}, \text{M})})$, Hz))	$\delta(\text{P}_\text{B})$ ($J(\text{P}_\text{B}, \text{P}_{\text{av}(\text{A}, \text{C}, \text{D})})$, Hz))	$\delta(\text{P}_\text{A})$
<i>cis</i> -2H	144.1 (353.5; 36.4)	3.6 (233.3; 17.4)	−3.7 (22.6)	−10.5 (15.7)	−16.3
<i>cis</i> -3H	139.4 (350.7; 21.9)	4.7 (230.0; 17.2)	−4.7 (22.7)	−11.7 (16.1)	−16.2
<i>cis</i> -4H	134.7 (353.3; 25.5)	2.3 (235.0; 17.4)	−3.4 (22.6)	−11.0 (15.6)	−19.3
<i>cis</i> -5H	6.1 (240.0; 21.1)	−6.1 (205.0; 20.0)	−12.6 (22.0)	−3.2 (20.0)	−17.3
<i>cis</i> -6H	3.0 (230.0; 19.9)	0.9 (221.0; 23.5)	−4.9 (24.9)	−4.8 (22.0)	−19.4

^a ABCDM spin system.**Table 6.** ^1H NMR Spectral Data (δ) for *cis*-[(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ Complexes in CD $_2$ Cl $_2$

compd no.	$\delta(\text{Ru}-\eta^2\text{-H}_2)$	$\delta(\text{L})$	J , Hz	$\delta(\text{CH}_2)$	$\delta(\text{Ph})$
<i>cis</i> -2H $_2$	−4.88 (br s, 2H)	3.17 (d, 9H)	12 ($J(\text{P}, \text{H})$)	5.65 (m, 4H)	6.60–7.93 (m, 40H)
<i>cis</i> -3H $_2$	−4.81 (br s, 2H)	3.61 (q, 6H) 0.85 (t, 9H)	8 ($J(\text{H}, \text{H})$)	5.62 (m, 4H)	6.69–7.98 (m, 40H)
<i>cis</i> -4H $_2$	−4.57 (br s, 2H)	4.50 (m, 2H) 0.87 (d, 12H)	6 ($J(\text{H}, \text{H})$)	5.88 (m, 4H)	6.80–7.95 (m, 40H)

Table 7. ^{31}P NMR Spectral Data (δ) for *cis*-[(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ Complexes in CD $_2$ Cl $_2$

compd no.	$\delta(\text{P}_\text{M})$	$\delta(\text{P}_\text{D})$	$\delta(\text{P}_\text{C})$	$\delta(\text{P}_\text{B})$	$\delta(\text{P}_\text{A})$
<i>cis</i> -2H $_2$ ^a	124.3 $J(\text{P}_\text{M}, \text{P}_\text{C}) = 35.0.8$ Hz $J(\text{P}_\text{M}, \text{P}_{\text{av}(\text{A}, \text{B})}) = 35.2$ Hz		−16.7 $J(\text{P}_\text{C}, \text{P}_{\text{av}(\text{A}, \text{B}, \text{M})}) = 28.0$ Hz	−21.0 $J(\text{P}_\text{B}, \text{P}_{\text{av}(\text{A}, \text{C}, \text{M})}) = 24.1$ Hz	−23.6 $J(\text{P}_\text{A}, \text{P}_{\text{av}(\text{B}, \text{C}, \text{M})}) = 24.8$ Hz
<i>cis</i> -3H $_2$ ^b	120.2 $J(\text{P}_\text{M}, \text{P}_\text{A}) = 34.6.0$ Hz $J(\text{P}_\text{M}, \text{P}_{\text{av}(\text{B}, \text{C}, \text{D})}) = 34.9$ Hz	−9.6 $J(\text{P}_\text{D}, \text{P}_\text{C}) = 204.0$ Hz	−17.8	−19.4	−22.9
<i>cis</i> -4H $_2$ ^b	124.6 $J(\text{P}_\text{M}, \text{P}_\text{B}) = 40.0.0$ Hz $J(\text{P}_\text{M}, \text{F}) = 1160.0$ Hz	5.9	−14.6 $J(\text{P}_\text{C}, \text{P}_\text{A}) = 258.0$ Hz	−22.6	−26.9

^a ABB'CM spin system. ^b ABCDM spin system.

$J(\text{H}_2, \text{P}_{\text{trans}}) = 46.8$ Hz), 0.74 (d, 12H, $\text{CH}(\text{CH}_3)_2$), $J(\text{H}, \text{H}) = 6$ Hz), 4.59 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 6.23 (m, 4H, CH_2). ^{31}P NMR (CD $_2$ Cl $_2$, rt): δ −1.27 (d, 4P, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), $J(\text{P}, \text{P}) = 34.3$ Hz), 121.5 (d qnt, 1P, $\text{PF}(\text{O}^i\text{Pr})_2$), $J(\text{P}, \text{F}) = 1120.0$ Hz).

Preparation of the Dihydrogen Complexes *trans*-[(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ (L = P(OMe) $_3$ (*trans*-2H $_2$), P(OEt) $_3$ (*trans*-3H $_2$), $\text{PF}(\text{O}^i\text{Pr})_2$ (*trans*-4H $_2$)) and *cis*-[(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ (L = P(OMe) $_3$ (*cis*-2H $_2$), P(OEt) $_3$ (*cis*-3H $_2$), $\text{PF}(\text{O}^i\text{Pr})_2$ (*cis*-4H $_2$)). Similar procedures were employed for the preparation of these derivatives. A 12 mg portion of *trans*-[(dppm) $_2$ Ru(H)(L)][BF $_4$] was dissolved in 0.9 mL of CD $_2$ Cl $_2$ in an NMR tube, and the solution was degassed. Then it was purged with H $_2$ gas for 5 min. Addition of ca. 8 equiv of HBF $_4$ ·Et $_2$ O (15 μL for L = P(OMe) $_3$; 14 μL for L = P(OEt) $_3$; 16 μL for L = $\text{PF}(\text{O}^i\text{Pr})_2$) gave the dihydrogen complexes which were characterized using NMR spectroscopy. The NMR data for these complexes are summarized in Tables 6 and 7.

