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Trans → Cis Isomerization of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OR)$_3$) Complexes: Preparation of *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$†

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A series of new dicationic dihydrogen complexes of ruthenium of the type *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (dppm = $Ph_2PCH_2PPh_2$; L = P(OMe)$_3$, P(OEt)$_3$, PF(O^{i}Pr)$_2$) have been prepared by protonating the precursor hydride complexes *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$, P(OEt)$_3$, P(O^{i}Pr)$_3$) using HBF$_4$·Et$_2$O. The *cis*-[(dppm)$_2$Ru(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*-[(dppm)$_2$Ru(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*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$], *cis*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$], and *cis*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][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*-[(dppe)$_2$Ru(η^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*-[($R_2PCH_2CH_2PR_2$)$_2$M(η^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*-[(P−P)$_2$Ru(η^2-H$_2$)(CN)]$^+$ and *trans*-[(P−P)$_2$Ru(η^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)$_4$Ru(η^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)$_2$Ru"H$_3$"]$^+$ fragment ([(P−P)$_2$Ru"H$_3$"]$^+$ = [(P−P)$_2$Ru(H)(η^2-H$_2$)]$^+$; P−P = dppb, diop, dpmb, dppe) and concluded that with an increasing bite angle of the

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(1) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(2) Mathew, N.; Jagirdar, B. R.; Gopalan, R. S.; Kulkarni, G. U. *Organometallics* **2000**, *19*, 4506.
(3) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375.
(4) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.
(5) Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4475.
(6) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (e) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (f) Morris, R. H. *Can. J. Chem.* **1996**, *74*, 1907.
(7) Maseras, F.; Koga, N.; Morokuma, K. *Organometallics* **1994**, *13*, 4008.

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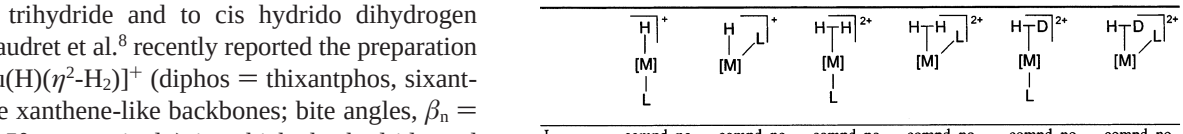
diphosphine the complexes change from trans hydrido dihydrogen to trihydride and to cis hydrido dihydrogen complexes. Chaudret et al.[8] recently reported the preparation of $[(diphos)_2Ru(H)(\eta^2\text{-}H_2)]^+$ (diphos = thixantphos, sixantphos; both have xanthene-like backbones; bite angles, β_n = 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 ^{31}P 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 $[Ph_2P(CH_2)_nPPh_2]NiX_2$ 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 $[(dppm)_2Ru(\eta^2\text{-}H_2)(L)][BF_4]_2$ (L = phosphite or phosphine); in addition, we wish to compare the present results with those of analogous dppe-containing derivatives that we reported earlier[2] 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 H_2 in a heterolytic manner; one could achieve this by having strong π-acceptor ligands trans to the η^2-H_2 moiety.

In the current work, we have attempted to carry out protonation reactions of a series of hydride complexes *trans*-$[(dppm)_2Ru(H)(L)][BF_4]$ (L = $P(OMe)_3$ (cone angle θ = 107°), $P(OEt)_3$ (θ = 109°), $P(O^iPr)_3$ (θ = 130°), PMe_3 (θ = 118°), and PMe_2Ph (θ = 122°)) with $HBF_4{\cdot}Et_2O$. We found that these hydrides, in the presence of ≤1 equiv of $HBF_4{\cdot}Et_2O$, isomerize to give new hydride complexes *cis*-$[(dppm)_2Ru(H)(L)][BF_4]$. Further addition of acid to the *cis*-$[(dppm)_2Ru(H)(L)][BF_4]$ complexes afforded the *cis*-$[(dppm)_2Ru(\eta^2\text{-}H_2)(L)][BF_4]_2$ complexes. These are the first examples in this class of complexes wherein the H_2 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-**1**H					
$P(OMe)_3$	trans-**2**H	cis-**2**H	trans-**2**H_2	cis-**2**H_2	trans-**2**HD	cis-**2**HD
$P(OEt)_3$	trans-**3**H	cis-**3**H	trans-**3**H_2	cis-**3**H_2	trans-**3**HD	cis-**3**HD
$P(O^iPr)_3$	trans-**4**H	cis-**4**H	trans-**4**H_2[b]	cis-**4**H_2[b]	trans-**4**HD[b]	cis-**4**HD[b]
PMe_3	trans-**5**H	cis-**5**H	trans-**5**H_2	cis-**5**H_2		
PMe_2Ph	trans-**6**H	cis-**6**H	trans-**6**H_2	cis-**6**H_2		
CH_3CN	trans-**7**H					
Cl	trans-**8**H[c]		trans-**8**H_2[d]		trans-**8**HD[d]	

[a] [M] = $(dppm)_2M$ fragment. [b] L = $PF(O^iPr)_2$. [c] Neutral. [d] +1.

Experimental Section

General Procedures. All reactions were carried out under N_2 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 H_2 or Ar just before use. $CHCl_3$ was purified using standard procedures.[13c] Although sufficient measures were taken to ensure that the $CHCl_3$ 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 $^{31}P\{^1H\}$ NMR spectra were measured in CD_2Cl_2 relative to 85% H_3PO_4 (aqueous solution) as an external standard and ^{19}F NMR spectra with respect to $CFCl_3$. Elemental analyses were carried out using a Heraues CHNO Rapid elemental analyzer. Bis(diphenylphosphino)methane (dppm),[15] *cis*-$[(dppm)_2RuCl_2]$,[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*-$[(dppm)_2Ru(H)(L)][BF_4]$ (L = $P(OMe)_3$ (trans-2H), $P(OEt)_3$ (trans-3H), $P(O^iPr)_3$ (trans-4H), PMe_3 (trans-5H), PMe_2Ph (trans-6H), CH_3CN (trans-7H)). All of these compounds were prepared using similar procedures. The preparation of *trans*-**2**H only is described here: To a CH_2Cl_2 (10 mL) solution of *cis*/*trans*-$[(dppm)_2RuH_2]$ (0.200 g, 0.2 mmol) was added 1 equiv (32 μL) of 54% $HBF_4{\cdot}Et_2O$. To this solution containing the *trans*-$[(dppm)_2Ru(\eta^2\text{-}H_2)(H)][BF_4]$ (*trans*-**1**H) 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 N_2 was introduced and the volume increased to ca. 30 mL by adding CH_2Cl_2. Addition of excess petroleum ether caused the precipitation of a cream colored product

(8) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, W. N. M.; Chaudret, B. *Chem. Commun.* **1997**, 373.
(9) (a) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095. (b) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435.
(10) McGarvey, J. J.; Wilson, J. *J. Am. Chem. Soc.* **1975**, *97*, 2531.
(11) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.
(12) (a) Szczepura, L. F.; Giambra, J.; See, R. F.; Lawson, H.; Janik, T. S.; Jircitano, A. J.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chim. Acta* **1995**, *239*, 77. (b) Ruiz, J.; Mosquera, M. E. G.; Riera, V. *J. Organomet. Chem.* **1997**, *527*, 35. (c) Winter, R. F.; Scheiring, T. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1196.
(13) (a) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986. (b) Herzog, S.; Dehnert, J.; Luhder, K. In *Techniques of Inorganic Chemistry*; Johnassen, H. B., Ed.; Interscience: New York, 1969; Vol. VII. (c) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Singapore, 1996; p 399. (d) The concentration of the acid impurity (HCl) was found to be approximately 4×10^{-7} M.
(14) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.
(15) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.
(16) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.
(17) Hill, G. S.; Holah, D. G.; Hughes, A. N.; Prokopchuk, E. M. *Inorg. Chim. Acta* **1998**, *278*, 226.

