Inorg. Chem. **1994,** *33,* 6278−6288

Influence of Chloride versus Hydride on H−H Bonding and Acidity of the Trans Dihydrogen Ligand in the Complexes *trans*-$[Ru(H_2)X(PR_2CH_2CH_2PR_2)_2]^+$, X = Cl, H, R = Ph, Et. Crystal Structure Determinations of $[RuCl(dppe)_2]PF_6$ and *trans*-$[Ru(H_2)Cl(dppe)_2]PF_6$

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Received April 22, 1994[⊗]

The complex $[RuCl(dppe)_2]PF_6$, **1**, dppe = $Ph_2PCH_2CH_2PPh_2$, is prepared by reacting *cis*-$RuCl_2(dppe)_2$ with $NaPF_6$. It has a distorted trigonal bipyramidal geometry with a $Ru(P)_2Cl$ "Y" shaped equatorial plane. In weakly coordinating solvents it is mainly five-coordinate. Under FAB MS conditions it is ionized to $[RuCl(PF_6)(dppe)_2]^+$. It reacts with Cl^- or L = CO, CH_3CN to give complexes *cis*-$RuCl_2(dppe)_2$ or *cis*-$[Ru(Cl)(L)(dppe)_2]PF_6$, respectively. Dihydrogen reacts with **1** to give *trans*-$[Ru(H_2)Cl(dppe)_2]PF_6$, **2a**. The reaction of HA, A = BF_4 or PF_6, with complexes *trans*-$RuH(Cl)(dppe)_2$ or *trans*-$RuHCl(depe)_2$, depe = $PEt_2CH_2CH_2PEt_2$, gives dihydrogen complexes *trans*-$[Ru(H_2)Cl(dppe)_2]A$, **2a**, and *trans*-$[Ru(H_2)Cl(depe)_2]A$, **2b**. The H−H distances in complexes **2** are longer than those found in analogous complexes *trans*-$[Ru(H_2)H(diphos)_2]^+$ **3** probably because of the π effect of the Cl^-. Associated with the H−H lengthening is a dramatic reduction in the pK_a of **2a** (6) vs **3a** (15). An electron-rich trihydride complex $[Ru(H)_3(dppf)_2]^+$ (**4**), dppf = 1,1′-bis(diphenylphosphino)ferrocene, with no H−H bond is found to be, paradoxically, the most acidic (p$K_a \approx 4$). Bond dissociation energies calculated for complexes **2a**, **3a**, and **4** from pK_a and electrochemical data also suggest that the amount of the H−H bonding has a major influence on the acidity of the complexes. Complex **2a** in CH_2Cl_2 under Ar appears to slowly lose HCl at 233 K; it reacts with CO at 273 K to give HCl and *trans*-$[Ru(CO)H(dppe)_2]^+$ and with H_2 in the presence of Na^+ to give **3a**. Complex **1** crystallizes in the space group $P2_1/c$ with a = 12.427(2) Å, b = 15.565(3) Å, c = 26.759(5) Å, β = 95.94(3)°, V = 5148.1 Å^3, and D_{calcd} = 1.391 g cm^{-3} for Z = 4. Least squares refinement of the model based on 4383 observed reflections ($F > 6.0\sigma(F)$) converged to a final R_F = 5.4%. Complex **2a** crystallizes in the space group $P2_1/n$ with a = 15.315(1) Å, b = 17.479(1) Å, c = 18.608(1) Å, β = 101.79(1)°, V = 4875.9(7) Å^3, and D_{calcd} = 1.472 g cm^{-3} for Z = 4. Least squares refinement of the model based on 9208 observed reflections ($F > 4.0\sigma(F)$) converged to a final R_F = 5.1%. There is electron density associated with the H_2 ligand trans to the chloride in octahedral **2a**.

Introduction

The nature of the ancillary ligands in a dihydrogen complex can have a dramatic influence on the structure and reactivity of the dihydrogen ligand. We have determined how the structure and acidity of dihydrogen complexes *trans*-$[M(H_2)H(PR_2CH_2CH_2PR_2)_2]^+$ change with a systematic change in cis bidentate phosphine ligands; when the R substituents are changed from *p*-$CF_3C_6H_4$ to *p*-$MeOC_6H_4$ the pK_a of the ruthenium dihydrogen complex changes from 9 to 16 while the H−H bond lengthens only slightly.[1] Other variations in the cis ligands, L, in the complexes $[Ru(H_2)H(L)_4]^+$, have been made by several research groups[2−7a] and the effects of these variations on the spectroscopic and H atom exchange properties of these complexes have been reviewed.[8] Li and Taube[9,10] have described how the spectroscopic properties of the complexes *trans*-$[Os(H{\cdot\cdot}D)X(en)_2]^+$ and *trans*-$[Os(H{\cdot\cdot}D)X(NH_3)_4]^+$ [11] change substantially as the trans ligand is varied; J(H,D) decreases as X = I > Br > Cl.[9b] Neutral ligands trans to the H··D ligand in these osmium complexes also change J(H,D).[9] There is evidence that the isomer of $Ir(H{\cdot\cdot}H)(H)Cl_2(P^iPr_3)_2$ with H_2 trans to Cl is more stable with respect to H_2 loss than the one with H_2 trans to H.[12]

We report here the preparation of the complexes *trans*-$[Ru(H_2)Cl(dppe)_2]^+$ (**2a**)[13] and $[Ru(H_2)Cl(depe)_2]^+$ (**2b**)[13] and the characterization of their physical properties in order to compare the effect of Cl versus hydride on the ligand trans to H_2. A communication described how these complexes act as intermediates in the synthesis of complexes $[Ru(H_2)HL_2]^+$ and RuH_2L_2

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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(13) Ligand abbreviations: $PR_2CH_2CH_2PR_2$, R = phenyl (dppe), ethyl (depe), cyclohexyl (dcype).

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from the reaction of *cis*-$\mathrm{RuCl_2L_2}$, $\mathrm{NaBPh_4}$ and $\mathrm{H_2}$ gas.[14] Mezzetti et al.[7a] have already established that the complexes *trans*-$[\mathrm{M(H{\cdot\cdot}D)(Cl)(dcype)_2}]^+$ (M = Ru (**2c**); M = Os)[13] have elongated H−D bonds with a small J(H,D) couplings of 16 and 10.5 Hz, respectively, while $[\mathrm{Os(D)(H)_2(dcype)_2}]^+$ presumably has no H−D bond because it has no observable H−D coupling. The recently reported technetium complexes $\mathrm{TcCl(dppe)_2}$ and *trans*-$\mathrm{Tc(H_2)Cl(dppe)_2}$[15] are isoelectronic with the complexes $[\mathrm{RuCl(dppe)_2}]^+$ (**1**) and *trans*-$[\mathrm{Ru(H_2)Cl(dppe)_2}]^+$ (**2a**) described here. A similar relationship holds between the rhenium complex *trans*-$\mathrm{Re(H{\cdot\cdot}H)Cl(dppe)_2}$[16] and the osmium complex *trans*-$[\mathrm{Os(H{\cdot\cdot}H)Cl(dppe)_2}]^+$.[14,17]

Experimental Section

Oxygen and water were excluded at all times by the use of a glovebox supplied with purified nitrogen or vacuum lines supplied with purified $\mathrm{N_2}$ or Ar; $\mathrm{N_2}$ was used unless otherwise stated. Benzene, tetrahydrofuran (THF), diethyl ether, and hexanes were dried over and distilled from sodium−benzophenone ketyl. Methanol was dried over magnesium methoxide, and ethanol, over magnesium ethoxide. Acetone was dried over potassium carbonate. Dichloromethane was distilled from calcium hydride. Deuterated solvents were dried over Linde type 4A molecular sieves and degassed prior to use. The phosphine ligands were used as purchased from Strem Chemicals or Digital Specialty Chemicals Ltd. The complexes *cis*-$\mathrm{RuCl_2(dppe)_2}$,[18] *cis*-$\mathrm{RuH_2(dppe)_2}$,[18] *trans*-$\mathrm{RuH(Cl)(depe)_2}$,[19] $[\mathrm{RuH(cod)(NH_2NMe_2)_3}]\mathrm{PF_6}$[20] and *trans*-$[\mathrm{Ru(H_2)H(dppe)_2}]\mathrm{BPh_4}$[18] were prepared by literature methods. The protonated phosphine compounds were prepared as described previously.[1]

NMR spectra were recorded on Varian XL-400 (400 MHz for ^{1}H, 162 MHz for ^{31}P), Varian XL-200 (200 MHz for ^{1}H, 81 MHz for ^{31}P), Varian Gemini 200 (200 MHz for ^{1}H) or Varian Gemini 300 (300 MHz for ^{1}H, 120.5 MHz for ^{31}P) spectrometers. All ^{31}P NMR were proton decoupled, unless stated otherwise. ^{31}P NMR chemical shifts were measured relative to ~1% $\mathrm{P(OMe)_3}$ in $\mathrm{C_6D_6}$ sealed in coaxial capillaries and are reported relative to $\mathrm{H_3PO_4}$ by use of $\delta(\mathrm{P(OMe)_3}) = 140.4$ ppm. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. In all cases, high frequency shifts are reported as positive. T_1 measurements were made at 400 or 200 MHz, as specified, using the inversion recovery method. The temperature of the probes were calibrated with the temperature dependence of the chemical shifts of MeOH. The CP MAS ^{31}P NMR spectra were run on a Chemagnetics CMX 300 MHz spectrometer; the 7.5 mm o.d. zirconium spinners were packed with about 200 mg of sample in a glovebag under $\mathrm{N_2}$. The samples were spun at about 6000 Hz. The shifts of the isotropic peaks were referenced relative to external $\mathrm{H_3PO_4}$ and to $\mathrm{PF_6^-}$ in the sample. Further experimental details were as published.[21] Microanalyses were performed on a sample handled under an inert atmosphere by Canadian Microanalytical Services, Delta, BC. Fast atom bombardment mass spectra (FAB MS) were obtained with a VG 70-250S mass spectrometer using a nitrobenzyl alcohol (NBA) or nitrophenyl octyl ether (NPOE) matrix.