Protonation Reactions of *trans*-[(dppm) $_2$ Ru(H)(L)][BF $_4$] (L = PMe $_3$ (*trans*-5H), PMe $_2$ Ph (*trans*-6H)). The protonation reactions of these complexes were carried out in a manner similar to that of *trans*-2H. Upon addition of 1 equiv of HBF $_4$ ·Et $_2$ O (1.6 μL for L = PMe $_3$; 1.8 μL for L = PMe $_2$ Ph) the ^1H NMR spectrum evidenced the formation of *cis*-[(dppm) $_2$ Ru(H)(L)][BF $_4$] (L = PMe $_3$

(*cis*-5H), PMe $_2$ Ph (*cis*-6H)), *trans*-[(dppm) $_2$ Ru(η^2 -H $_2$)(H)][BF $_4$] (*trans*-1H), *trans*-[(dppm) $_2$ Ru(η^2 -H $_2$)(Cl)][BF $_4$] (*trans*-8H $_2$), and *cis*-[(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ (L = PMe $_3$ (*cis*-5H $_2$), PMe $_2$ Ph (*cis*-6H $_2$)) complexes. When ca. 10 equiv of acid was added, no signals were found in the hydride region of the spectrum except that of the *trans*-8H $_2$ complex. The ^{31}P NMR spectrum, in addition to indicating *trans*-8H $_2$, showed *trans*-[(dppm) $_2$ Ru(BF $_4$)Cl] (*trans*-9) (37%) and free ligand. The presence of the bound BF $_4$ moiety was confirmed using ^{19}F NMR spectroscopy in the presence of a large excess of acid. Characterization data for *trans*-9 are as follows. ^{31}P NMR (CD $_2$ Cl $_2$, rt): δ 12.5 (br s, 2P), −17.8 (t, 2P). The signal at 12.5 ppm sharpens to a triplet at 223 K. ^{19}F NMR (CD $_2$ Cl $_2$, rt): δ −132.3 (s, 4F, Ru−BF $_4$), −150.5 (br s, free BF $_4$ $^-$). Attempts to measure the T_1 and $J(\text{H}, \text{D})$ for [(dppm) $_2$ Ru(η^2 -H $_2$)(L)][BF $_4$] $_2$ (L = PMe $_3$, PMe $_2$ Ph) complexes failed due to the high lability of the dihydrogen ligand in these complexes.

Protonation Reaction of *cis*/*trans*-[(dppm) $_2$ Ru(H) $_2$]. To an NMR tube charged with 15 mg of *cis*/*trans*-[(dppm) $_2$ Ru(H) $_2$] was transferred CD $_2$ Cl $_2$ (0.9 mL) saturated with Ar or H $_2$ just before inserting the tube into the NMR probe; this was done due to the instability of the dihydride complex in CD $_2$ Cl $_2$ for long periods of time. The ^1H NMR spectrum showed the presence of a small amount of *trans*-[(dppm) $_2$ Ru(H)(Cl)][BF $_4$] (*trans*-8H). Addition of

ca. 1 equiv of 54% HBF₄·Et₂O (2.6 μL) gave *trans*-[(dppm)₂Ru(η²-H₂)(H)][BF₄] (*trans*-1H) along with some *trans*-8H₂. Addition of further acid resulted in the disappearance of *trans*-1H; however, the *trans*-8H₂ remained intact. The ³¹P NMR spectrum of this mixture was identical to that of *trans*-9 observed in the protonation of the PMe₃ and PMe₂Ph hydrides. In the presence of excess acid, the signals due to *trans*-9 broaden as well as shift slightly downfield.

Preparation of *trans*-[(dppm)₂Ru(η²-H₂)(Cl)][BF₄] (*trans*-8H₂). A 15 mg portion of *trans*-[(dppm)₂Ru(H)(Cl)] (*trans*-8H) dissolved in 0.7 mL of CD₂Cl₂ in an NMR tube was degassed and then saturated with Ar or H₂. Then ca. 1 equiv of HBF₄·Et₂O (2.2 μL) was added. The dihydrogen complex was characterized using NMR spectroscopy. Characterization data for *trans*-8H₂ are as follows. ¹H NMR (CD₂Cl₂): δ -9.07 (br s, 2H, η²-H₂, J(H₂-P_{cis}) = 6 Hz (HD isotopomer)), 4.54 (m, 2H, PCH₂P), 5.04 (m, 2H, PCH₂P), 6.31–7.89 (m, 40H, PPh₂). ³¹P NMR (CD₂Cl₂): δ -6.57 (s, 4P, Ph₂PCH₂PPh₂). T₁ (400 MHz, CD₂Cl₂, 298 K): η²-H₂ ligand, 15.87 ms; J(H,D) = 26 Hz, d_{HH} = 0.99 Å.

¹H NMR Spin–Lattice Relaxation Time Measurements. The dihydrogen ligand in the complexes *cis*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = phosphite or phosphine) and *trans*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ were found to be quite labile. Although variable-temperature T₁ measurements were carried out, precise values of T₁ could not be obtained because the data were rendered unreliable by the high lability of the H₂ ligand. Therefore, we report here (Table 10) only the room-temperature T₁ data for all the complexes. These measurements were carried out within few minutes of the generation of the dihydrogen complexes. The short T₁ values for our complexes evidence the intact nature of the H–H bond in these derivatives.

Observation of the H–D Isotopomers. The HD isotopomers were obtained as follows: (a) D₂ gas was purged through a CD₂-Cl₂ solution of *trans/cis*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = P(OMe)₃ (*trans*-2HD and *cis*-2HD), P(OEt)₃ (*trans*-3HD and *cis*-3HD)) for ca. 10 min. (b) Excess DBF₄·Et₂O (prepared from HBF₄·Et₂O and D₂O in a 3:1 ratio) was added to a CD₂Cl₂ solution of *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OⁱPr)₃ (*trans*-4H)) (12 mg)/*cis*-[(dppm)₂Ru(H₂)] (12 mg)/*trans*-[(dppm)₂Ru(H)(Cl)] (*trans*-8H) (12 mg). The H–D isotopomers formed were observed by ¹H NMR spectroscopy.

X-ray Structure Determination of *trans*-[(dppm)₂Ru(H)(P(OMe)₃)]₂[BF₄] (*trans*-2H) and *cis*-[(dppm)₂Ru(H)(L)]₂[BF₄] (L = P(OMe)₃ (*cis*-2H), P(OⁱPr)₃ (*cis*-4H)). Suitable crystals of *trans*-2H, *cis*-2H, and *cis*-4H were chosen after examination under a microscope. X-ray diffraction intensities were measured by ω scans using a Siemens three-circle diffractometer attached with a CCD area detector and a graphite monochromator for the Mo Kα radiation (50 kV, 40 mA). The crystals of *cis*-2H and *cis*-4H were cooled to 130 K on the diffractometer using a stream of cold N₂ gas from a vertical nozzle; this temperature was maintained during the data collection. In the case of *trans*-2H, the data collection was carried out at 298 K. The unit cell parameters and the orientation matrix were initially determined using 80 reflections from 25 frames collected over a small ω scan of 7.5° sliced at 0.3° intervals. A hemisphere of reciprocal space was then collected using the SMART software¹⁸ and 2θ settings of the detector at 28°. Data reduction was done using the SAINT program,¹⁸ 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 are summarized in Table 8. An empirical absorption correction based on symmetry-equivalent reflections was applied using the