Table 2. ^{1}H NMR Spectral Data (δ) for *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] Complexes in CD_2Cl_2

compd no.	δ(Ru−H)	J(H,P$_{tr\ ans}$), Hz	J(H,P$_{cis}$), Hz	δ(CH$_2$)	δ(L)	J(H,E), Hz	δ(Ph)
trans-**2**H	−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-**3**H	−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-**4**H	−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-**5**H	−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-**6**H	−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-**7**H	−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. ^{31}P{^{1}H} NMR Spectral Data (δ) for *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] Complexes in CD_2Cl_2

compd no.	P(L)	P(dppm)	J(P,P), Hz
trans-**2**H	136.6 (qnt, 1P)	−1.2 (d, 4P)	33.2
trans-**3**H	135.9 (qnt, 1P)	−1.3 (d, 4P)	33.3
trans-**4**H	133.3 (qnt, 1P)	−3.5 (d, 4P)	32.7
trans-**5**H	−30.8 (qnt, 1P)	−2.9 (d, 4P)	23.8
trans-**6**H	−15.8 (qnt, 1P)	−3.5 (d, 4P)	23.8
trans-**7**H		−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 $C_{53}H_{54}BF_4O_3P_5Ru\cdot CH_2Cl_2$: C, 55.59; H, 4.83. Found: C, 56.09; H, 5.13. Yield of *trans*-**3**H): 80%. Anal. Calcd for $C_{56}H_{60}BF_4O_3P_5Ru\cdot 0.5CH_2Cl_2$: C, 58.19; H, 5.27. Found: C, 58.25; H, 5.43. Yield of *trans*-**4**H: 85%. This product contained certain impurities, and purification procedures resulted in its partial decomposition. Anal. Calcd for $C_{59}H_{66}BF_4O_3P_5Ru\cdot 0.5CH_2Cl_2$: C, 59.14; H, 5.59. Found: C, 59.91; H, 5.57. Yield of *trans*-**5**H: 84%. Anal. Calcd for $C_{53}H_{54}BF_4P_5Ru$: C, 61.58; H, 5.27. Found: C, 61.24; H, 5.12. Yield of *trans*-**6**H: 78%. Anal. Calcd for $C_{58}H_{56}BF_4P_5Ru\cdot CH_2Cl_2$: C, 60.02; H, 4.95. Found: C, 60.49; H, 4.89. Yield of *trans*-**7**H: 84%. Anal. Calcd for $C_{52}H_{48}BF_4NP_4Ru$: 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 ^{1}H NMR spectra in $CDCl_3$ and measuring the integrals for the CH_2Cl_2 (δ 5.3) of solvation (if present) with respect to the dppm $-CH_2$ 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)$_2$Ru(η^2-H$_2$)(H)][BF$_4$] (*trans*-**1**H) are as follows. ^{1}H NMR (CD_2Cl_2): δ −6.63 (qnt, 1H, Ru−*H*, J(H,P$_{cis}$) = 18.7 Hz); −2.34 (br s, 2H, η^2-*H*$_2$), 4.10 (m, 2H, PC*H*$_2$P), 4.54 (m, 2H, PC*H*$_2$P), 6.28−7.79 (m, 40H, P*Ph*$_2$). ^{31}P NMR (CD_2Cl_2): δ −0.03 (s, 4P, Ph$_2$*P*CH$_2$*P*Ph$_2$). T_1 (400 MHz, CD_2Cl_2, 298 K): η^2-H$_2$ ligand, 17.3 ms; J(H,D) = 29 Hz, d_{HH} = 0.94 Å; hydride ligand, 216 ms.

Isomerization of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ (trans-2H), P(OEt)$_3$ (trans-3H), P(O^{i}Pr)$_3$ (trans-4H), PMe$_3$ (trans-5H), PMe$_2$Ph (trans-6H)). **Method A**. A $CHCl_3$ solution (30 mL) of *trans*-**2**H (0.150 g, 0.13 mmol) was refluxed for 20 h and then cooled to room temperature, filtered, and concentrated. Addition of Et_2O (2 mL) and excess petroleum ether caused the precipitation of a mixture of *trans*-**2**H and *cis*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (*cis*-**2**H) complexes. ^{1}H NMR spectroscopy evidenced the presence of the trans and the cis isomers in a ratio of 19:81. The product was washed with Et_2O and petroleum ether and then dried in vacuo. Yield: 0.090 g. It was crystallized from a CH_2Cl_2 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*-**3**H, *trans*-**4**H, *trans*-**5**H, and *trans*-**6**H were also carried out using this method. ^{1}H NMR of the products in CD_2Cl_2: (a) L = P(OEt)$_3$, mixture of *trans*- and *cis*-[(dppm)$_2$Ru(H)(P(OEt)$_3$)][BF$_4$] (*trans*- and *cis*-**3**H) complexes in a ratio of 3 and 97%; (b) L = P(O^{i}Pr)$_3$, the cis isomer, 100%; *cis*-**4**H complex crystallized from a CH_2Cl_2 solution via diffusion of petroleum ether; (c) L = PMe$_3$, ratio of trans to cis, 42 to 58%; (d) L = PMe$_2$Ph, 41% trans to 59% cis. The NMR data for these compounds are summarized in Tables 4 and 5.

Method B. To a $CHCl_3$ solution (7 mL) of *trans*-**2**H (0.100 g, 0.09 mmol) under H_2 atmosphere was added 1 equiv (13 μL) of HBF$_4\cdot$Et$_2$O. This solution was stirred for 1 min, and Et_2O (2 mL) and excess petroleum ether were added. The precipitated product was washed with Et_2O and petroleum ether and dried in vacuo. ^{1}H NMR spectrum indicated the presence of *trans*-**2**H (minor) and *cis*-**2**H (major) complexes.