$[\mathrm{RuCl(dppe)_2}]\mathrm{PF_6}$ (1). *cis*-$\mathrm{RuCl_2(dppe)_2}$ (226 mg, 0.232 mmol) and $\mathrm{NaPF_6}$ (46.0 mg, 1.18 equiv) were stirred in THF (2 mL) and EtOH (1 mL) under Ar overnight. The solution was red and the yellow solids never disappeared. After evaporation, the solids were dissolved in $\mathrm{CH_2Cl_2}$ and filtered and washed with $\mathrm{CH_2Cl_2}$ (15 mL total) through Celite. Evaporation of solvent left behind 286 mg of red solid (99% yield). FAB MS: calcd for $\mathrm{C_{52}H_{50}ClP_4{}^{102}Ru}$, 933; obsd (NBA matrix), 1064 ($\mathrm{M^+ + PF_6^-}$), 933 ($\mathrm{M^+}$), 897 ($\mathrm{M^+ - H - Cl}$); obsd (NPOE matrix): 933 ($\mathrm{M^+}$), 987 ($\mathrm{M^+ - H - Cl}$). ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz): δ 7.8−6.7 (m, $\mathrm{PC_6}H_5$), 2.7 (br s, 2H), 2.5 (br s, 4H), 1.6 (br s, 2H) (PCH_2CH_2P). ^{31}P{^{1}H} NMR ($\mathrm{CH_2Cl_2}$): δ 82.4 (br t), 54.5 (t, J(P,P) = 11.3 Hz), −144.9 (sept, J(P,F) = 711 Hz). CP MAS ^{31}P NMR (120 MHz): δ 90.3 (br s), 81.0 (br s), 53.0 (A of AB), 49.8 (B of AB, J(A,B) = 265 Hz), −142 (sept, J(P,F) = 700 Hz). The isotropic peaks assigned to the cation are shown in Figure 1.

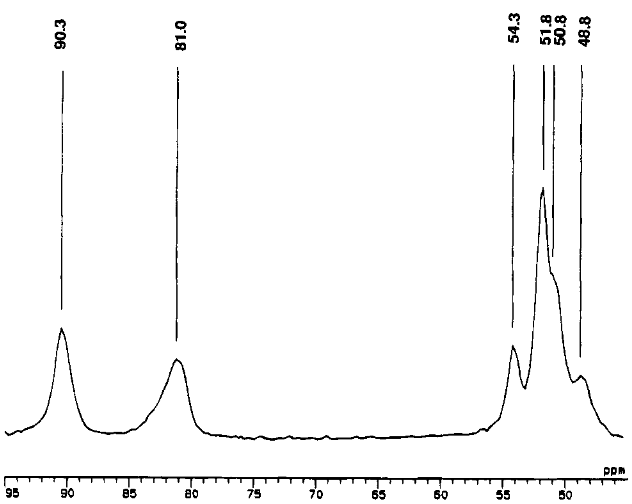

Figure 1. Isotropic peaks of the cation of $[\mathrm{RuCl(dppe)_2}]\mathrm{PF_6}$ in the CP MAS ^{31}P NMR spectrum.

***trans*-RuHCl(dppe)$_2$.** $[\mathrm{Ru(H_2)(H)(dppe)_2}]\mathrm{BPh_4}$ (0.200 g, 0.163 mmol) was dissolved in 8 mL acetone and LiCl (0.138 g, 3.27 mmol) was added. This mixture was stirred overnight after which time the solvent was removed under reduced pressure and the residue redissolved in benzene. This was then filtered through Celite and the volume of the filtrate reduced to 1 mL. Addition of cold hexanes produced a yellow solid (0.100 g, 65%) with properties as reported in the literature.[19] ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 8.1−7.0 (m, $\mathrm{PC_6}H_5$), 2.9 and 2.3 (2 m, PCH_2CH_2P), −18.4 (quint, RuH, ^2J(H,P) = 19.5 Hz). ^{31}P{^{1}H} NMR (toluene): δ 62.5 (s).

***trans*-$[\mathrm{Ru(H_2)Cl(dppe)_2}]^+\mathrm{X^-}$, $\mathrm{X^-}$ = $\mathrm{BF_4}$, $\mathrm{PF_6}$ (2a). Method 1.** Under 1 atm of $\mathrm{H_2(g)}$, *trans*-$\mathrm{RuHCl(dppe)_2}$ (0.050 g, 0.053 mmol) was dissolved in 3 mL of THF and with stirring, a slight excess of $\mathrm{HBF_4{\cdot}Et_2O}$ or $\mathrm{HPF_6(aq)}$ was added. Reduction of solvent volume and addition of diethyl ether caused the precipitation of a cream colored solid. This solid was allowed to settle and the supernatant liquid was syringed off. The solid was then washed with diethyl ether (2 × 3 mL) to remove the excess acid. Yield: >90%.

Method 2. Under 1 atm of $\mathrm{H_2}$, $\mathrm{RuCl_2(dppe)_2}$ (4.30 g, 4.40 mmol) was dissolved in 20 mL of THF and 10 mL of EtOH. $\mathrm{NaPF_6}$ (2.22 g, 13.2 mmol) was added and the yellow mixture immediately changed to an orange-red color. The mixture, which turned back to a pale yellow color after approximately 1.5 min, was stirred for 4 h. The solvent was then removed under reduced pressure leaving a deep red residue which was dissolved under Ar, in 40 mL of $\mathrm{CH_2Cl_2}$ and filtered through Celite. The volume of the dark red solution was reduced to 5 mL and put under 1 atm of $\mathrm{H_2}$. This caused the solution to discolor to a pale yellow. Addition of diethyl ether caused the precipitation of a cream colored solid which was washed with ether (2 × 10 mL) and dried under a stream of $\mathrm{H_2}$ affording 2.4 g of product. Yield: 58%. The color of this solid could be changed back and forth from orange to cream by simply passing Ar and then $\mathrm{H_2}$ over the solid.

Method 3. A $\mathrm{CH_2Cl_2}$ solution of **1** was exposed to 1 atm of $\mathrm{H_2}$ with stirring. The solution immediately turned from red to light yellow. ^{31}P NMR showed quantitative conversion to **2a**.

FAB MS: calcd for $\mathrm{C_{52}H_{50}ClP_4{}^{102}Ru}$, 935; obsd, 933 ($\mathrm{M^+ - 2H}$), 898 ($\mathrm{M^+ - 2H - Cl}$). Anal. Calcd for $\mathrm{C_{52}H_{50}ClF_6P_5Ru}$: C, 57.80; H, 4.67. Found: C, 57.67; H, 4.66. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 200 MHz): δ 7.8−6.8 (m, $\mathrm{PC_6}H_5$), 2.9 and 2.3 (2 m, PCH_2CH_2P), −12.3 (br s, RuH_2).

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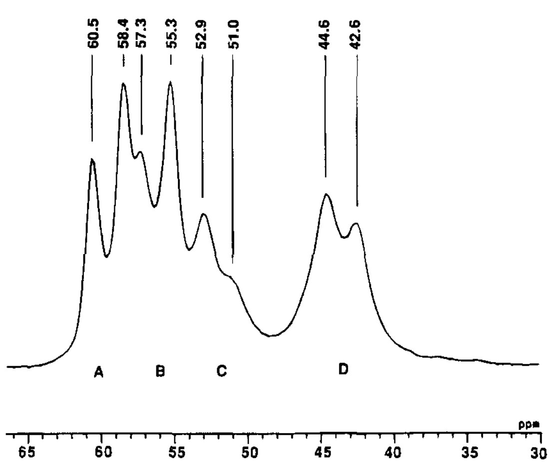

Figure 2. Isotropic peaks of the cation of $[Ru(H_2)Cl(dppe)_2]PF_6$ in the CP MAS ^{31}P NMR spectrum.