Table 8. Crystallographic Data for *trans*-[(dppm)₂Ru(H)(P(OMe)₃)]₂[BF₄] (*trans*-2H), *cis*-[(dppm)₂Ru(H)(P(OMe)₃)]₂[BF₄] (*cis*-2H), and *cis*-[(dppm)₂Ru(H)(P(OⁱPr)₃)]₂[BF₄] (*cis*-4H)

	<i>trans</i> -2H	<i>cis</i> -2H	<i>cis</i> -4H
formula	C ₅₄ H ₅₆ BCl ₂ F ₄ ·O ₃ P ₃ Ru	C ₅₃ H ₅₃ BF ₄ ·O ₃ P ₃ Ru	C ₅₉ H ₆₂ BF ₄ ·O ₃ P ₃ Ru
fw	1165.61	1080.68	1161.82
cryst syst	monoclinic	triclinic	monoclinic
space group	P2 ₁ /c	P1	P2 ₁ /n
a, Å	10.21610(10)	9.77640(10)	12.5092(3)
b, Å	24.6584(3)	15.0833(2)	33.9863(7)
c, Å	22.0474(2)	20.72300(10)	12.9395(2)
α, deg	89.9970(10)	75.75	89.95
β, deg	91.3580(10)	76.1020(10)	92.4970(10)
γ, deg	90.0780(10)	77.1270(10)	89.9820(10)
V, Å ³	5552.45(10)	2831.23(5)	5495.89(19)
Z	4	2	4
D _{calcd} , g/cm ³	1.394	1.268	1.404
T, K	293(2)	130(2)	130(2)
λ, Å	0.710 73	0.710 73	0.710 73
μ, mm ⁻¹	0.577	0.469	0.489
R ^a	0.0536	0.0635	0.0386
R _w ^a	0.1192	0.2032	0.0780

^a R = Σ(|F_o| - |F_c|)/Σ|F_o|; R_w = [Σw(|F_o| - |F_c|)²/Σw|F_o|²]^{1/2} (based on reflections with I > 2σ(I)).

SADABS program,¹⁹ 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 respectively 0.1 and 0.0688, 0.0433 and 0.0338, and 0.56 and 0.0481 for *trans*-2H, *cis*-2H, and *cis*-4H. 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.²⁰ H atoms other than those on ruthenium were fixed and refined isotropically.

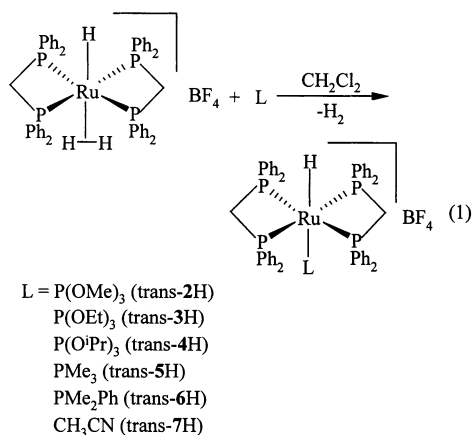
Results and Discussion

Synthesis of New Hydride Complexes. The new ruthenium hydride complexes *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (*trans*-2H), P(OEt)₃ (*trans*-3H), P(OⁱPr)₃ (*trans*-4H), PMe₃ (*trans*-5H), PMe₂Ph (*trans*-6H), CH₃CN (*trans*-7H)) were prepared from *trans*-[(dppm)₂Ru(η²-H₂)(H)][BF₄] (*trans*-1H) (generated in situ) similar to the preparation of the analogous dppe hydride derivatives reported by us² and the *trans*-[(dppe)₂Os(H)(CH₃CN)][BF₄] by Schlaf et al.²¹ (eq 1). The reaction mixtures have to be worked up rapidly, typically 1 min after the addition of the phosphorus ligands, otherwise the trans hydrides isomerize to give mixtures of trans and cis hydride phosphite/phosphine derivatives (see text later).

trans-1H was prepared by reacting *cis/trans*-[(dppm)₂Ru(H₂)] with exactly 1 equiv of HBF₄·Et₂O in Et₂O under H₂ atmosphere. It was characterized using NMR spectroscopy (see Experimental Section).²² For the preparation of *trans*-

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$[(\text{dppm})_2\text{Ru}(\text{H})(\text{L})][\text{BF}_4]$ complexes ($\text{L} = \text{P}(\text{OR})_3$, PR_3 , CH_3CN) the amount of phosphorus/ CH_3CN ligand that was reacted with *trans*-1H was based on the concentration of the starting dihydride complex. All the new hydrides were obtained in good yields as off-white to dull cream-colored solids. They were purified by crystallization from CH_2Cl_2 -petroleum ether solutions in the presence of a slight excess of the appropriate phosphite or phosphine or acetonitrile in the crystallization mixture in the absence of which the *trans* hydrides isomerize with time to give a mixture of the *trans* and *cis* isomers. This means that the *trans* P ligand is very labile in these complexes.

The ^1H NMR spectra of the *trans*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{L})][\text{BF}_4]$ ($\text{L} = \text{P}(\text{OR})_3$ or PR_3) complexes show a doublet of quintets for the hydride ligand due to coupling with the *trans* P ($\text{P}(\text{OR})_3$ or PR_3) and the four *cis* P (dppm) nuclei. The $J(\text{H}, \text{P}_{\text{trans}})$ is on the order of 100 Hz for the $\text{P}(\text{OR})_3$ and 50 Hz for the *trans* PR_3 complexes. We² and others²³ observed this trend earlier. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a doublet ($J(\text{P}, \text{P}) = 23\text{--}33$ Hz) for the dppm P nuclei due to coupling with the phosphite/phosphine ligand and a quintet for the phosphite/phosphine coupled to the four dppm phosphorus nuclei.

Our attempts to prepare the PBU_3 , PPh_3 , and PCy_3 hydride complexes failed, and the starting *trans*-1H complex was recovered. To understand the steric effects of the dppm ligand, we carried out an X-ray crystallographic study of *trans*-2H.