Protonation Reaction of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ (trans-2H), P(OEt)$_3$ (trans-3H)). A 12 mg portion of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] was dissolved in 0.9 mL of CD_2Cl_2 in an NMR tube. This solution was freeze−pump−thaw degassed and then purged with H_2 gas for 5 min. Upon addition of 1 equiv of HBF$_4\cdot$Et$_2$O (1.8 μL for L = P(OMe)$_3$; 1.4 μL for L = P(OEt)$_3$) the ^{1}H NMR spectrum evidenced the formation of the cis isomer, *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ (*cis*-**2**H), P(OEt)$_3$ (*cis*-**3**H)). Thereafter, the acid was added in small increments. Addition of excess acid gave a mixture of *trans*- and *cis*-dihydrogen complexes [(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = P(OMe)$_3$ (*trans*-**2**H$_2$ and *cis*-**2**H$_2$); P(OEt)$_3$ (*trans*-**3**H$_2$ and *cis*-**3**H$_2$)), respectively. Characterization data for *trans*-**2**H$_2$ are as follows. ^{1}H NMR (CD_2Cl_2): δ −3.07 (d, 2H, Ru−η^2-*H*$_2$, J(H$_2$,P$_{trans}$) = 50 Hz). Signals due to other moieties could not be assigned with confidence. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 116.25 (qnt, 1P, *P*(OMe)$_3$, J(P,P) = 41.8 Hz), −10.01 (d, 4P, *dppm*). Characterization data for *trans*-**3**H$_2$ are as follows. ^{1}H NMR (CD_2Cl_2): δ −3.11 (br d, 2H, η^2-*H*$_2$, J(H$_2$,P$_{trans}$) = 43 Hz). Signals due to other moieties could not be assigned definitively. ^{31}P NMR (CD_2Cl_2): δ 114.5 (qnt, 1P, *P*(OEt)$_3$), J(P,P) = 40.2 Hz), −10.8 (d, 4P, Ph$_2$*P*CH$_2$*P*Ph$_2$).

Protonation Reaction of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(O^{i}Pr)$_3$ (trans-4H)). The protonation of *trans*-**4**H was carried out in a manner similar to that of *trans*-**2**H. Upon addition of 1 equiv of 54% HBF$_4\cdot$Et$_2$O new hydride complexes were formed, *cis*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (*cis*-**4**H) and *trans*-[(dppm)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$]. When excess acid was added, *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*trans*-**4**H$_2$) and *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*cis*-**4**H$_2$), respectively, were obtained. Characterization data for *trans*-**4**H$_2$ are as follows. ^{1}H NMR (CD_2Cl_2, rt (room temperature)): δ −2.94 (br d, 2H, η^2-*H*$_2$,

Table 4. ^{1}H NMR Spectral Data (δ) for *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] Complexes in CD_2Cl_2

compd no.	δ(Ru−H)[a]	J(H,P$_{trans}$), Hz	J(H,P$_{cis-av}$), Hz	δ(L)	J(H,E), Hz	δ(CH$_2$)	δ(Ph)
cis-**2**H	−8.51 (1H)	68.0	8.5	3.07 (d, 9H)	20[b]	5.95 (m, 4H)	6.57−7.81 (m, 40H)
cis-**3**H	−8.49 (1H)	68.0	10.2	3.43 (m, 6H)	8[c]	5.90 (m, 4H)	6.63−7.70 (m, 40H)
				0.68 (t, 9H)			
cis-**4**H	−8.52 (1H)	80.4	9.0	4.27 (m, 3H)	32[b]	5.62 (m, 4H)	6.40−7.90 (m, 40H)
				0.8 (dd, 18H)	8[c]		
cis-**5**H	−8.73 (1H)	82.0	9.5	0.76 (d, 9H)	4[c]	5.95 (m, 4H)	6.73−7.79 (m, 40H)
cis-**6**H	−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_2Cl_2

compd no.	δ(P$_M$) (J(P$_M$,P$_B$); J(P$_M$,P$_{av(A,C,D)}$, Hz))	δ(P$_D$) (J(P$_D$,P$_C$); J(P$_D$,P$_{av(A,B,M)}$, Hz))	δ(P$_C$) (J(P$_C$,P$_{av(A,B,M)}$, Hz))	δ(P$_B$) (J(P$_B$,P$_{av(A,C,D)}$, Hz))	δ(P$_A$)
cis-**2**H	144.1 (353.5; 36.4)	3.6 (233.3; 17.4)	−3.7 (22.6)	−10.5 (15.7)	−16.3
cis-**3**H	139.4 (350.7; 21.9)	4.7 (230.0; 17.2)	−4.7 (22.7)	−11.7 (16.1)	−16.2
cis-**4**H	134.7 (353.3; 25.5)	2.3 (235.0; 17.4)	−3.4 (22.6)	−11.0 (15.6)	−19.3
cis-**5**H	6.1 (240.0; 21.1)	−6.1 (205.0; 20.0)	−12.6 (22.0)	−3.2 (20.0)	−17.3
cis-**6**H	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. ^{1}H NMR Spectral Data (δ) for *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ Complexes in CD_2Cl_2

compd no.	δ(Ru−(η^2-H$_2$))	δ(L)	J, Hz	δ(CH$_2$)	δ(Ph)
cis-**2**H$_2$	−4.88 (br s, 2H)	3.17 (d, 9H)	12 (J(P,H))	5.65 (m, 4H)	6.60−7.93 (m, 40H)
cis-**3**H$_2$	−4.81 (br s, 2H)	3.61 (q, 6H)	8 (J(H,H))	5.62 (m, 4H)	6.69−7.98 (m, 40H)
		0.85 (t, 9H)			
cis-**4**H$_2$	−4.57 (br s, 2H)	4.50 (m,2H)	6 (J(H,H))	5.88 (m, 4H)	6.80−7.95 (m, 40H)
		0.87 (d,12H)			

Table 7. ^{31}P NMR Spectral Data (δ) for *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ Complexes in CD_2Cl_2

compd no.	δ(P$_M$)	δ(P$_D$)	δ(P$_C$)	δ(P$_B$)	δ(P$_A$)
cis-**2**H$_2$[a]	124.3		−16.7	−21.0	−23.6
	J(P$_M$,P$_C$) = 35 0.8 Hz		J(P$_C$,P$_{av(A,B,M))}$ = 28.0 Hz	J(P$_B$,P$_{av(A,C,M)}$) = 24.1 Hz	J(P$_A$,P$_{av(B,C,M)}$) = 24.8 Hz
	J(P$_M$,P$_{av(A,B)}$) = 35.2 Hz				
cis-**3**H$_2$[b]	120.2	−9.6	−17.8	−19.4	−22.9
	J(P$_M$,P$_A$) = 34 6.0 Hz	J(P$_D$,P$_C$) = 204.0 Hz			
	J(P$_M$,P$_{av(B,C,D)}$) = 34.9 Hz				
cis-**4**H$_2$[b]	124.6	5.9	−14.6	−22.6	−26.9
	J(P$_M$,P$_B$) = 40 0.0 Hz		J(P$_C$,P$_A$) = 258.0 Hz		
	J(P$_M$,F) = 1160.0 Hz				

[a] ABB′CM spin system. [b] ABCDM spin system.