^{31}P NMR (THF): δ 51.5 (s), −144 (sept, J(P,F) = 711 Hz). CP MAS ^{31}P NMR (120 MHz): δ 59.0 (br d, J(P,P) = 254 Hz), 56.1 (br d, J(P,P) = 229 Hz), 51.7 (br d, J(P,P) = 269 Hz), 43.3 (br d, J(P,P) = 239 Hz), −142 (sept, J(P,F) = 700 Hz); see Figure 2 for the isotropic peaks of the cation.

***cis*-[Ru(CH₃CN)Cl(dppe)₂]PF₆.** One drop of CH_3CN was added to a CH_2Cl_2 solution (5 mL) of **2a** (90.2 mg) with stirring to give a light yellow solution of the product (quantitative conversion by ^{31}P NMR). Addition of acetone caused the precipitation of yellow crystals. FAB MS: only peaks due to $\mathbf{1}PF_6^+$ and $\mathbf{1}^+$ were observed (see above). IR (CH_2Cl_2): 2306 cm^{-1}, ν(CN). ^{31}P NMR (CH_2Cl_2): δ 59.6 (m), 42.9 (m).

Observation of *cis*-[Ru(CO)Cl(dppe)₂]PF₆. A CH_2Cl_2 solution of **1** was exposed to 1 atm of CO with stirring. The solution immediately turned from red to colorless with quantitative conversion to the product according to the ^{31}P NMR spectrum. FAB MS: calcd for $C_{53}H_{50}ClOP_4{}^{102}Ru$, 961; obsd, 961 ($M^+$), 898 ($M^+$ − 2H − Cl). ^{31}P NMR (CH_2Cl_2): ABCD multiplets at 45.9, 38.8, 51.5, 24.6 ppm with J_{AB} 256, J_{AC} 18.9, J_{AD} 18.9, J_{BC} 10.5, J_{BD} 29.4, J_{CD} 25.9 Hz.

***trans*-[Ru(H₂)Cl(depe)₂]⁺X⁻ = BF₄⁻, PF₆⁻ (2b).** These were prepared by use of method 1 for the synthesis of **1**. Under Ar as a solid, this compound slowly turned irreversibly from white to green. FAB MS: calcd for $C_{20}H_{50}ClP_4{}^{102}Ru$, 551; obsd, 549 ($M^+$ − 2H), 515 (M^+ − H − Cl). ^1H NMR (acetone-d_6, 200 MHz): δ 2.4 and 2.1 (2 m, PCH_2CH_2P), 1.9 (m, PCH_2CH_3), 1.1 (m, PCH_2CH_3), −14.2 (quint, RuH_2, ^2J(H,P) = 7.2 Hz). ^{31}P NMR (THF): δ 53.3 (s).

Observation of *trans*-[Ru(HD)Cl(dppe)₂]PF₆. When *trans*-[Ru(H₂)Cl(dppe)₂]PF₆ was dissolved in acetone-d_6, changes were observed in the shape of the H_2 signal in the ^1H NMR (200 MHz) due to intermolecular H/D exchange with the acetone-d_6. The ^1J(HD) coupling value for *trans*-[Ru(HD)Cl(dppe)₂]PF₆ was found to be 25.9 Hz by simulation of and comparison to the observed spectra.

Observation of *trans*-[Ru(HD)Cl(depe)₂]BF₄. Method 1. After leaving a solution of *trans*-[Ru(H₂)Cl(depe)₂]BF₄ in acetone-d_6 for a 24 h period, by ^1H NMR it was found that some *trans*-[Ru(HD)Cl(depe)₂]BF₄ had formed.

Method 2. Under 1 atm of Ar, RuHCl(depe)₂ (0.020 g, 0.034 mmol) was suspended in diethyl ether (3 mL) and D_2O (0.043 mL, 1.7 mmol). With vigorous stirring, 2 drops (excess) $HBF_4{\cdot}Et_2O$ were added resulting in the immediate formation of a white precipitate. After allowing the solid to settle, the supernatant liquid was decanted and the precipitate was washed with diethyl ether (2 × 5 mL). A ^1H NMR spectrum of the sample in acetone-d_6 was then obtained and a ^1J(H,D) = 25.2 Hz was confirmed by performing an inversion recovery pulse sequence on the sample in order to null out the η^2-H_2 signal (Figure 3).

Preparation of Ru(H)₂(dppf)₂ (4). Under Ar, [RuH(cod)(NH₂NMe₂)₃]PF₆ (0.294 g, 0.55 mmol) was dissolved in ethanol and transferred to an addition funnel. This pale beige solution was added slowly to a solution of bright yellow dppf (0.628 g, 1.14 mmol) in ethanol under Ar and refluxed for 1.5 h. The solution immediately turned orange but with continuous stirring faded to a pale yellow. The solution was cooled and the yellow precipitate was filtered out and washed with ethanol and ether and dried under vacuum to yield 0.45 (60%) of **4**. This product is also obtained if the reaction is done under 1 atm of H_2. The complex can be recrystallized by addition of hexanes to a concentrated solution of **4** in CH_2Cl_2. FAB MS: calcd for $C_{68}H_{58}Fe_2P_4{}^{102}Ru$, 1212; obsd, 1211 ($M^+$ − H), 1210 (M^+ − 2H), 655 (M^+ − 3H − dppf). Anal. Calcd for $C_{68}H_{58}Fe_2P_4Ru$: C, 67.4; H, 4.8. Found: C, 66.9; H, 4.8. ^1H NMR (CD_2Cl_2, 200 MHz): δ −10.4 (AA′MM′X₂ spin system containing pseudo dt, ^2J(H,P) = 39, 30 Hz, RuH_2). ^{31}P NMR (CD_2Cl_2): δ 37.4 (br s), 49.3 (br s).

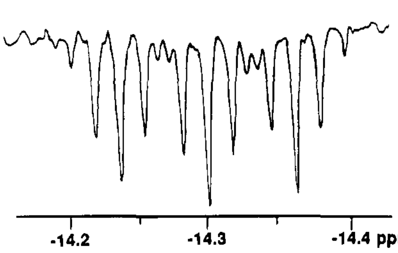

Figure 3. HD resonance in the ^1H NMR spectrum of *trans*-[Ru(HD)Cl(depe)₂]BF₄ in CD_2Cl_2 observed by nulling the peak due to $[Ru(H_2)Cl(depe)_2]^+$ by use of an inversion recovery method.

Acidity Measurements. Approximately 6 mg of **1** and an equimolar amount of base were dissolved in either CD_2Cl_2 or THF-d_8 at 20 °C. The ^1H NMR and ^{31}P NMR spectra were taken within 30 min and again after 24 h. Resonances were integrated with care as described previously.[1] When the base was $PEtPh_2$, the equilibrium constant was 0.070 ± 0.005 in CD_2Cl_2.

Complex **4** (30 mg) and an excess of acid ([HPPh₃]BF₄, [HPCy₂Ph]BF₄, [HPEtPh₂]BF₄ or [HPCy₃]BF₄) were dissolved in 1.5 mL of CD_2Cl_2. The ^1H NMR and ^{31}P NMR spectra were taken within 30 min. The ^1H NMR spectra of the reaction of either [HPCy₂Ph]BF₄ or [HPEtPh₂]BF₄ with **1** showed separate peaks for hydride-containing reactants and products: −10.4 (m, **4**) and −7.9 ppm (q, ^2J(H,P) = 10 Hz, $[Ru(H)_3(dppf)_2]^+$ ($\mathbf{4H^+}$)[6]). These were integrated to determine the equilibrium constants (0.008 ± 0.004 and 0.34 ± 0.10, respectively). The ^{31}P NMR spectrum of the reaction with $[HPCy_2Ph]^+$ showed peaks at 65.5 (bs, $\mathbf{4H^+}$), 49.3 (br s, **4**), 37.4 (br s, **4**) and 27.3 ppm (br s, average of shifts of $HPCy_2Ph^+$ and PCy_2Ph) with intensities consistent with the equilibrium constant. There was very little reaction with [HPCy₃]BF₄; only **4** and a trace of $\mathbf{4H^+}$ were observed. The reaction with [HPPh₃]BF₄ completely converted **4** to $\mathbf{4H^+}$.

X-ray Structure Determinations of [RuCl(dppe)₂]PF₆ (1) and *trans*-[Ru(H₂)Cl(dppe)₂]PF₆ (2a). Crystals of **1** were prepared by slow diffusion of diethyl ether into a solution of 47 mg of complex in 0.35 mL of CH_2Cl_2. This was done without protection from the air. A red block was mounted on a glass fiber. Crystals of **2a** were prepared by slow diffusion of diethyl ether into a saturated solution of the complex in CH_2Cl_2 under 1 atm of Ar. A pale yellow crystal was mounted on a glass fiber.

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer for **1** and on a Siemens P4 diffractometer for **2a**, using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω-2θ scan technique was applied with variable scan speeds. In each case the intensities of 3 standard reflections measured at constant intervals showed no decay. Data for the compounds were corrected for Lorentz and polarization effects and for absorption.[22] For both structures the Ru atom position was solved by the Patterson method and other nonhydrogen atoms were located by successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares to minimize $\sum w(F_o - F_c)^2$ where $w = 1/(\sigma^2(F_o) + g(F_o)^2)$. Hydrogen atoms were positioned on geometric grounds (C−H 0.96 Å, U_{iso} = 0.065(4) Å² for **1** and 0.089(3) Å² for **2a**). Crystal data, data collection, and least-squares parameters are listed in Table 1. All calculations were performed and diagrams created using SHELXTL-PC[23] on a 486-66 personal computer.