Structure of *trans*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)][\text{BF}_4]$ (*trans*-2H). The structure of *trans*-2H cation is shown in Figure 1. The cation is made up of a nearly perfect square pyramid defined by four coplanar dppm phosphorus atoms and the $\text{P}(\text{OMe})_3$ moiety perpendicular to this plane. In addition to a discrete $[\text{BF}_4]^-$ counterion a molecule of CH_2Cl_2 is also present. The hydride ligand that occupies the sixth coordination site on the metal was not located; however, ^1H NMR spectroscopy provides evidence of its presence. The dppm

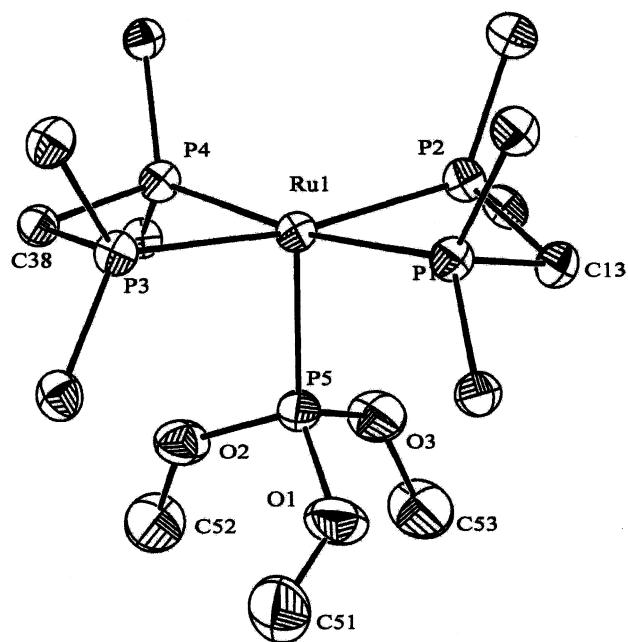


Figure 1. ORTEP view of the *trans*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)]^+$ (*trans*-2H) cation at the 50% probability level. The phenyl groups on the dppm phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for *trans*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)][\text{BF}_4]$ (*trans*-2H), *cis*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)][\text{BF}_4]$ (*cis*-2H), and *cis*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{P}(\text{O}^i\text{Pr})_3)][\text{BF}_4]$ (*cis*-4H)

	<i>trans</i> -2H	<i>cis</i> -2H	<i>cis</i> -4H
Ru(1)–P(5)	2.3153(17)	2.249(2)	2.2924(9)
Ru(1)–P(4)	2.3375(16)	2.417(2)	2.4252(9)
Ru(1)–P(3)	2.3347(15)	2.349(2)	2.3380(9)
Ru(1)–P(2)	2.3554(16)	2.316(2)	2.3466(9)
Ru(1)–P(1)	2.3680(16)	2.379(2)	2.4048(9)
P(5)–O(1)	1.579(5)	1.612(5)	1.602(2)
P(5)–O(2)	1.600(5)	1.585(5)	1.605(3)
P(5)–O(3)	1.596(5)	1.605(5)	1.600(2)
P(5)–Ru(1)–P(4)	92.45(6)	92.15(7)	92.97(3)
P(5)–Ru(1)–P(3)	94.53(6)	93.22(7)	92.51(3)
P(4)–Ru(1)–P(3)	71.95(5)	70.89(7)	69.64(3)
P(5)–Ru(1)–P(2)	95.50(6)	90.20(7)	94.95(3)
P(3)–Ru(1)–P(2)	169.95(6)	176.23(7)	172.38(3)
P(5)–Ru(1)–P(1)	95.53(6)	152.14(8)	159.03(3)
P(4)–Ru(1)–P(1)	171.84(6)	113.58(7)	107.04(3)

bite angles $\text{P}(1)\text{--Ru}(1)\text{--P}(2)$ and $\text{P}(3)\text{--Ru}(1)\text{--P}(4)$ are $69.59(5)$ and $71.95(5)^\circ$, respectively. The $\text{Ru}\text{--P}(\text{dppm})$ bond lengths vary from $2.3347(15)$ to $2.3680(16)$ Å while the $\text{Ru}\text{--P}$ distance ($\text{P}(\text{OMe})_3$) is $2.3153(17)$ Å. The $\text{Ru}\text{--P}(\text{P}(\text{OMe})_3)$ bond of the *trans*-2H complex is elongated by ca. 0.07 Å compared to its *cis* isomer (see later). The plane of the four dppm phosphorus atoms in *trans*-2H is nearly perfect whereas the analogous dppe derivative² is slightly puckered. The $\text{P}(1)\text{--C}(13)\text{--P}(2)$ and $\text{P}(3)\text{--C}(38)\text{--P}(4)$ bond angles are 92.7 and $95.6(3)^\circ$, respectively, falling in the lower end of the range of $\text{P}\text{--C}\text{--P}$ bond angles ($92\text{--}133^\circ$) that dppm ligand exhibits in its complexes. The selected bond lengths and angles have been summarized in Table 9.

Protonation Reaction of the Hydride Complexes *trans*- $[(\text{dppm})_2\text{Ru}(\text{H})(\text{L})][\text{BF}_4]$ ($\text{L} = \text{P}(\text{OMe})_3$ (*trans*-2H), $\text{P}(\text{OEt})_3$ (*trans*-3H), $\text{P}(\text{O}^i\text{Pr})_3$ (*trans*-4H)). The hydride com-

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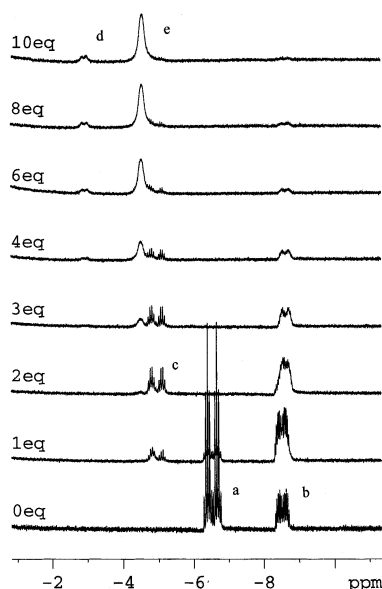


Figure 2. Hydride region of the ¹H NMR spectrum for the titration of *trans*-[(dppm)₂Ru(H)(P(OⁱPr)₃)] [BF₄] (*trans*-4H) with HBF₄·Et₂O in CD₂Cl₂. The number of equivalents of acid added with respect to the starting hydride complex is indicated on the left of each spectrum. Key: (a) *trans*-[(dppm)₂Ru(H)(P(OⁱPr)₃)] [BF₄] (*trans*-4H); (b) *cis*-[(dppm)₂Ru(H)(P(OⁱPr)₃)] [BF₄] (*cis*-4H); (c) *trans*-[(dppm)₂Ru(H)(PF(OⁱPr)₂)] [BF₄]; (d) *trans*-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (*trans*-4H₂); (e) *cis*-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (*cis*-4H₂).