J(H$_2$,P$_{trans}$) = 46.8 Hz), 0.74 (d, 12H, CH(CH_3)$_2$, J(H,H) = 6 Hz), 4.59 (m, 2H, CH(CH$_3$)$_2$), 6.23 (m, 4H, CH_2). ^{31}P NMR (CD_2Cl_2, rt): δ −1.27 (d, 4P, Ph$_2$$PCH_2$$PPh_2$, J(P,P) = 34.3 Hz), 121.5 (d qnt, 1P, PF(O^{i}Pr)$_2$, J(P,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$_2$), PF(O^{i}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$_2$), PF(O^{i}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_2Cl_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 = P(O^{i}Pr)$_3$) 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*-**2**H. 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 ^{1}H NMR spectrum evidenced the formation of *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$ (*cis*-**5**H), PMe$_2$Ph (*cis*-**6**H)), *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(H)][BF$_4$] (*trans*-**1**H), *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(Cl)][BF$_4$] (*trans*-**8**H$_2$), and *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = PMe$_3$ (*cis*-**5**H$_2$), PMe$_2$Ph (*cis*-**6**H$_2$)) 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*-**8**H$_2$ complex. The ^{31}P NMR spectrum, in addition to indcating *trans*-**8**H$_2$, 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_2Cl_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_2Cl_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(H,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_2Cl_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_2Cl_2 for long periods of time. The ^{1}H NMR spectrum showed the presence of a small amount of *trans*-[(dppm)$_2$Ru(H)(Cl)][BF$_4$] (*trans*-**8**H). Addition of

ca. 1 equiv of 54% $HBF_4 \cdot Et_2O$ (2.6 μL) gave *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(H)][BF$_4$] (*trans*-**1**H) along with some *trans*-**8**H$_2$. Addition of further acid resulted in the disappearance of *trans*-**1**H; however, the *trans*-**8**H$_2$ remained intact. The ^{31}P NMR spectrum of this mixture was identical to that of *trans*-**9** observed in the protonation of the PMe_3 and PMe_2Ph hydrides. In the presence of excess acid, the signals due to *trans*-**9** broaden as well as shift slightly downfield.

Preparation of *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(Cl)][BF$_4$] (trans-8H$_2$). A 15 mg portion of *trans*-[(dppm)$_2$Ru(H)(Cl)] (*trans*-**8**H) dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube was degassed and then saturated with Ar or H_2. Then ca. 1 equiv of $HBF_4 \cdot Et_2O$ (2.2 μL) was added. The dihydrogen complex was characterized using NMR spectroscopy. Characterization data for *trans*-**8**H$_2$ are as follows. ^{1}H NMR (CD_2Cl_2): δ −9.07 (br s, 2H, η^2-*H*$_2$, $J(H_2,P_{cis})$ = 6 Hz (HD isotopomer)), 4.54 (m, 2H, PC*H*$_2$P), 5.04 (m, 2H, PC*H*$_2$P), 6.31−7.89 (m, 40H, P*Ph*$_2$). ^{31}P NMR (CD_2Cl_2): δ −6.57 (s, 4P, $Ph_2PCH_2PPh_2$). T_1 (400 MHz, CD_2Cl_2, 298 K): η^2-H$_2$ ligand, 15.87 ms; J(H,D) = 26 Hz, d_{HH} = 0.99 Å.

^{1}H NMR Spin−Lattice Relaxation Time Measurements. The dihydrogen ligand in the complexes *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = phosphite or phosphine) and *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ were found to be quite labile. Although variable-temperature T_1 measurements were carried out, precise values of T_1 could not be obtained because the data were rendered unreliable by the high lability of the H$_2$ ligand. Therefore, we report here (Table 10) only the room-temperature T_1 data for all the complexes. These measurements were carried out within few minutes of the generation of the dihydrogen complexes. The short T_1 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) D_2 gas was purged through a CD_2Cl_2 solution of *trans*/*cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = $P(OMe)_3$ (*trans*-**2**HD and *cis*-**2**HD), $P(OEt)_3$ (*trans*-**3**HD and *cis*-**3**HD)) for ca. 10 min. (b) Excess $DBF_4 \cdot Et_2O$ (prepared from $HBF_4 \cdot Et_2O$ and D_2O in a 3:1 ratio) was added to a CD_2Cl_2 solution of *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = $P(O^iPr)_3$ (*trans*-**4**H)) (12 mg)/*cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] (12 mg)/*trans*-[(dppm)$_2$Ru(H)Cl] (*trans*-**8**H) (12 mg). The H−D isotopomers formed were observed by ^{1}H NMR spectroscopy.

X-ray Structure Determination of *trans*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (trans-2H) and *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ (cis-2H), P(O^{i}Pr)$_3$ (cis-4H)). Suitable crystals of *trans*-**2**H, *cis*-**2**H, and *cis*-**4**H 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*-**2**H and *cis*-**4**H were cooled to 130 K on the diffractometer using a stream of cold N_2 gas from a vertical nozzle; this temperature was maintained during the data collection. In the case of *trans*-**2**H, 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 software[18] 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 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*-**2**H, *cis*-**2**H, and *cis*-**4**H. 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.

Table 8. Crystallographic Data for *trans*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (*trans*-**2**H), *cis*-(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (*cis*-**2**H), and *cis*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (*cis*-**4**H)

	trans-**2**H	*cis*-**2**H	*cis*-**4**H
formula	$C_{54}H_{56}BCl_2F_4O_3P_5Ru$	$C_{53}H_{53}BF_4O_3P_5Ru$	$C_{59}H_{62}BF_4O_3P_5Ru$
fw	1165.61	1080.68	1161.82
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
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] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ (based on reflections with $I > 2\sigma(I)$).

Results and Discussion

Synthesis of New Hydride Complexes. The new ruthenium hydride complexes *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = $P(OMe)_3$ (*trans*-**2**H), $P(OEt)_3$ (*trans*-**3**H), $P(O^iPr)_3$ (*trans*-**4**H), PMe_3 (*trans*-**5**H), PMe_2Ph (*trans*-**6**H), CH_3CN (*trans*-**7**H)) were prepared from *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(H)][BF$_4$] (*trans*-**1**H) (generated in situ) similar to the preparation of the analogous dppe hydride derivatives reported by us[2] and the *trans*-[(dppe)$_2$Os(H)(CH_3CN)][BF$_4$] 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-**1**H was prepared by reacting *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] with exactly 1 equiv of $HBF_4 \cdot Et_2O$ in Et_2O under H_2 atmosphere. It was characterized using NMR spectroscopy (see Experimental Section).[22] For the preparation of *trans*-

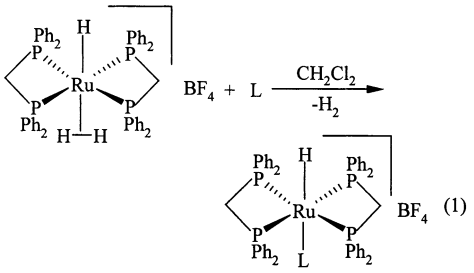
(18) Siemens Analytical Instruments, Inc., Madison, WI, 1995.

(19) Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, Germany, 1993.

(20) *SHELXTL (SGI version)*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

(21) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270.