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(22) Sheldrick, G. M. SHELXA-90 absorption correction program. *J. Appl. Crystallogr.*, in press.

(23) Sheldrick, G. M. SHELXTL-PC; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1993.

Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters[a]

	complex **1**	complex **2a**
chem formula	$C_{52}H_{48}ClF_6P_5Ru$	$C_{52}H_{50}ClF_6P_5Ru$
a, Å	12.427(2)	15.315(1)
b, Å	15.565(3)	17.479(1)
c, Å	26.759(5)	18.608(1)
β, deg	95.94(4)	101.79(1)
V, Å^3	5148.1(13)	4875.9(7)
Z	4	4
fw	1078.3	1080.3
space group	$P2_1/c$	$P2_1/n$
T, °C	21	21
λ, Å	0.710 73 Å	0.710 73
ϱ_{calc}, g cm^{-3}	1.39	1.472
μ, cm^{-1}	5.7	5.99
transm coeff	0.4843−0.9622	0.4483−0.9556
$R(F_o)$, %	$R(F_o > 6.0\sigma(F_o)) = 5.36$	$R(F_o > 4.0\sigma(F_o)) = 5.05$
$R_w(F_o)$, %	6.72	6.38

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + g(F_o)^2)$ where $g = 0.0016$ for **1** and $g = 0.0007$ for **2a**.

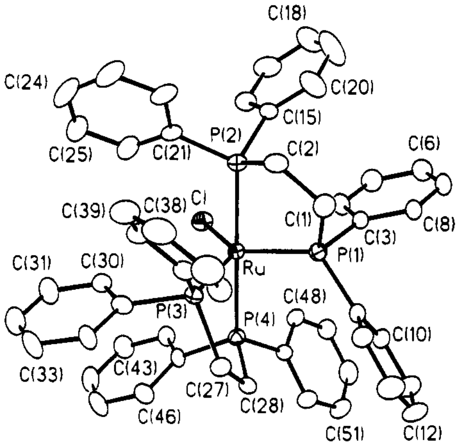

Figure 4. Structure of the cation of $[RuCl(dppe)_2]PF_6$ showing thermal displacements at the 25% probability level.

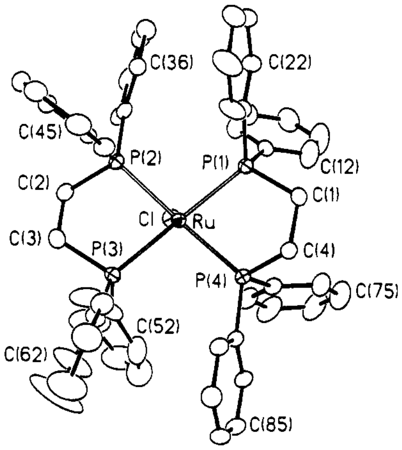

Figure 5. Structure of the cation of $[Ru(H_2)Cl(dppe)_2]PF_6$ showing thermal displacements at the 25% probability level.

Table 2. Selected Positional Parameters and Equivalent Isotropic Displacement Coefficients (Å^2) for **1**[a]

	x	y	z	U(eq)[b]
Ru	0.76718(5)	0.79644(4)	0.83068(2)	0.0326(2)
Cl	0.7110(2)	0.6761(1)	0.7786(1)	0.052(1)
P(1)	0.8043(2)	0.9353(1)	0.8180(1)	0.040(1)
P(2)	0.5896(2)	0.8541(2)	0.8237(1)	0.041(1)
P(3)	0.8017(2)	0.8030(1)	0.9143(1)	0.037(1)
P(4)	0.9475(2)	0.7445(1)	0.8409(1)	0.037(1)
C(1)	0.7036(7)	1.0079(6)	0.8420(4)	0.057(4)
C(2)	0.5990(7)	0.9621(5)	0.8518(3)	0.049(3)
C(3)	0.7854(6)	0.9535(5)	0.7506(3)	0.043(3)
C(9)	0.9352(7)	0.9869(5)	0.8348(4)	0.044(3)
C(15)	0.5171(6)	0.8680(6)	0.7609(3)	0.046(3)
C(21)	0.4911(6)	0.7989(7)	0.8580(3)	0.045(3)
C(27)	0.9459(6)	0.8285(6)	0.9336(3)	0.044(3)
C(28)	1.0204(6)	0.8053(5)	0.8927(3)	0.040(3)
C(29)	0.7832(6)	0.6975(6)	0.9426(3)	0.045(3)
C(36)	0.7655(8)	0.9464(6)	0.9755(4)	0.055(4)
C(41)	0.9654(6)	0.6306(5)	0.8583(3)	0.038(3)
C(47)	1.0301(6)	0.7544(5)	0.7889(3)	0.035(3)

[a] Only ipso carbons of phenyls. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Ru−Cl	2.395(2)	Ru−P(1)	2.243(2)
Ru−P(2)	2.371(2)	Ru−P(3)	2.238(2)
Ru−P(4)	2.372(2)	P(1)−C(1)	1.851(10)
P(1)−C(3)	1.815(9)	P(1)−C(9)	1.828(9)
P(2)−C(2)	1.842(9)	P(2)−C(15)	1.835(9)
P(2)−C(21)	1.821(9)	P(3)−C(27)	1.856(8)
P(3)−C(29)	1.833(9)	P(3)−C(35)	1.826(9)
P(4)−C(28)	1.837(8)	P(4)−C(41)	1.841(8)
P(4)−C(47)	1.820(9)	C(1)−C(2)	1.528(12)
C(27)−C(28)	1.547(12)		
Cl−Ru−P(1)	135.8(1)	Cl−Ru−P(2)	92.1(1)
P(1)−Ru−P(2)	80.1(1)	Cl−Ru−P(3)	129.2(1)
P(1)−Ru−P(3)	95.0(1)	P(2)−Ru−P(3)	98.2(1)
Cl−Ru−P(4)	90.9(1)	P(1)−Ru−P(4)	98.0(1)
P(2)−Ru−P(4)	177.0(1)	P(3)−Ru−P(4)	79.6(1)
Ru−P(1)−C(1)	112.2(3)	Ru−P(1)−C(3)	107.1(3)
C(1)−P(1)−C(3)	103.1(4)	Ru−P(1)−C(9)	125.3(3)
C(1)−P(1)−C(9)	105.2(4)	C(3)−P(1)−C(9)	101.4(4)
Ru−P(2)−C(2)	107.1(3)	Ru−P(2)−C(15)	118.8(3)
C(2)−P(2)−C(15)	105.7(4)	Ru−P(2)−C(21)	116.8(3)
C(2)−P(2)−C(21)	104.0(4)	C(15)−P(2)−C(21)	103.1(4)
Ru−P(3)−C(27)	111.5(3)	Ru−P(3)−C(29)	110.6(3)
C(27)−P(3)−C(29)	103.7(4)	Ru−P(3)−C(35)	126.1(3)
C(27)−P(3)−C(35)	103.8(4)	C(29)−P(3)−C(35)	98.5(4)
Ru−P(4)−C(28)	107.3(3)	Ru−P(4)−C(41)	116.5(3)
C(28)−P(4)−C(41)	105.5(4)	Ru−P(4)−C(47)	118.9(3)
C(28)−P(4)−C(47)	105.1(4)	C(41)−P(4)−C(47)	102.3(4)
P(1)−C(1)−C(2)	113.1(6)	P(2)−C(2)−C(1)	112.0(6)
P(3)−C(27)−C(28)	112.7(5)	P(4)−C(28)−C(27)	111.7(5)

[a] Only ipso carbons of phenyls.

The structures of the cations of **1** and **2a**, including the crystallographic labeling schemes, are shown in Figures 4 and 5. Selected positional parameters and bond distances and angles are listed in Tables 2–5.

Results and Discussion

Synthesis of $[RuCl(dppe)_2]PF_6$, 1. Attempts to make this useful starting complex by the reaction of *trans*-$RuX_2(dppe)_2$, X = Cl or Br, with NH_4PF_6 in refluxing ethanol were unsuccessful.[24] *trans*-$RuCl_2(dppe)_2$ does not react with reagents such as $NaPF_6$ or $NaBF_4$, or $NaBPh_4$ that precipitate NaCl; there does appear to be a slow reaction under an H_2 atmosphere. However reaction of *cis*-$RuCl_2(dppe)_2$ with $NaPF_6$ in THF/ethanol at 20 °C (eq 1) rapidly produces a yellow precipitate,

$$cis\text{-}RuCl_2(dppe)_2 + NaPF_6 \xrightarrow{THF} \xrightarrow{CH_2Cl_2} \underset{\mathbf{1}}{[RuCl(dppe)_2]PF_6} + NaCl \quad (1)$$

thought to be $[Ru(THF)Cl(dppe)_2]PF_6$, which upon recrystallization from CH_2Cl_2/Et_2O yields the red, five-coordinate complex $[RuCl(dppe)_2]PF_6$, **1**. The exclusive presence of the

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(24) Bressan, M.; Rigo, P. *Inorg. Chem.* **1975**, *14*, 2286.