Table 10. *T*₁ (400 MHz, 298 K) Data for the Dihydrogen Complexes

complex	<i>T</i> ₁ (ms)	complex	<i>T</i> ₁ (ms)
<i>trans</i> -2H ₂	15.8	<i>cis</i> -3H ₂	12.3
<i>cis</i> -2H ₂	13.7	<i>trans</i> -4H ₂	12.9
<i>trans</i> -3H ₂	14.4	<i>cis</i> -4H ₂	12.5

plexes were titrated with HBF₄·Et₂O in CD₂Cl₂. Addition of 1 equiv of the acid to the hydride complexes transformed the doublet of quintets into a multiplet pattern in the hydride region of the ¹H NMR spectrum. It was apparent from the coupling constants that the multiplet was due to a *cis* isomer, *cis*-[(dppm)₂Ru(H)(L)][BF₄]. Further acid addition led to a broad singlet due to *cis*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = P(OMe)₃, P(OEt)₃) complex that increased in intensity with increasing number of equivalents of the acid. The complete conversion required 6 equiv of the acid. The isomerization proceeds slowly in the presence of ≤ 1 equiv of the acid. In addition to the broad singlet, a weak broad doublet due to *trans*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ was also obtained.

In the case of *trans*-4H, the addition of 1 equiv of acid affords the *cis* isomer. A small amount of another hydride, *trans*-[(dppm)₂Ru(H)(PF(OⁱPr)₂)] [BF₄] (observation of *J*(P,F) in the ³¹P NMR), was also seen. We reported the mechanism of the formation of an analogous dppe-containing species earlier.² The *cis*-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (*cis*-4H₂) and *trans*-[(dppm)₂Ru(η²-H₂)(PF(OⁱPr)₂)] [BF₄]₂ (*trans*-4H₂) complexes resulted upon addition of more acid (Figure 2). The cone angle reduction (in PF(OⁱPr)₂) in the otherwise sterically crowded P(OⁱPr)₃ to give the *trans*-[(dppm)₂Ru(H)(PF(OⁱPr)₂)] [BF₄] that was observed spectroscopically seems reasonable. In the cases of the P(OMe)₃ and P(OEt)₃ (smaller cone angles) hydrides, no fluorine substitution was observed. We, however, found that, in all the three cases, a

small amount of *cis* isomer was already present in solution before the addition of the acid.

Synthesis of *cis*-[(dppm)₂Ru(H)(L)][BF₄] Complexes (L = P(OMe)₃ (*cis*-2H), P(OEt)₃ (*cis*-3H), P(OⁱPr)₃ (*cis*-4H), PMe₃ (*cis*-5H), PMe₂Ph (*cis*-6H)). The protonation of the *trans* hydride phosphite/phosphine complexes with 1 equiv of HBF₄·Et₂O in CHCl₃ yielded the isomerized derivatives. Upon workup of the reaction mixture, the products were obtained as off-white solids containing both the isomers. Separation of the *trans* and the *cis* hydride phosphite complexes was accomplished via crystallization in the case of P(OMe)₃ derivative. The *cis* isomer crystallized as pale orange crystals whereas the *trans* one was colorless; thus, manual separation was possible.

When CHCl₃ solutions of the *trans* hydrides were refluxed, they isomerized, the facilities of which are dependent on the cone angles of the phosphorus ligands: easier for ligands that have larger cone angles, that is, P(OⁱPr)₃ > P(OEt)₃ > P(OMe)₃.²⁴ ¹H NMR spectroscopy of the products showed the presence of the *trans* and the *cis* isomers in ratios of 19:81 (P(OMe)₃), 3:97 (P(OEt)₃), 0:100 (P(OⁱPr)₃), 42:58 (PMe₃), and 41:59 (PMe₂Ph), respectively. We have determined the *K*_{eq} values for the isomerization using NMR spectroscopy, and the data have been deposited in the Supporting Information.²⁵

The ¹H NMR spectra of the *cis* hydride complexes show multiplet pattern (spin system XABCDM) for the hydride ligand. The hydride region of the spectrum of *cis*-4H was simulated using a simulation program,²⁶ which matched the observed spectrum. The *cis* conformation was also ascertained from the ³¹P NMR coupling constants (Table 5).^{4,27} In addition, we determined the X-ray crystal structures of [(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ and P(OⁱPr)₃) complexes to prove the *cis* conformation without any ambiguity.

The *trans* phosphorus ligands in the hydride complexes were found to be labile. We found small amounts of the free ligand in CH₂Cl₂ solutions of the *trans* hydrides as evidenced by ³¹P NMR spectroscopy. When these solutions were refluxed, the *trans* hydrides isomerized slowly to give small quantities of the *cis* isomers over a period of several days. Addition of free ligand to these solutions suppressed the isomerization (Scheme 1). However, when the *trans* hydrides were refluxed in CHCl₃ solvent (with traces of acid impurities), the isomerization proceeded much faster. We monitored the *trans*-2H to *cis*-2H isomerization in CHCl₃ (with traces of acid impurities; CDCl₃ as external lock) in a sealed NMR tube using ³¹P NMR. A small amount of HP(OMe)₃⁺ (25.0 ppm)^{23a} was found initially along with some free ligand (138.4 ppm).^{23a} As the reaction progressed, the integral of the signal due to free ligand reduced and did not undergo

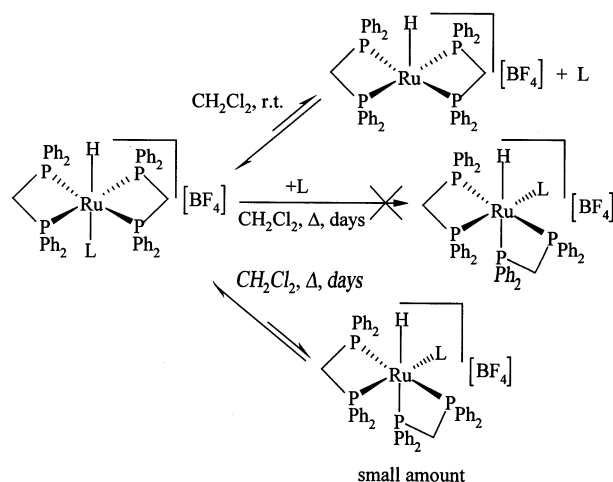
(24) We are studying the kinetics of the isomerization reactions currently, the results of which will be published shortly.

(25) We were unable to determine the *K*_{eq} values for the acid-accelerated isomerization reactions because some amounts of dihydrogen complexes were also formed in the protonation reactions with HBF₄·Et₂O and not just the two isomers.