(22) The following two references report partial NMR data: (a) Jessop, P. G.; Rastar, G.; James, B. R. *Inorg. Chim. Acta* **1996**, *250*, 351. (b) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000.



L = $P(OMe)_3$ (trans-**2**H)
$P(OEt)_3$ (trans-**3**H)
$P(O^iPr)_3$ (trans-**4**H)
PMe_3 (trans-**5**H)
PMe_2Ph (trans-**6**H)
CH_3CN (trans-**7**H)

$[(dppm)_2Ru(H)(L)][BF_4]$ complexes (L = $P(OR)_3$, PR_3, CH_3CN) the amount of phosphorus/CH_3CN ligand that was reacted with *trans*-**1**H 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*-$[(dppm)_2Ru(H)(L)][BF_4]$ (L = $P(OR)_3$ or PR_3) complexes show a doublet of quintets for the hydride ligand due to coupling with the trans P ($P(OR)_3$ or PR_3) and the four cis P (dppm) nuclei. The $J(H,P_{trans})$ is on the order of 100 Hz for the $P(OR)_3$ and 50 Hz for the trans PR_3 complexes. We[2] and others[23] observed this trend earlier. The $^{31}P\{^1H\}$ NMR spectra show a doublet ($J(P,P)$ = 23−33 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*-**1**H complex was recovered. To understand the steric effects of the dppm ligand, we carried out an X-ray crystallographic study of *trans*-**2**H.

Structure of *trans*-$[(dppm)_2Ru(H)(P(OMe)_3)][BF_4]$ (trans-2H). The structure of *trans*-**2**H 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 $P(OMe)_3$ moiety perpendicular to this plane. In addition to a discrete $[BF_4]^-$ 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

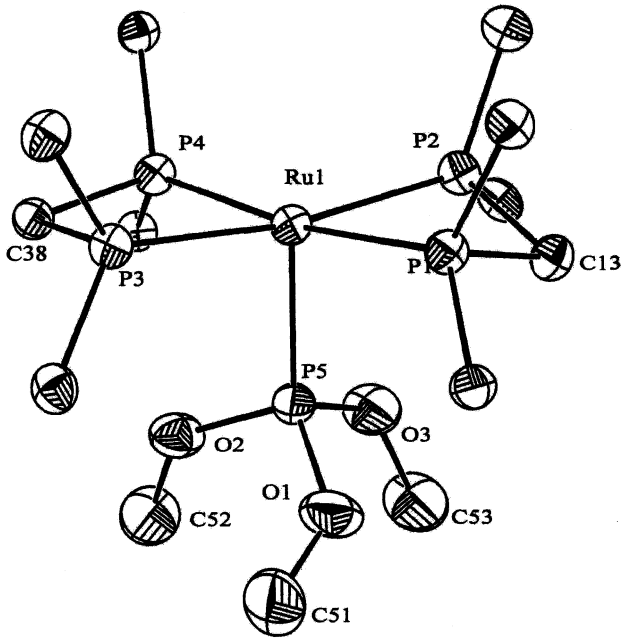


Figure 1. ORTEP view of the *trans*-$[(dppm)_2Ru(H)(P(OMe)_3)]^+$ (*trans*-**2**H) cation at the 50% probability level. The phenyl groups on the dppm phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$(dppm)_2Ru(H)(P(OMe)_3)][BF_4]$ (*trans*-**2**H), *cis*-$[(dppm)_2Ru(H)(P(OMe)_3)][BF_4]$ (*cis*-**2**H), and *cis*-$[(dppm)_2Ru(H)(P(O^iPr)_3)][BF_4]$ (*cis*-**4**H)

	trans-**2**H	*cis*-**2**H	*cis*-**4**H
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 P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are 69.59(5) and 71.95(5)°, respectively. The Ru−P(dppm) bond lengths vary from 2.3347(15) to 2.3680(16) Å while the Ru−P distance ($P(OMe)_3$) is 2.3153(17) Å. The Ru−P($P(OMe)_3$) bond of the *trans*-**2**H 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*-**2**H is nearly perfect whereas the analogous dppe derivative[2] is slightly puckered. The P(1)−C(13)−P(2) and P(3)−C(38)−P(4) bond angles are 92.7 and 95.6(3)°, respectively, falling in the lower end of the range of P−C−P bond angles (92−133°) 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*-$[(dppm)_2Ru(H)(L)][BF_4]$ (L = $P(OMe)_3$ (trans-2H), $P(OEt)_3$ (trans-3H), $P(O^iPr)_3$ (trans-4H)). The hydride com-

(23) (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. (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.

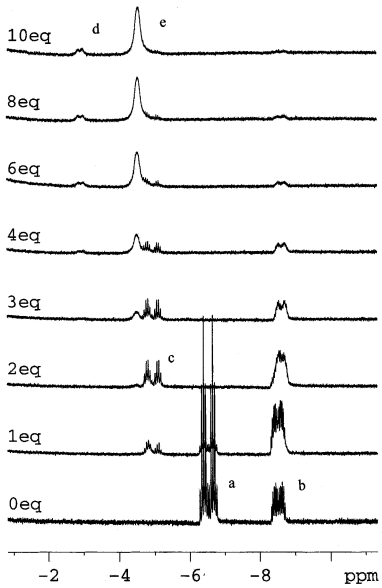


Figure 2. Hydride region of the ^{1}H NMR spectrum for the titration of *trans*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (*trans*-**4**H) with HBF$_4$·Et$_2$O in CD_2Cl_2. The number of equivalents of acid added with respect to the starting hydride complex is indicated on the left of each spectrum. Key: (a) *trans*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (*trans*-**4**H); (b) *cis*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (*cis*-**4**H); (c) *trans*-[(dppm)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$]; (d) *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*trans*-**4**H$_2$); (e) *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*cis*-**4**H$_2$).

Table 10. T_1 (400 MHz, 298 K) Data for the Dihydrogen Complexes

complex	T_1 (ms)	complex	T_1 (ms)
trans-**2**H$_2$	15.8	*cis*-**3**H$_2$	12.3
cis-**2**H$_2$	13.7	*trans*-**4**H$_2$	12.9
trans-**3**H$_2$	14.4	*cis*-**4**H$_2$	12.5

plexes were titrated with HBF$_4$·Et$_2$O in CD_2Cl_2. 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 ^{1}H NMR spectrum. It was apparent from the coupling constants that the multiplet was due to a cis isomer, *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$]. Further acid addition led to a broad singlet due to *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (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 $\leq$1 equiv of the acid. In addition to the broad singlet, a weak broad doublet due to *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ was also obtained.