Table 4. Selected Positional Parameters and Equivalent Isotropic Displacement Coefficients (Å^2) for **2a**[a]

	x	*y*	*z*	*U*(eq)[b]
Ru	0.26489(2)	0.18502(2)	0.02495(1)	0.03251(8)
Cl	0.3846(1)	0.1283(1)	−0.0227(1)	0.0488(3)
P(1)	0.1812(1)	0.0683(1)	0.0135(1)	0.0395(3)
P(2)	0.3583(1)	0.1617(1)	0.1417(1)	0.0360(3)
P(3)	0.3496(1)	0.3005(1)	0.0339(1)	0.0449(3)
P(4)	0.1694(1)	0.2047(1)	−0.0914(1)	0.0360(3)
C(1)	0.0699(3)	0.0879(3)	−0.0453(3)	0.060(2)
C(2)	0.4593(3)	0.2204(3)	0.1459(2)	0.053(1)
C(3)	0.4307(3)	0.2988(3)	0.1222(3)	0.062(2)
C(4)	0.0623(2)	0.1678(2)	−0.0781(2)	0.045(1)
C(11)	0.2247(3)	−0.0150(2)	−0.0269(2)	0.045(1)
C(21)	0.1489(2)	0.0300(2)	0.0963(2)	0.042(1)
C(31)	0.4022(3)	0.0661(2)	0.1650(2)	0.041(1)
C(41)	0.3243(3)	0.1919(2)	0.2261(2)	0.039(1)
C(51)	0.4139(3)	0.3151(3)	−0.0367(3)	0.064(2)
C(61)	0.2998(4)	0.3939(3)	0.0436(3)	0.063(2)
C(71)	0.1903(3)	0.1556(2)	−0.1723(2)	0.047(1)
C(81)	0.1408(2)	0.3013(2)	−0.1252(2)	0.041(1)

[a] Only ipso carbons of phenyls. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Bond Lengths (Å) and Angles (deg) for **2a**[a]

Ru−Cl	2.407(1)	Ru−P(1)	2.396(1)
Ru−P(2)	2.379(1)	Ru−P(3)	2.387(1)
Ru−P(4)	2.377(1)	P(1)−C(1)	1.859(4)
P(1)−C(11)	1.825(4)	P(1)−C(21)	1.838(4)
P(2)−C(2)	1.845(4)	P(2)−C(31)	1.819(4)
P(2)−C(41)	1.832(4)	P(3)−C(3)	1.847(4)
P(3)−C(51)	1.814(6)	P(3)−C(61)	1.826(5)
P(4)−C(4)	1.825(4)	P(4)−C(71)	1.818(4)
P(4)−C(81)	1.825(4)	C(1)−C(4)	1.520(6)
C(2)−C(3)	1.478(6)		

Cl−Ru−P(1)	92.9(1)	Cl−Ru−P(2)	84.5(1)
P(1)−Ru−P(2)	98.4(1)	Cl−Ru−P(3)	86.0(1)
P(1)−Ru−P(3)	178.7(1)	P(2)−Ru−P(3)	82.2(1)
Cl−Ru−P(4)	95.6(1)	P(1)−Ru−P(4)	79.9(1)
P(2)−Ru−P(4)	178.2(1)	P(3)−Ru−P(4)	99.5(1)
Ru−P(1)−C(1)	107.7(1)	Ru−P(1)−C(11)	118.8(1)
C(1)−P(1)−C(11)	105.8(2)	Ru−P(1)−C(21)	117.8(1)
C(1)−P(1)−C(21)	100.9(2)	C(11)−P(1)−C(21)	103.8(2)
Ru−P(2)−C(2)	106.6(1)	Ru−P(2)−C(31)	120.0(1)
C(2)−P(2)−C(31)	103.6(2)	Ru−P(2)−C(41)	120.7(1)
C(2)−P(2)−C(41)	100.7(2)	C(31)−P(2)−C(41)	102.5(2)
Ru−P(3)−C(3)	107.7(2)	Ru−P(3)−C(51)	115.8(2)
C(3)−P(3)−C(51)	106.3(2)	Ru−P(3)−C(61)	122.1(2)
C(3)−P(3)−C(61)	98.3(2)	C(51)−P(3)−C(61)	104.3(2)
Ru−P(4)−C(4)	103.2(1)	Ru−P(4)−C(71)	120.5(1)
C(4)−P(4)−C(71)	105.1(2)	Ru−P(4)−C(81)	120.5(1)
C(4)−P(4)−C(81)	102.4(2)	C(71)−P(4)−C(81)	102.7(2)
P(1)−C(1)−C(4)	113.1(3)	P(2)−C(2)−C(3)	107.9(3)
P(3)−C(3)−C(2)	112.6(3)	P(4)−C(4)−C(1)	112.4(3)

[a] Only ipso carbons of phenyls.

two triplet resonances for **1** in the ^{31}P NMR spectrum of the reaction mixture in CH_2Cl_2 suggests that the yield of eq 1 is quantitative. We have preliminary evidence that the complex can also be prepared by the reaction of $AgBF_4$ with *trans*-$RuCl_2(dppe)_2$ in CH_2Cl_2 at room temperature. The parent ion for **1** in an NPOE matrix was detected by FAB MS. In an NBA matrix, the ion $[RuCl(PF_6)(dppe)_2]^+$ was the most intense peak in the FAB MS. This unusual observation of a cationic complex associating with the anion suggests that the PF_6^- anion is coordinated in the gas phase. **1** was also characterized by a single crystal X-ray diffraction study and by solid-state and solution NMR studies (see below).

Structure of [RuCl(dppe)$_2$]PF$_6$ in the Solid State. The crystal structure of **1** consists of distorted trigonal bipyramidal (tbp) cations $[RuCl(dppe)_2]^+$ (Figure 4) and discrete octahedral PF_6^- anions. The bidentate dppe ligands span axial and equatorial positions and the chloride ligand is equatorial. The axial phosphorus atoms P(2) and P(4) (P_{ax}) are each 2.372(2) Å away from the ruthenium, with the P(2)−Ru−P(4) angle being 177.0(1)°. The bite angles of the dppe ligands are 80.1(1) and 79.7(1)° for P(1)−Ru−P(2) and P(3)−Ru−P(4), respectively. The major distortion from tbp geometry is a change from a trigonal to a Y-shape in the equatorial plane. The two equatorial phosphorus−ruthenium bonds form the top of the "Y" with a P(1)−Ru−P(3) angle of only 95.0(1)°. There is definitely a strong electronic preference for such a distortion because the close approach of such large groups seems very unfavorable on the basis of steric repulsion considerations.

The origin of this Y type of distortion has been explained by Rachidi et al.[25] and Thorn and Hoffmann.[26] For a d^6 metal, the tbp geometry would give a triplet state since the highest occupied molecular orbitals would be degenerate E type orbitals lying in the equatorial plane. This degeneracy can be lifted if the molecule distorts from a trigonal geometry in the equatorial plane. It has been predicted that strong σ-donors such as tertiary phosphines prefer to distort to the two top arms of the "Y". Weak π-donors such as chloride prefer the lower leg. This is why the two bulky PPh_2 groups of P(1) and P(3) in **1** adopt the unusually small angle of 95.0(1)°.

The "Y" is distorted because the chloride in **1** is closer to P(3); P(1)−Ru−Cl = 135.8(1)° and P(3)−Ru−Cl = 129.2(1)°. This distortion is so great in the complex $[RuCl(dcype)_2]PF_6$[7b] that the complex becomes almost square pyramidal with the equatorial planar arrangement of atoms described by a T-shape. The chloride in that complex is moved much more toward P(1): P(1)−Ru−Cl = 119.1(1)° and P(3)−Ru−Cl = 147.4(1)°. Despite the larger bulk of the cyclohexyl groups relative to the phenyl groups, the two equatorial P atoms in $[RuCl(dcype)_2]^+$ are actually closer together than in the dppe complex: P(1)−Ru−P(3) = 93.1(1)°. The complex $Ir(H)_2Cl(P^tBu_2Ph)_2$ has a distorted Y in the equatorial plane with an HIrH angle of 72.7° and unequal ClIrH angles of 131.1 and 156.2°.[12] HF *ab initio* calculations suggest that the Y can distort toward the T in this way as long as the two pure σ-bonding ligands (H in the iridium case and therefore P in the case of **1**) maintain a constant, small angle with the metal. The complexes $MCl(dppe)_2$, M = Tc,[15] Re,[27] have equatorial angles and distortions that are comparable to those of **1** while the symmetrical complex $Re(H_2BEt_2)$(*rac*-tetraphos-1) is undistorted with equal P_{eq}−Re−B angles.[28]

The Ru−Cl distance of 2.394(3) Å in **1** is marginally shorter than that observed in $[Ru(H_2)Cl(dppe)_2]^+$ (see below). This distance is within one standard deviation of the Ru−Cl distance (2.41(4) Å) obtained by averaging over 102 Ru−Cl distances in six-coordinate complexes, where Cl is not trans to hydride.[29] It is near the lower quartile of Ru−Cl distances for 7 five-coordinate complexes.[29] Therefore if there is Ru−Cl π bonding in **1**, it is similar to that observed in other complexes. The Ru−Cl bond in **1** is shorter than the Tc−Cl bond in $TcCl(dppe)_2$ (2.432(2) Å)[15] presumably because of the positive charge on Ru(II) vs Tc(I).