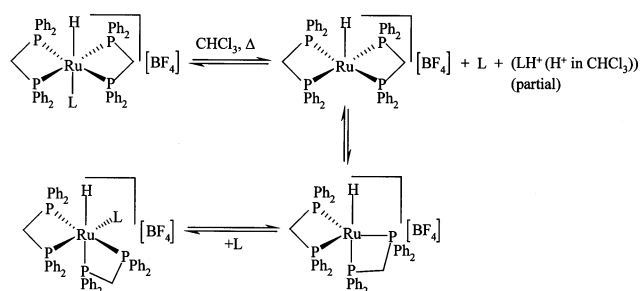
(26) Bruker WIN-DAISY, 4.05 version.

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Scheme 1



Scheme 2



further change with time. The mechanism thus involves the trans phosphorus ligand loss that is trapped by some external acid thereby accelerating the isomerization; some free ligand still remains in equilibrium that binds back to the metal cis to the hydride to give the isomerized derivative (Scheme 2). On the other hand, the $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ added in the protonation of the trans hydrides serves to trap the free phosphorus ligand and thus accelerating the isomerization. It must be noted that acid is not required for the isomerization; however, the presence of it accelerates the reaction.

In the case of the *trans*-4H complex, a competing reaction takes place in the presence of excess $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 : protonation of the trans phosphite ligand to generate a new *trans*- $[(\text{dppe})_2\text{Ru}(\eta^2\text{-H}_2)(\text{PF}(\text{O}^i\text{Pr})_2)][\text{BF}_4]_2$ (*trans*-4H₂) derivative through the intermediacy of *trans*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{PF}(\text{O}^i\text{Pr})_2)][\text{BF}_4]$. This hydride complex could not be isolated; however, it was observed in the ^1H NMR spectrum. In the presence of excess acid, the *cis*-4H complex gives *cis*-4H₂ presumably via the *cis*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{PF}(\text{O}^i\text{Pr})_2)][\text{BF}_4]$ species which could not be observed spectroscopically.

Structure of *cis*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)][\text{BF}_4]$ (*cis*-2H). An ORTEP diagram of the *cis*-2H cation is shown in Figure 3. The structure consists of a severely distorted octahedron: three of the four dppe P atoms define a plane whereas the fourth phosphorus is approximately trans to the phosphite ligand that is perpendicular to the plane of the three dppe P atoms. The hydride ligand that occupies the sixth coordination site on the metal was not located. The dppe bite angles $\text{P}(1)\text{--Ru}(1)\text{--P}(2)$ and $\text{P}(3)\text{--Ru}(1)\text{--P}(4)$ are respectively $71.40(7)$ and $70.89(7)^\circ$. The notable feature

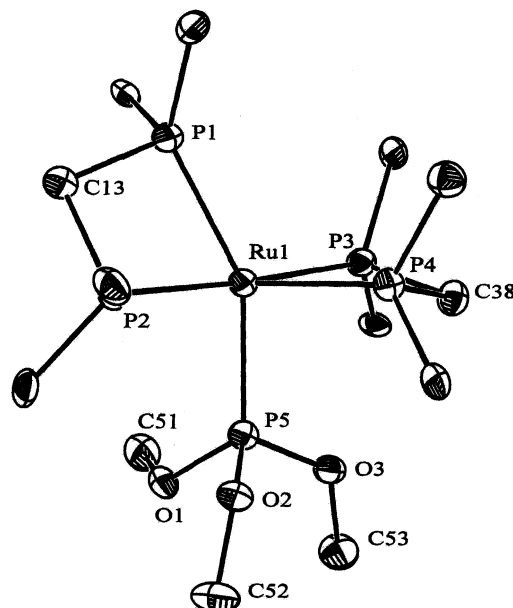


Figure 3. ORTEP view of the *cis*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{P}(\text{OMe})_3)]^+$ (*cis*-2H) cation at the 50% probability level. The phenyl groups on the dppe phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

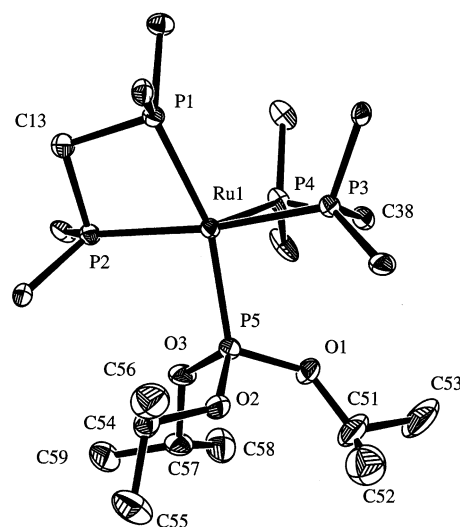
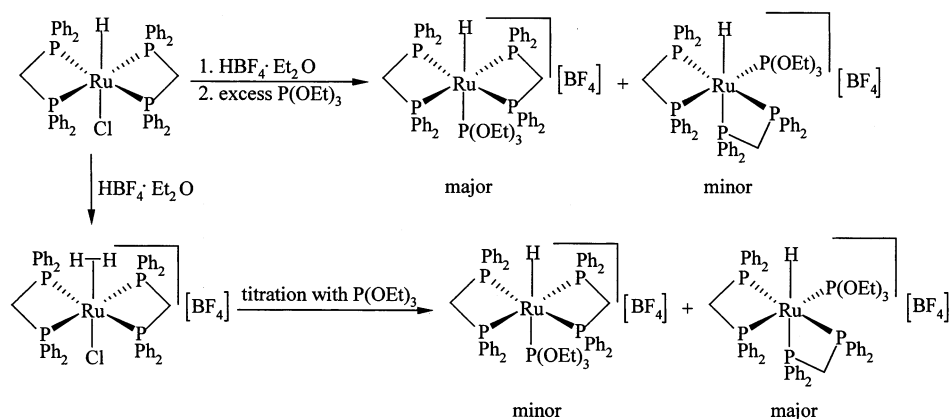


Figure 4. ORTEP view of the *cis*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{P}(\text{O}^i\text{Pr})_3)]^+$ (*cis*-4H) cation at the 50% probability level. The phenyl groups on the dppe phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

of the structure is the *tightening* of the $\text{Ru}(1)\text{--P}(5)$ bond ($2.249(2)$ Å) compared to that of the *trans* isomer ($2.3153(17)$ Å). The pertinent bond lengths and angles are listed in Table 9.