In the case of *trans*-**4**H, the addition of 1 equiv of acid affords the cis isomer. A small amount of another hydride, *trans*-[(dppm)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$] (observation of J(P,F) in the ^{31}P NMR), was also seen. We reported the mechanism of the formation of an analogous dppe-containing species earlier.[2] The *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*cis*-**4**H$_2$) and *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(PF(O^{i}Pr)$_2$)][BF$_4$]$_2$ (*trans*-**4**H$_2$) complexes resulted upon addition of more acid (Figure 2). The cone angle reduction (in PF(O^{i}Pr)$_2$) in the otherwise sterically crowded P(O^{i}Pr)$_3$ to give the *trans*-[(dppm)$_2$Ru(H)(PF(O^{i}Pr)$_2$)][BF$_4$] 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)$_2$Ru(H)(L)][BF$_4$] Complexes (L = P(OMe)$_3$ (cis-2H), P(OEt)$_3$ (cis-3H), P(O^{i}Pr)$_3$ (cis-4H), PMe$_3$ (cis-5H), PMe$_2$Ph (cis-6H)). The protonation of the trans hydride phosphite/phosphine complexes with 1 equiv of HBF$_4$·Et$_2$O in $CHCl_3$ 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.

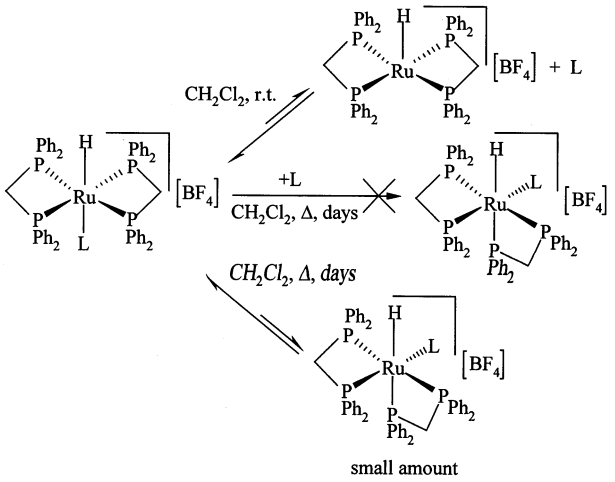
When $CHCl_3$ solutions of the trans hydrides were refluxed, they isomerized, the facilities of which are dependent on the cone angles of the phosphorus ligands: easier for ligands that have larger cone angles, that is, P(O^{i}Pr)$_3$ > P(OEt)$_3$ > P(OMe)$_3$.[24] ^{1}H NMR spectroscopy of the products 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(O^{i}Pr)$_3$), 42:58 (PMe$_3$), and 41:59 (PMe$_2$Ph), 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 ^{1}H 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*-**4**H was simulated using a simulation program,[26] which matched the observed spectrum. The cis conformation was also ascertained from the ^{31}P NMR coupling constants (Table 5).[4,27] In addition, we determined the X-ray crystal structures of [(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ and P(O^{i}Pr)$_3$) complexes to prove the cis conformation without any ambiguity.

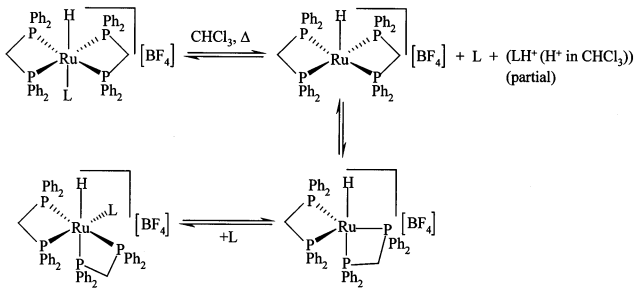
The trans phosphorus ligands in the hydride complexes were found to be labile. We found small amounts of the free ligand in CH_2Cl_2 solutions of the trans hydrides as evidenced by ^{31}P NMR spectroscopy. When these solutions were refluxed, the trans hydrides isomerized slowly to give small quantities 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 $CHCl_3$ solvent (with traces of acid impurities), the isomerization proceeded much faster. We monitored the *trans*-**2**H to *cis*-**2**H isomerization in $CHCl_3$ (with traces of acid impurities; $CDCl_3$ as external lock) in a sealed NMR tube using ^{31}P 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 HBF$_4$·Et$_2$O and not just the two isomers.
(26) Bruker WIN-DAISY, 4.05 version.
(27) Mezzetti, A.; Del Zotto, A.; Rigo, P.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

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 $HBF_4 \cdot Et_2O$ added in the protonation of the trans hydrides serves to trap the free phosphorus ligand 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*-**4**H complex, a competing reaction takes place in the presence of excess $HBF_4 \cdot Et_2O$ in CH_2Cl_2: protonation of the trans phosphite ligand to generate a new *trans*-$[(dppm)_2Ru(\eta^2\text{-}H_2)(PF(O^iPr)_2)][BF_4]_2$ (*trans*-**4**H_2) derivative through the intermediacy of *trans*-$[(dppm)_2Ru(H)(PF(O^iPr)_2)][BF_4]$. This hydride complex could not be isolated; however, it was observed in the ^1H NMR spectrum. In the presence of excess acid, the *cis*-**4**H complex gives *cis*-**4**H_2 presumably via the *cis*-$[(dppm)_2Ru(H)(PF(O^iPr)_2)][BF_4]$ species which could not be observed spectroscopically.

Structure of *cis*-[(dppm)$_2$Ru(H)(P(OMe)$_3$)][BF$_4$] (cis-2H). An ORTEP diagram of the *cis*-**2**H cation is shown in Figure 3. The structure consists of a severely distorted octahedron: three of the four dppm 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 dppm P atoms. The hydride ligand that occupies the sixth coordination site on the metal was not located. The dppm bite angles P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are respectively 71.40(7) and 70.89(7)°. The notable feature

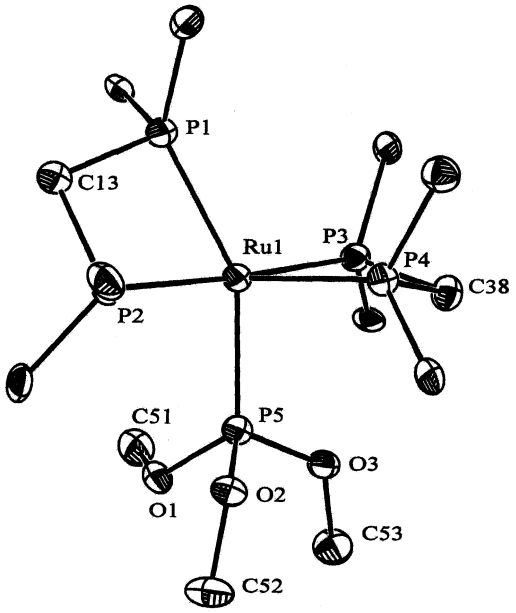


Figure 3. ORTEP view of the *cis*-$[(dppm)_2Ru(H)(P(OMe)_3)]^+$ (*cis*-**2**H) cation at the 50% probability level. The phenyl groups on the dppm phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