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(25) Rachidi, I. E.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671−677.

(26) Thorn, D. L.; Hoffmann, R. *New J. Chem.* **1979**, *3*, 39.

(27) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1983**, *248*, C26−C28.

(28) Jia, G.; Lough, A. J.; Morris, R. H. *J. Organomet. Chem.* **1993**, *461*, 147−156. Only the equatorial P and B atoms in the complex $Re(H_2BEt_2)$(*rac*-tetraphos-1) are used to define the "Y"; the bridging hydrides are ignored.

(29) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

The equatorial Ru−P bond distances in **1** of 2.243(2) and 2.238(2) Å are exceptionally short, suggesting that these P-donors are forming strong dative bonds. Usual Ru(II)−P distances for phosphines of this size are in the range 2.35−2.40 Å.[29] Therefore it appears that these P atoms as well as the chloride are making up for the electron deficiency of the Ru(II).

The solid state CP MAS ^{31}P NMR spectrum of **1** is shown in Figure 1. The two singlets at 90.4 and 81.0 ppm are assigned to the equatorial phosphorus atoms (P_{eq} or P_1 and P_3 of Figure 1) while the AB pattern centered at 51 ppm is assigned to the axial atoms (P_{ax} or P_2 and P_4) with a characteristically large trans coupling, $J(P_{ax},P'_{ax})$, of 266 Hz.

Solution NMR Spectroscopy of 1. The $^{31}P\{^1H\}$ NMR spectrum of a dilute solution (2 mM) of **1** in CH_2Cl_2 consists of two triplets at 82.4 (P_{eq}) and 54.5 ppm (P_{ax}) with $J(P_{ax},P_{eq})$ of 11.3 Hz. Clearly the equatorial atoms, P_{eq}, which were inequivalent in the solid state are rendered equivalent in solution, probably by movement of the chloride ligand. The line widths become greater with increasing concentration (2 to 25 mM), changing from 7 to 10 Hz for P_{ax} and from 7 to 13 Hz for P_{eq}, respectively. Above 25 mM the line widths for P_{ax} and P_{eq} approach limiting values of 12 and 15 Hz, respectively. This behavior might be explained by a monomer to chloride-bridged dimer equilibrium at the fast exchange limit (eq 2). Such dimers

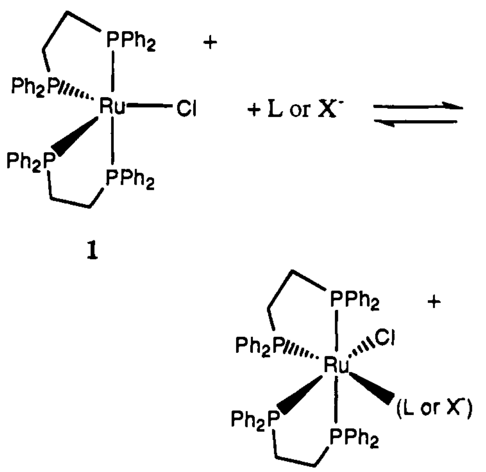
$$2[RuCl(dppe)_2]^+ \rightleftharpoons [(dppe)_2Ru(\mu\text{-}Cl)_2Ru(dppe)_2]^{2+} \qquad (2)$$

have been observed for the complexes $[L_2Ru(\mu\text{-}Cl)_2RuL_2]^{2+}$, L = $PPh_2CH_2CH_2$-2-py[30] and $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$.[31] However, there is no change in the chemical shifts with concentration which is inconsistent with this interpretation. The chemical shifts do change with temperature. The ^{31}P NMR peak due to P_{eq} shifted from 82.4 ppm at 298 K to 86.4 ppm at 193 K; the other peak shifted from 54.5 to 55.9 ppm under similar conditions. No other resonances are present at 193 K.

The $^{13}C\{^1H\}$ NMR spectrum (80 MHz) in $CDCl_3$ shows multiplets at δ 135−127 for the phenyl carbons and two kinds of methylene carbons: a multiplet at 30 ppm and a triplet at 18 ppm. The triplet is a second order $A(^{13}C)X(^{31}P_{ax})X'(^{31}P_{ax})$ spin system with $J(C,P_{ax})$ = 18.4 Hz.

Reactions of 1. Despite the fact that **1** is formally a coordinatively unsaturated complex, it is diamagnetic and stable in solution in air for weeks (i.e. there is no reaction with O_2, N_2 or H_2O). It forms red solutions in alcohols, THF, acetone, $CHCl_3$, CH_2Cl_2 and toluene. It can be precipitated with Et_2O or alkanes. In THF or acetone a pale yellow precipitate forms, presumably $[RuCl(solvent)(dppe)_2]PF_6$. However, red **1** is reformed when this complex is redissolved. The yellow complex *cis*-$[RuCl(CH_3CN)(dppe)_2]PF_6$ is formed from a solution of CH_3CN in CH_2Cl_2. The cis stereochemistry is indicated by a complex $P_MP_XP_YP_Z$ spin system observed in the $^{31}P\{^1H\}$ NMR spectrum. This complex partially converts back to **1** when dissolved in CH_2Cl_2 according to eq 3 (L = CH_3CN, THF, acetone). The CH_3CN ligand is also lost from this complex under the conditions of running a FAB MS spectrum because only the ion for **1** is observed.

Complex **1** reacts with LiCl according to eq 3 (X = Cl) to give *cis*-$RuCl_2(dppe)_2$. At higher temperatures *trans*-$RuCl_2(dppe)_2$ is formed which is much less reactive than *cis*-$RuCl_2(dppe)_2$ (see above).



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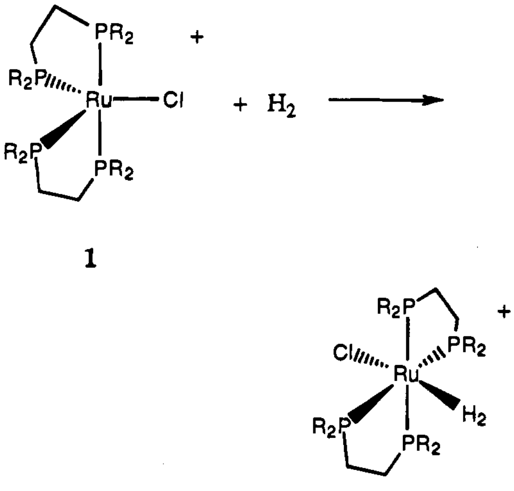
(3)

Complex **1** instantly picks up carbon monoxide at 1 atm, to give a clear colorless solution of *cis*-$[Ru(Cl)(CO)(dppe)_2]^+$ according to eq 3, L = CO; however this is irreversible. The properties of the trans isomer $[Ru(Cl)(CO)(dppe)_2]SbF_6$ have already been reported.[32] The analogous dcype compound $[RuCl(dcype)_2]BPh_4$ reacts with ligands L = CO or MeCN at −60 °C to give *cis*-$[Ru(Cl)(L)(dcype)_2]^+$ which rearrange at room temperature to *trans*-$[Ru(L)Cl(dcype)_2]BPh_4$.[7a,c] One of the chelating dcype ligands might become monodentate after coordination of L to permit this rearrangement.