Structure of *cis*- $[(\text{dppe})_2\text{Ru}(\text{H})(\text{P}(\text{O}^i\text{Pr})_3)][\text{BF}_4]$ (*cis*-4H). An ORTEP view of the *cis*-4H cation is shown in Figure 4. The structure consists of a severely distorted octahedron around the metal center with three of the four dppe P atoms forming a plane, phosphite and the fourth dppe phosphorus being approximately perpendicular to this plane. The hydride ligand that could not be located completes the sixth coordination site around ruthenium. The $\text{Ru}\text{--P}$ bond lengths (dppe) are in the range $2.3380(9)\text{--}2.4252(9)$ Å whereas the $\text{Ru}\text{--P}$ bond distance ($\text{P}(\text{O}^i\text{Pr})_3$) is $2.2924(9)$ Å. The dppe

Scheme 3



bite angles P(1)–Ru(1)–P(2) and P(3)–Ru(1)–P(4) are respectively 72.23(3) and 69.64(3)°. We found that one of the CH₃ groups on the P(OⁱPr)₃ ligand was disordered with occupancies of 44% and 56%, respectively. The figure shows only one of the orientations. The salient bond distances and angles are listed in Table 9.

Reactivity of *trans*-[(dppm)₂RuH(Cl)] (*trans*-8H). The *trans*-8H complex was prepared from *cis*/*trans*-[(dppm)₂RuH₂] using a method adapted from literature: the dihydrides are unstable in CHCl₃; upon dissolving in CHCl₃, the hydride chloride complex was obtained.¹⁶ Protonation of *trans*-8H with 1 equiv of HBF₄·Et₂O gave the corresponding dihydrogen complex, *trans*-[(dppm)₂Ru(η²-H₂)(Cl)][BF₄] (*trans*-8H₂). In the context of losing HCl instead of H₂ in its reactivity *trans*-8H₂ is similar to *trans*-[(dppe)₂Ru(η²-H₂)(Cl)][BF₄].⁴ When *trans*-8H was reacted with 1 equiv of the acid in the presence of excess P(OEt)₃ [(dppm)₂RuH(P(OEt)₃)] [BF₄] (*cis*-3H (minor) and *trans*-3H (major)) were obtained. The reaction could involve an intermediate η²-H₂ complex that loses HCl. We have not detected the HCl directly. The phosphite attacks the metal on the vacant site generated by the elimination of HCl resulting in [(dppm)₂RuH(P(OEt)₃)] [BF₄]. When *trans*-8H was first protonated with 1 equiv of acid followed by a titration with phosphite (1–5 equiv in increments of 1 equiv), *cis*-3H was obtained as the major product with a small amount of the *trans* isomer. These reactions are shown in Scheme 3.

Protonation Reactions of *cis*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OMe)₃ (*cis*-2H), P(OEt)₃ (*cis*-3H), P(OⁱPr)₃ (*cis*-4H)). The protonation reactions of mixtures of *trans* (minor) and *cis* hydride phosphite (major) complexes were carried out under an H₂ atmosphere in CD₂Cl₂ using excess HBF₄·Et₂O. When the protonation was carried out in an Ar atmosphere, signals due to the η²-H₂ complexes *cis*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = P(OMe)₃ (*cis*-2H₂), P(OEt)₃ (*cis*-3H₂), P(OⁱPr)₃ (*cis*-4H₂)) were not observed. In fact no resonances were observed in the hydride region which could mean that although protonation did take place, the H₂ ligand due to its lability is eliminated under argon. We found a singlet at δ 4.6 ppm assignable to free H₂ in the ¹H NMR spectrum.

The ¹H NMR spectrum of the dihydrogen complex shows a broad singlet in the hydride region for the η²-H₂ ligand.

Loss of H₂ takes place in our complex with time; we found that the loss of H₂ is reversible. When H₂ gas is purged through the solutions, the dihydrogen complexes were recovered.

Protonation Reaction of the Hydride Complexes *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = PMe₃ (*trans*-5H), PMe₂Ph (*trans*-6H)). The protonation of these complexes in CD₂Cl₂ with 1 equiv of HBF₄·Et₂O led to the complete disappearance of the starting hydride accompanied by the appearance of *cis*-[(dppm)₂Ru(H)(L)][BF₄], *cis*-[(dppm)₂Ru(η²-H₂)(L)][BF₄]₂ (L = PMe₃ (*cis*-5H, *cis*-5H₂), PMe₂Ph (*cis*-6H, *cis*-6H₂)), *trans*-[(dppm)₂Ru(η²-H₂)(H)][BF₄] (*trans*-1H), and *trans*-[(dppm)₂Ru(η²-H₂)Cl][BF₄] (*trans*-8H₂) complexes in the ¹H NMR spectrum. Further acid addition resulted in the disappearance of all the species except *trans*-8H₂. When excess acid was used, two new signals were observed in the ³¹P NMR spectrum assignable to *trans*-[(dppm)₂Ru(BF₄)Cl] (*trans*-9) along with that of the free ligand. The pathway to these species is unclear. In the presence of a large excess acid, the ³¹P NMR signals of *trans*-9 broaden and at the same time move slightly downfield. A similar observation was made by Morris et al.⁴ for [(dppe)₂RuCl]⁺. The signal broadening was explained as a monomer to chloride-bridged dimer equilibrium as observed for [L₂Ru(μ-Cl)₂RuL₂]²⁺ (L = Ph₂PCH₂CH₂-2-py)²⁸ and [(PMe₃)₄Ru(μ-Cl)]₂[Cl]₂.²⁹

H–D Isotopomers. The H–D isotopomers were obtained by exposing the η²-H₂ complexes to D₂ gas or by the use of DBF₄·Et₂O to deuterate the starting hydrides. Albeniz et al.³⁰ proposed that a combination of the lability and the acidity of the H₂ ligand is responsible for the isotopic scrambling to form the HD isotopomers. The η²-HD ligand was observed in the ¹H NMR spectrum by nullifying the residual η²-H₂ signal by an inversion recovery pulse sequence.^{31,32} The spectra exhibit triplet signals for the *cis*-[(dppm)₂Ru(η²-HD)(L)][BF₄]₂ complexes the intensity ratios of which are

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Table 11. Properties of Dihydrogen Complexes of Ruthenium

complex	$E_{1/2}$, V ^a	$J(\text{H,D})$, Hz	d_{HH} , Å ^b	stability ^c
<i>trans</i> -[(dppm) ₂ Ru(H ₂)Cl] ⁺	2.0	26	0.99	s
<i>trans</i> -[(dppe) ₂ Ru(H ₂)Cl] ⁺ ^d	1.8	26	0.99	s
<i>trans</i> -[(dppp) ₂ Ru(H ₂)Cl] ⁺ ^e	1.8	24	1.00	u
<i>trans</i> -[(dppm) ₂ Ru(H ₂)H] ⁺	1.9	29	0.94	s
<i>trans</i> -[(dppm) ₂ Ru(H ₂)(P(OR) ₃)] ²⁺	2.7	32 (R = Me) 30 (R = Et)	0.88 (R = Me) 0.92 (R = Et)	u u
<i>cis</i> -[(dppm) ₂ Ru(H ₂)(P(OR) ₃)] ²⁺	2.7	29 (R = Me) 26 (R = Et)	0.94 (R = Me) 0.99 (R = Et)	u u
<i>trans</i> -[(dppe) ₂ Ru(H ₂)(PF(OR) ₂)] ²⁺ ^f	na ^g	29 (R = Me) 28 (R = Et)	0.94 (R = Me) 0.95 (R = Et)	1d ^h 1d ^h
<i>trans</i> -[(dppm) ₂ Ru(H ₂)(CNH)] ²⁺ ⁱ	na ^g	32.2	0.88	u