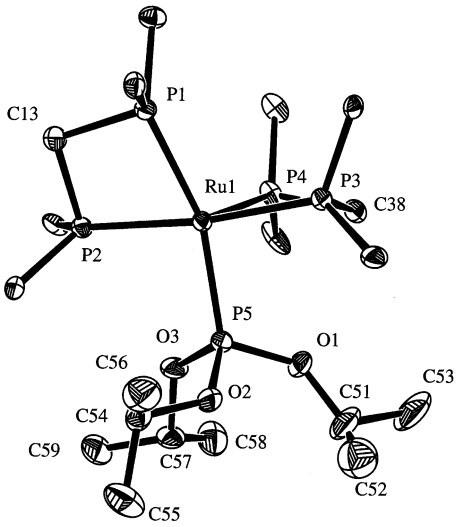
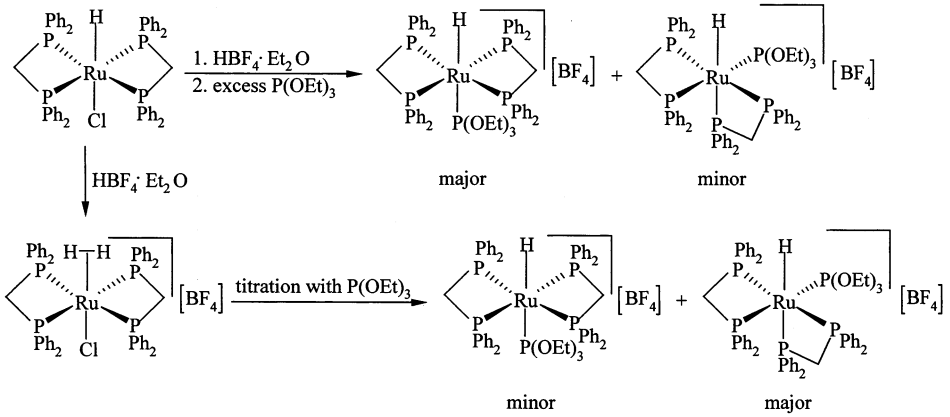


Figure 4. ORTEP view of the *cis*-$[(dppm)_2Ru(H)(P(O^iPr)_3)]^+$ (*cis*-**4**H) cation at the 50% probability level. The phenyl groups on the dppm phosphorus atoms have been omitted for clarity; only one carbon atom of each of the phenyl groups is shown.

of the structure is the *tightening* of the Ru(1)−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*-[(dppm)$_2$Ru(H)(P(O^{i}Pr)$_3$)][BF$_4$] (cis-4H). An ORTEP view of the *cis*-**4**H cation is shown in Figure 4. The structure consists of a severely distorted octahedron around the metal center with three of the four dppm P atoms forming a plane, phosphite and the fourth dppm phosphorus being approximately perpendicular to this plane. The hydride ligand that could not be located completes the sixth coordination site around ruthenium. The Ru−P bond lengths (dppm) are in the range 2.3380(9)−2.4252(9) Å whereas the Ru−P bond distance ($P(O^iPr)_3$) is 2.2924(9) Å. The dppm

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 CH_3 groups on the P(O^{i}Pr)$_3$ 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)$_2$RuH(Cl)] (trans-8H). The *trans*-**8**H complex was prepared from *cis*/*trans*-[(dppm)$_2$RuH$_2$] using a method adapted from literature: the dihydrides are unstable in $CHCl_3$; upon dissolving in $CHCl_3$, the hydride chloride complex was obtained.[16] Protonation of *trans*-**8**H with 1 equiv of HBF$_4$·Et$_2$O gave the corresponding dihydrogen complex, *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(Cl)][BF$_4$] (*trans*-**8**H$_2$). In the context of losing HCl instead of H_2 in its reactivity *trans*-**8**H$_2$ is similar to *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(Cl)][BF$_4$].[4] When *trans*-**8**H was reacted with 1 equiv of the acid in the presence of excess P(OEt)$_3$ [(dppm)$_2$RuH(P(OEt)$_3$)][BF$_4$] (*cis*-**3**H (minor) and *trans*-**3**H (major)) were obtained. The reaction could involve an intermediate η^2-H_2 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)$_2$RuH(P(OEt)$_3$)][BF$_4$]. When *trans*-**8**H was first protonated with 1 equiv of acid followed by a titration with phosphite (1−5 equiv in increments of 1 equiv), *cis*-**3**H 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)$_2$Ru(H)(L)][BF$_4$] (L = P(OMe)$_3$ (cis-2H), P(OEt)$_3$ (cis-3H), P(O^{i}Pr)$_3$ (cis-4H)). The protonation reactions of mixtures of trans (minor) and cis hydride phosphite (major) complexes were carried out under an H_2 atmosphere in CD_2Cl_2 using excess HBF$_4$·Et$_2$O. When the protonation was carried out in an Ar atmosphere, signals due to the η^2-H_2 complexes *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = P(OMe)$_3$ (*cis*-**2**H$_2$), P(OEt)$_3$ (*cis*-**3**H$_2$), PF(O^{i}Pr)$_2$ (*cis*-**4**H$_2$)) were not observed. In fact no resonances were observed in the hydride region which could mean that although protonation did take place, the H_2 ligand due to its lability is eliminated under argon. We found a singlet at δ 4.6 ppm assignable to free H_2 in the ^{1}H NMR spectrum.

The ^{1}H NMR spectrum of the dihydrogen complex shows a broad singlet in the hydride region for the η^2-H_2 ligand. Loss of H_2 takes place in our complex with time; we found that the loss of H_2 is reversible. When H_2 gas is purged through the solutions, the dihydrogen complexes were recovered.

Protonation Reaction of the Hydride Complexes *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = PMe$_3$ (trans-5H), PMe$_2$Ph (trans-6H)). The protonation of these complexes in CD_2Cl_2 with 1 equiv of HBF$_4$·Et$_2$O led to the complete disappearance of the starting hydride accompanied by the appearance of *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$], *cis*-[(dppm)$_2$Ru(η^2-H$_2$)(L)][BF$_4$]$_2$ (L = PMe$_3$ (*cis*-**5**H, *cis*-**5**H$_2$), PMe$_2$Ph (*cis*-**6**H, *cis*-**6**H$_2$)), *trans*-[(dppm)$_2$Ru(η^2-H$_2$)(H)][BF$_4$] (*trans*-**1**H), and *trans*-[(dppm)$_2$Ru(η^2-H$_2$)Cl][BF$_4$] (*trans*-**8**H$_2$) complexes in the ^{1}H NMR spectrum. Further acid addition resulted in the disappearance of all the species except *trans*-**8**H$_2$. When excess acid was used, two new signals were observed in the ^{31}P NMR spectrum assignable to *trans*-[(dppm)$_2$Ru(BF$_4$)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 ^{31}P 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)$_2$RuCl]$^+$. The signal broadening was explained as a monomer to chloride-bridged dimer equilibrium as observed for [L$_2$Ru(μ-Cl)$_2$RuL$_2$]$^{2+}$ (L = Ph$_2$PCH$_2$CH$_2$-2-py)[28] and [(PMe$_3$)$_4$Ru(μ-Cl)]$_2$[Cl]$_2$.[29]