Preparation of *trans*-$[Ru(H_2)(Cl)(dppe)_2]PF_6$, 2a. A CH_2Cl_2 solution of **1** reacts with dihydrogen (1 atm) at 298 or 193 K to give the yellow compound *trans*-$[Ru(H_2)Cl(dppe)_2]PF_6$, **2a** (eq 4, R = Ph). The reaction of H_2 with **1** in CD_2Cl_2 at 193 K was monitored by ^1H (300 MHz) and ^{31}P NMR (121.4 MHz). Only peaks due to the reactant **1** and the product **2a** are observed. However the ^{31}P resonances of **1** are broadened anomalously: the peak due to P_{eq} of **1** at 86.4 ppm has a width at half height of about 190 Hz under H_2 (approximately 90 Hz under Ar) while the P_{ax} peak due **1** at 55.9 ppm has a width of 100 Hz (approximately 90 Hz under Ar). This is likely due to rapid exchange with a small amount of *cis*-$[Ru(H_2)Cl(dppe)_2]^+$, the cis isomer of **2a**. There are no resonances in the ^1H NMR spectrum assignable to this isomer but there is also no resonance for free H_2, usually observed at 4.5 ppm; rapid exchange of H_2 with the cis isomer would be likely to shift and broaden this



1

2

(4)

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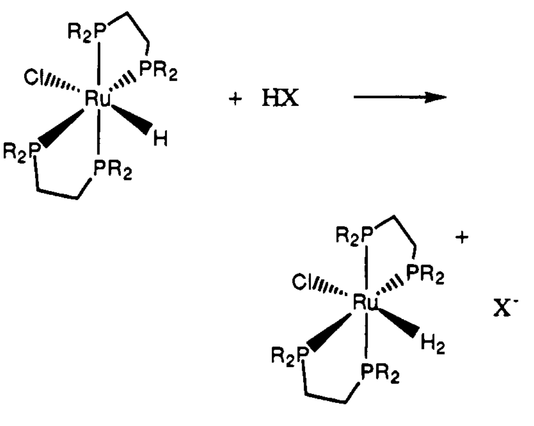
resonance. Warming this solution to 203 K produces spectra providing evidence for **1** and more of the product **2a**. The reason that a trans complex is produced in eq 4 while only cis complexes are produced by other ligands (eq 3) might be that *cis*-$[Ru(H_2)Cl(dppe)_2]^+$ isomerizes to the more stable *trans*-**2a** via a fluxional, seven-coordinate dihydride intermediate $[Ru(H)_2Cl(dppe)_2]^+$. It might also be that H_2 is small enough to attack between the P_{eq}−Ru−P_{eq} angle to give *trans*-**2a** while CO and larger ligands can only attack cis to the chloride as in eq 3. Whichever pathway is followed must be irreversible because **2a** loses HCl in preference to loss of H_2 (see below).

Complex **2a** was also prepared as the PF_6^- or BF_4^- salts by reacting *trans*-$RuH(Cl)(dppe)_2$ in THF with HPF_6(aq) or $HBF_4{\cdot}Et_2O$, respectively (eq 5, R = Ph, X = PF_6 or BF_4). This reaction is not as direct as the one using **1** as an intermediate (eq 4) since the preparation of the *trans*-$RuH(Cl)(dppe)_2$ complex is more involved. The isotopomer $[Ru(HD)Cl(dppe)_2]^+$ was generated in solution by reacting **2a** with acetone-d_6 at 20 °C for 20 min. The mechanism of this H/D exchange process is unknown. After a few hours, complete exchange takes place and the resulting species *trans*-$[Ru(D_2)Cl(dppe)_2]PF_6$ has no signal in the hydride region.



(5)

2

The identity of the PF_6 salt of **2a** was verified by elemental analysis, FAB MS, solid state and solution phase NMR and by a single crystal X-ray diffraction study. The BF_4 salt was characterized by NMR.

Preparation of $[Ru(H_2)(Cl)(depe)_2]PF_6$, 2b. Pure *trans*-$[Ru(H_2)Cl(depe)_2]^+$ could be produced by protonating *trans*-$RuHCl(depe)_2$ with HBF_4 or HPF_6 (eq 5, R = Et, X = BF_4 or PF_6). The white salts of **2b** were characterized by FAB MS and ^1H and ^{31}P NMR. Attempts at converting these products to the tetraphenylborate salt by adding $NaBPh_4$ to a solution of *trans*-$[Ru(H_2)Cl(depe)_2]BF_4$ or *trans*-$[Ru(H_2)Cl(depe)_2]PF_6$ under 1 atm H_2 always converted some of the dihydrogen chloride compound to *trans*-$[Ru(H_2)(H)(depe)_2]BPh_4$. Sodium salts were, therefore, excluded from solutions of **2b** at all times. When **2b** was in solution (acetone) or in the solid state for a period of days under 1 atm Ar, it changed color from pale yellow to green indicating that some decomposition was probably occurring. The complex $[Ru(HD)Cl(depe)_2]BF_4$ was prepared as in eq 5 by use of an HBF_4/D_2O mixture. This isotopomer also forms when **2b** is left in acetone-d_6 for 24 h.

Solid State Structure of 2a. Figure 5 shows the structure of the cation as determined by an X-ray diffraction study at 294 K. There is also a regular PF_6 anion. The cation appears to be a distorted square pyramid with the chloride in the apical position. There is residual electron density associated with the dihydrogen ligand at 1.6 Å from the Ru but H atom positions could not be refined. A ^1H NMR spectrum of the crystals dissolved in CD_2Cl_2 verified the presence of the H_2 ligand.

The four phosphorus atoms and the ruthenium atom are in a plane. This is similar to the structure of *trans*-$[Os(H_2)(H)(dppe)_2]BF_4$ where the OsP_4 unit forms a plane[33] and the dihydrogen ligand is somewhat staggered with respect to the *trans*-P−Os−P vectors.[34] In $[Fe(H_2)(H)(dppe)_2]^+$ salts, the dihydrogen ligand eclipses a P−Fe−P vector and that P−Fe−P angle distorts to less than 170°.[35] Therefore, the H_2 ligand in **2a** might not be parallel to a P−Ru−P vector. The Ru−P bond lengths fall in the normal range (2.39 Å average distance) and are comparable to those found in the X-ray crystal structure of *trans*-Ru(H)(Cl){(+)-diop}$_2$ (2.38 Å average distance).[36] The phenyl groups attached to P(3) have somewhat larger thermal ellipsoids than the other rings; the reason for this has not yet been determined.

The Ru−Cl vector is not exactly at 90° to the RuP_4 plane. It is tilted toward phosphorus atoms P(2) and P(3). The Ru−Cl bond length (2.407(1) Å) is shorter by 0.15 Å than the analogous bond in the (+)-diop complex. The longer Ru−Cl bond in the latter complex is likely due to the higher trans influence of the hydride ligand compared to the dihydrogen in **2a**. The dihydrogen ligand must have a low trans influence on the Ru−Cl bond length because the distances in **1** and **2a** are identical. This contrasts with the analogous Tc−Cl distances of 2.432(2) and 2.629(4) Å in $TcCl(dppe)_2$ and *trans*-$Tc(H_2)Cl(dppe)_2$ where there is large bond lengthening. The disorder in the crystal of the latter complex leaves the Tc−Cl bond length somewhat uncertain.[37]

The solid state CP MAS ^{31}P NMR spectrum (121 MHz) of **2a** shows four doublets attributable to two pairs of mutually trans but inequivalent phosphorus atoms. The couplings ^2J(P,P) range from 231 to 257 Hz (see Figure 2).

Structure and Dynamics of Dihydrogen Complexes 2 in Solution. The trans geometry of these complexes appears to be maintained in solution on the basis of the observation of a singlet in the $^{31}P\{^1H\}$ NMR spectra of these complexes. The dihydrogen resonance for both complexes in solution at low temperature (180 K) is a broad singlet at −12.30 ppm for **2a** and −14.25 ppm for **2b**, again consistent with the presence of a single trans isomer. At temperatures warmer than 180 K these chemical shifts remain constant but the peaks sharpen as expected because the T_2 becomes longer. The resonance of **2a** in CD_2Cl_2 remains a broad singlet at room temperature while that of **2b** in acetone-d_6 resolves into a broadened quintet with ^2J(H,P) of 7.2 Hz.

Variable temperature measurements of the T_1 of the H_2 resonance of **2a** and **2b** establish that these complexes can be classified as dihydrogen complexes. The T_1 data of Table 6 were fit with a temperature-dependent T_1 equation by use of a temperature dependent correlation time, $\tau = \tau_0 e^{E_a/RT}$, as described previously.[38] The calculated values match the observed ones well when the parameters d(H−H), E_a and T(min) are optimized to the ones of Table 7. This analysis does not reveal whether the dihydrogen ligand is rapidly spinning (rate ≫ 400 MHz) with a short H−H distance of 0.92 Å for **2a** or slowly spinning (rate ≪ 400 MHz) with an H⋯H distance of 1.16 Å.

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Table 6. Observed and Calculated T_1 Values of the Dihydrogen Ligand in the Complexes *trans*-$[M(H_2)Cl(L)_2]^+$ [a]

$[Ru(H_2)Cl(dppe)_2]^+$ (**2a**) in CD_2Cl_2			$[Ru(H_2)Cl(depe)_2]^+$ (**2b**) in CD_2Cl_2		
T, K	T_1(obs), ms	T_1(calc), ms	*T*, K	T_1(obs), ms	T_1(calc), ms
291	33	34	289	86	81
272	28	29	277	64	68
250	25	25	247	45	42
228	26	26	227	33	31
206	33	32	206	28	29
186	47	49	186	34	36
			176	47	48

[a] Refer to Table 7 for the parameters used in the calculations.