^a Calculated $E_{1/2}$ values of the N₂ complexes.⁴¹ ^b Calculated from the $J(\text{H,D})$ values of the HD isotopomers using the equation given in ref 34. ^c Stability with respect to loss of H₂ at room temperature (s = stable; u = unstable); see ref 41 for definition of categories. ^d Reference 4. ^e Reference 39. ^f Reference 2. ^g Not available. ^h Loss of H₂ starts to occur after ca. 24–36 h. ⁱ Reference 5.

approximately 1:1:1 with $J(\text{H,D})$ of 29, 26, and 29 Hz for *cis*-2HD, *cis*-3HD, and *cis*-4HD, respectively. The *trans*-[(dppm)₂Ru(η^2 -HD)(P(OMe)₃)](BF₄)₂ (*trans*-2HD) and *trans*-[(dppm)₂Ru(η^2 -HD)(P(OEt)₃)](BF₄)₂ (*trans*-3HD) complexes gave doublets of triplets with $J(\text{H,D})$ of 32 and 30 Hz, respectively. The H–H distances (d_{HH}) calculated from the inverse relationship between d_{HH} and $J(\text{H,D})$ of the HD isotopomers^{33,34} are 0.88, 0.94, 0.92, 0.99, and 0.94 Å respectively for *trans*-2H₂, *cis*-2H₂, *trans*-3H₂, *cis*-3H₂, and *cis*-4H₂.

Comments on H–H Distances and the Stabilities of the Dihydrogen Complexes. The complexation of H₂ to a metal is considered to result from the σ (η^2 -H₂) donation to the empty d (M) orbital and π back-donation from the filled d (M) orbital to the σ^* (η^2 -H₂) orbital. Table 11 shows a comparison of some of the properties of our H₂ complexes and also the ones reported by others. The weak trans influence of Cl[−], a π -donor ligand, favors the σ donation from H₂ to metal d orbitals and an increased back-donation from the metal to the σ^* orbital of H₂. These effects, consequently, weaken the H–H bond and increase the M–H₂ interaction. Thus, a relatively long H–H distance (d_{HH} = 0.99 Å) is consistent with the tight binding of H₂ to the metal as found in *trans*-8H₂. When solutions containing *trans*-8H₂ were exposed to D₂ gas for prolonged periods, no observable deuterium incorporation was found. This is in contrast to the observations made by Kubas et al.³⁵ on the neutral tungsten complex, by Heinekey et al.³⁶ on the cationic rhenium derivatives, and by us^{2,37} on certain ruthenium dppe complexes that undergo rapid H₂/D₂ exchange. It was earlier suggested that complexes bearing elongated H–H bond are less acidic compared to those with a short H–H bond.^{6e} However, we speculate that *trans*-8H₂ might show greater acidity than expected. This is demonstrated by its reactions with phosphites. It eliminates HCl to give the phosphite

hydrides. With respect to exhibiting high reactivity toward heterolysis combined with tight binding of H₂ to the metal, *trans*-8H₂ behaves similar to certain other derivatives reported (highly acidic) in the literature.^{4,38–40}

In light of the calculated oxidation potentials of the corresponding N₂ complexes as suggested by Morris,⁴¹ our dihydrogen complexes may be categorized as having labile H₂ ligands. It was suggested that if the $E_{1/2}$ value of the corresponding N₂ complex is >2.0 V, the dihydrogen complex can be predicted to be unstable with respect to loss of H₂ at 298 K under Ar. The dihydrogen complexes reported in this work are fully formed under 1 atm of H₂; upon loss of the H₂ ligand, the dihydrogen complex could be recovered by purging the solution containing the [(dppm)₂Ru(P(OR)₃)]²⁺ with H₂ gas.⁴² This is in contrast to our earlier findings² on the dppe analogues wherein we noted that the *trans*-[(dppe)₂Ru(η^2 -H₂)(PF(OR)₂)]²⁺ complexes could be generated either under Ar or H₂ atmosphere.⁴³ Those derivatives were stable with respect to loss of H₂ ligand; however, upon loss of H₂ (typically ca. 24–36 h), the dihydrogen complexes could not be recovered which could mean that the 5 coordinate species is highly reactive. We⁴⁴ found that this species picks up either a water molecule (residual water in the solvent) or dioxygen and generates species that we have not able to identify.

One another observation is the long H–H bond in the *cis* H₂ phosphite complexes compared to the *trans* ones. The *cis* complexes have phosphine ligands (not as strong as phosphites in terms of π acidity) *trans* to the H₂ that results in this bond elongation.^{45,46}

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Conclusions

The protonation reactions of the hydride complexes *trans*-[(dppm)₂Ru(H)(L)][BF₄] (L = P(OR)₃) with HBF₄·Et₂O gave pure *cis* hydride phosphite derivative, *cis*-[(dppm)₂Ru(H)(L)][BF₄] for L = P(OⁱPr), whereas, for L = P(OMe)₃ and P(OEt)₃, equilibrium mixtures of both the *cis* and *trans* isomers are produced, the separation of which is somewhat difficult. The isomerization seems to be accelerated by acid via the trapping of the labile *trans* phosphorus ligand by the added acid. Further addition of acid to the *cis* hydride complexes results in the corresponding dihydrogen complexes, the first examples in this class of complexes wherein the H₂ and the monodentate phosphorus ligands are in *cis* conformations. The dihydrogen ligand in these systems was found to be quite labile.

The starting *trans* hydride complexes bearing the phosphine ligands (PR₃) also behave in a similar manner with respect to isomerization. However, further addition of the acid to mixtures of the *cis* and the *trans* hydrides results in *trans*-[(dppm)₂Ru(BF₄)Cl]. From this study it can be concluded that the bite angles of the diphosphine moieties and

the cone angles and the π -acidities of the monodentate phosphorus ligands can have a profound effect on the properties of the dihydrogen complexes.

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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 *trans*-2H, *cis*-2H, and *cis*-4H, in CIF format, a table of K_{eq} data for the *trans*/*cis* isomerization reaction, and a figure showing the ¹H NMR spectra of the hydride region for the titration of *trans*-2H with HBF₄·Et₂O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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