H−D Isotopomers. The H−D isotopomers were obtained by exposing the η^2-H_2 complexes to D_2 gas or by the use of DBF$_4$·Et$_2$O to deuterate the starting hydrides. Albeniz et al.[30] proposed that a combination of the lability and the acidity of the H_2 ligand is responsible for the isotopic scrambling to form the HD isotopomers. The η^2-HD ligand was observed in the ^{1}H NMR spectrum by nullifying the residual η^2-H_2 signal by an inversion recovery pulse sequence.[31,32] The spectra exhibit triplet signals for the *cis*-[(dppm)$_2$Ru(η^2-HD)(L)][BF$_4$]$_2$ complexes the intensity ratios of which are

(28) Costella, L.; Del Zotto, A.; Mezzetti, A.; Zangrando, E.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1993**, 3001.
(29) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511.
(30) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632.
(31) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031.
(32) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

Table 11. Properties of Dihydrogen Complexes of Ruthenium

complex	$E_{1/2}$, V[a]	J(H,D), Hz	d_{HH}, Å[b]	stability[c]
trans-$[(dppm)_2Ru(H_2)Cl]^+$	2.0	26	0.99	s
trans-$[(dppe)_2Ru(H_2)Cl]^+$ [d]	1.8	26	0.99	s
trans-$[(dppp)_2Ru(H_2)Cl]^+$ [e]	1.8	24	1.00	u
trans-$[(dppm)_2Ru(H_2)H]^+$	1.9	29	0.94	s
trans-$[(dppm)_2Ru(H_2)(P(OR)_3)]^{2+}$	2.7	32 (R = Me)	0.88 (R = Me)	u
		30 (R = Et)	0.92 (R = Et)	u
cis-$[(dppm)_2Ru(H_2)(P(OR)_3)]^{2+}$	2.7	29 (R = Me)	0.94 (R = Me)	u
		26 (R = Et)	0.99 (R = Et)	u
trans-$[(dppe)_2Ru(H_2)(PF(OR)_2)]^{2+}$ [f]	na[g]	29 (R = Me)	0.94 (R = Me)	1d[h]
		28 (R = Et)	0.95 (R = Et)	1d[h]
trans-$[(dppm)_2Ru(H_2)(CNH)]^{2+}$ [i]	na[g]	32.2	0.88	u

[a] Calculated $E_{1/2}$ values of the N_2 complexes.[41] [b] Calculated from the J(H,D) values of the HD isotopomers using the equation given in ref 34. [c] Stability with respect to loss of H_2 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 H_2 starts to occur after ca. 24−36 h. [i] Reference 5.

approximately 1:1:1 with J(H,D) of 29, 26, and 29 Hz for *cis*-**2**HD, *cis*-**3**HD, and *cis*-**4**HD, respectively. The *trans*-$[(dppm)_2Ru(\eta^2\text{-HD})(P(OMe)_3)][BF_4]_2$ (*trans*-**2**HD) and *trans*-$[(dppm)_2Ru(\eta^2\text{-HD})(P(OEt)_3)][BF_4]_2$ (*trans*-**3**HD) complexes gave doublets of triplets with J(H,D) of 32 and 30 Hz, respectively. The H−H distances (d_{HH}) calculated from the inverse relationship between d_{HH} and J(H,D) of the HD isotopomers[33,34] are 0.88, 0.94, 0.92, 0.99, and 0.94 Å respectively for *trans*-**2**H_2, *cis*-**2**H_2, *trans*-**3**H_2, *cis*-**3**H_2, and *cis*-**4**H_2.

Comments on H−H Distances and the Stabilities of the Dihydrogen Complexes. The complexation of H_2 to a metal is considered to result from the σ (η^2-H_2) donation to the empty d (M) orbital and π back-donation from the filled d (M) orbital to the σ^* (η^2-H_2) orbital. Table 11 shows a comparison of some of the properties of our H_2 complexes and also the ones reported by others. The weak trans influence of Cl^-, a π-donor ligand, favors the σ donation from H_2 to metal d orbitals and an increased back-donation from the metal to the σ^* orbital of H_2. These effects, consequently, weaken the H−H bond and increase the M−H_2 interaction. Thus, a relatively long H−H distance (d_{HH} = 0.99 Å) is consistent with the tight binding of H_2 to the metal as found in *trans*-**8**H_2. When solutions containing *trans*-**8**H_2 were exposed to D_2 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 H_2/D_2 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*-**8**H_2 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 H_2 to the metal, *trans*-**8**H_2 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 N_2 complexes as suggested by Morris,[41] our dihydrogen complexes may be categorized as having labile H_2 ligands. It was suggested that if the $E_{1/2}$ value of the corresponding N_2 complex is >2.0 V, the dihydrogen complex can be predicted to be unstable with respect to loss of H_2 at 298 K under Ar. The dihydrogen complexes reported in this work are fully formed under 1 atm of H_2; upon loss of the H_2 ligand, the dihydrogen complex could be recovered by purging the solution containing the $[(dppm)_2Ru(P(OR)_3)]^{2+}$ with H_2 gas.[42] This is in contrast to our earlier findings[2] on the dppe analogues wherein we noted that the *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(PF(OR)_2)]^{2+}$ complexes could be generated either under Ar or H_2 atmosphere.[43] Those derivatives were stable with respect to loss of H_2 ligand; however, upon loss of H_2 (typically ca. 24−36 h), the dihydrogen complexes could not be recovered which could mean that the 5 coordinate species is highly reactive. We[44] 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 H_2 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 H_2 that results in this bond elongation.[45,46]

(33) (a) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396. (b) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F. Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396. (c) King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782.

(34) d_{HH} (Å) = −0.0167[J(H,D) (Hz)] + 1.42.

(35) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390.

(36) Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515.

(37) Mathew, N.; Jagirdar, B. R. *Inorg. Chem.* **2000**, *39*, 5404.

(38) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127.

(39) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711.

(40) Forde, C. E.; Landau, S. E.; Morris, R. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1663.

(41) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.

(42) We have noted the five coordinate species to be quite stable; even after the complete loss of H_2 (typically overnight), the dihydrogen complex was recovered by purging the solution with H_2.

(43) The electrochemical parameter E_L for $PF(OR)_2$ ligands is not known.

(44) Mathew, N.; Jagirdar, B. R. Unpublished results.

(45) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.

(46) (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 384, 436. (c) Jones, C. E.; Coskran, K. J. *Inorg. Chem.* **1971**, *10*, 55.

Conclusions

The protonation reactions of the hydride complexes *trans*-[(dppm)$_2$Ru(H)(L)][BF$_4$] (L = P(OR)$_3$) with HBF$_4$·Et$_2$O gave pure cis hydride phosphite derivative, *cis*-[(dppm)$_2$Ru(H)(L)][BF$_4$] for L = P(O^{i}Pr), 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 H_2 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 (PR$_3$) 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)$_2$Ru(BF$_4$)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*-**2**H, *cis*-**2**H, and *cis*-**4**H, in CIF format, a table of K_{eq} data for the trans/cis isomerization reaction, and a figure showing the ^{1}H NMR spectra of the hydride region for the titration of *trans*-**2**H with HBF$_4$·Et$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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