Table 7. Parameters Used To Fit the Temperature Dependence of the T_1 Values Listed in Table 6[a]

					d(H−H), Å	
complex	*T*(min), K	T_1(min), ms	τ_0, ps	E_a, kcal/mol	fast spin	slow spin
$[Ru(H_2)Cl(dppe)_2]^+$, **2a**	240	25 ± 1	1.8	2.4	0.92	1.16
$[Ru(H_2)Cl(depe)_2]^+$, **2b**	210	28 ± 1	0.37	2.7	0.94	1.18
$[Ru(H_2)H(dppe)_2]^+$, **3a**	230	20 ± 1	1.1	2.5	0.88	1.12
$[Ru(H_2)H(depe)_2]^+$, **3b**	195	16 ± 1	0.18	2.8	0.85	1.08

[a] The observed minimum T_1 value, T_1(min), for the dihydrogen ligand (at temperature *T*(min) and at 400 MHz) obtained by direct observation and fitting to the temperature dependent T_1 equation using a temperature dependent correlation time $\tau = \tau_0 e^{E_a/RT}$.[38] The H−H distance of the dihydrogen ligand, *d*(H−H), is calculated for the case of rapid spinning of the dihydrogen with respect to the tumbling of the molecule and for the case of slow or no rotation.

Table 8. Comparison of the ^1H NMR Properties of the Complexes *trans*-$[Ru(H_2)X(L)_2]^+$ and *trans*-$[Ru(HD)X(L)_2]^+$

					^2J(H,P), Hz	
no.	X	L	T_1(min), ms (400 MHz)	^1J(H,D), Hz	H_2	H
2a	Cl	dppe[a]	25 (H_2)	25.9	7.4[e]	
2b	Cl	depe[b]	28 (H_2)	25.2	7.2 (7.1)[e]	
2c	Cl	dcype[a]	20 (H_2)[d]	16[c]	8[c]	
3a	H	dppe[b]	20 (H_2), 270 (H)	32.0	0 ± 2	18.1
3b	H	depe[b]	16 (H_2), 400 (H)	32.3	0 ± 2	18.2
3c	H	dcype[a]	15 (H_2),[d] 280 (H)[d]	31.5	not obsd	17.7

[a] CD_2Cl_2. [b] Acetone-d_6. [c] From simulation of a ^1H NMR of a partially resolved multiplet (due to η^2-HD proton). [d] Calculated for 400 MHz on the basis of values observed at 80 MHz. [e] ^2J(H,P) of *trans*-$[Ru(HD)Cl(L)_2]^+$.

There is also the possibility that there are rapidly interconverting spinning dihydrogen and cis dihydride forms as reported in the communication of this work.[14] The related complexes *trans*-$[Ru(H_2)H(L)_2]^+$, L = dppe (**3a**) and L = depe (**3b**), have similar parameters (Table 7) although the calculated H−H distances are somewhat shorter than those of **2a** and **2b**, respectively. Complexes **3** are thought to have rapidly spinning dihydrogen ligands[18] and the similarity with parameters of complexes **2** is an indicator that complexes **2** might also have such H_2 ligands. *In any case, it is clear that the effect of the trans chloride ligand is to lengthen the H−H bond relative to the trans hydride ligand.*

The observation of a sizeable coupling ^1J(H,D) in the Ru(HD) isotopomers of **2** is consistent with H−D bonding (Table 8). There is a weakened H−D interaction compared to that found in analogous complexes **3**; for example the coupling is 25.9 Hz for *trans*-$[Ru(HD)Cl(dppe)_2]^+$ compared to 32.0 Hz for *trans*-$[Ru(HD)H(dppe)_2]^+$. This adds further support to the conclusion that trans chloride weakens the H−H bond relative to trans hydride.

Complexes **2** have unusually large ^2J(H,P) coupling constants of 7−8 Hz (Table 8) for spinning dihydrogen complexes.[8] A decrease in *J*(H,D) is associated with an increase in ^2J(H,P), probably paralleling an increase in metal−dihydride versus metal−dihydrogen character. The trend is clear: the order of electron donation by the ligands is dcype > depe > dppe; this is the expected order on the basis of the inductive effects of Cy, Et and Ph groups, respectively.

The physical properties of complexes **2** might also be explained in terms of a rapid equilibrium between a spinning H_2 complex *trans*-$[Ru(H_2)Cl(L)_2]^+$ in about 65% abundance and a dihydride species $[Ru(H)_2Cl(L)_2]^+$ in 35% abundance. This is based on reasonable assumptions about the T_1, *J*(H,P) and *J*(H,D) values for the separate species and how they average.[39] Such an argument was made for the complex $[Os(H\cdot\cdot H)H(depe)_2]^+$ which has an ambiguous structure in solution.[40] We cannot conclusively prove or disprove this proposal.

Reactions of Complexes 2. Solid **2a** as the PF_6^- salt is stable with respect to H_2 loss under vacuum. The solid state CP MAS ^{31}P NMR spectrum showed no change even after pumping for 10 h at high vacuum. By contrast the CP MAS ^{31}P NMR spectrum of $[Ru(H_2)H(dppe)_2]BPh_4$ (**3a**) does change under these conditions because of the partial loss of H_2. Therefore complex **2a** is stable with respect to loss of H_2 relative to **3a**. Heating solid **2a** to 155 °C under vacuum gives an array of products including $[RuClL_2]^+$, $[Ru(H_2)ClL_2]^+$, $[Ru(H_2)HL_2]^+$ and $RuHClL_2$.

Complex **2a** has a complicated reactivity pattern in solution. It partially loses HCl instead of H_2 when Ar is bubbled into a CH_2Cl_2 solution at 233 K for 20 min (i.e. not the reverse of eq 4). The amount of conversion is small and the HCl has not yet been directly detected. Two new singlets appear in the ^{31}P NMR spectrum at 58.1 and 42.9 ppm. The latter peak rapidly disappears when the sample is warmed to 273 K while the former peak slowly decreases in intensity at this temperature with a corresponding increase in the intensity of peaks due to **1**. We tentatively suggest that these unstable species are $[RuH(dppe)_2]^+$ and *trans*-$[Ru(H)(CH_2Cl_2)(dppe)_2]^+$, respectively. These disappear at 273 K because they react with CH_2Cl_2 to give back **1** and other species. When Ar is bubbled through a THF solution of **3a**, a similar species at 58 ppm is observed. Complexes **2b** and $[Ru(H_2)Cl(dcype)_2]^+$ are stable in solution under Ar.

When CO is bubbled through a solution of **2a** in CH_2Cl_2 for 2 min, a new singlet appears in the ^{31}P NMR spectrum at 63.0 ppm (−77.4 vs $P(OMe)_3$) which matches the literature value for *trans*-$[RuH(CO)(dppe)_2]^+$.[41] The ^1H NMR spectrum of the product in CD_2Cl_2 has a quintet at −6.8 ppm, confirming the identity of the carbonyl product as in eq 6.

$$\textit{trans}\text{-}[Ru(H_2)Cl(dppe)_2]^+ + CO \rightarrow \textit{trans}\text{-}[RuH(CO)(dppe)_2]^+ + HCl \quad (6)$$

Complex **2a** in THF reacts with 1 atm H_2 in the presence of $NaBPh_4$ to give complex **3a** (eq 7). This reaction explains how

$$[Ru(H_2)Cl(dppe)_2]^+ + H_2 + NaBPh_4 \rightarrow [Ru(H_2)H(dppe)_2]BPh_4 + HCl + Na^+ \quad (7)$$

3a can be prepared directly from *cis*-$RuCl_2(dppe)_2$ and $NaBPh_4$ under 1 atm of H_2.[14,18] Complex **2b** is less acidic and requires a NaOEt/$NaBPh_4$ mixture to be completely converted into

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Table 9. J(H,D) Couplings, H–H Distances, pK_a Values, and H-Atom Bond Dissociation Energies (Eq 12) for Dihydrogen and Dihydride Complexes

complex	J(H,D), Hz	D(H–H),[a] Å fast spin	D(H–H),[a] Å slow spin	pK_a	ΔH_{BDE}, kcal/mol
$[Ru(H_2)H(dppe)_2]^+$	32	*0.88*	1.12	15.0	82 ± 2
$[Ru(H_2)Cl(dppe)_2]^+$	26	0.92	1.16	6.0	71 ± 3
$[Ru(H)_2H(dppf)_2]^+$			>1.8	4.4	58 ± 2
$[Cp^*Ru(H\cdot\cdot H)(dppm)]^+$	21[b]	0.87	*1.10*[c]	9.2[b]	73 ± 2[d]
$[Cp^*Ru(H)_2(dppm)]^+$	[e]		>1.8	8.8[b]	72 ± 2[d]

[a] The italic value has been established to be the correct one. [b] Reference 43. [c] Reference 35. [d] Reference 1. [e] Not observed.

complex **3b** (eq 8). Other reactions of **2** include their H/D

$$[Ru(H_2)Cl(depe)_2]^+ + H_2 + NaOEt \rightarrow [Ru(H_2)H(depe)_2]^+ + NaCl + HOEt \quad (8)$$

exchange with acetone-d_6 as described above and their deprotonation reactions as outlined below.

Acidity of 2a. The pK_a of **2a** in CH_2Cl_2 was estimated by studying its reaction with $PEtPh_2$ by ^1H and ^{31}P NMR (eq 9, L

$$[Ru(H_2)ClL_2]^+ + PEtPh_2 \rightleftharpoons trans\text{-}RuHClL_2 + [HPEtPh_2]^+ \quad (9)$$

= dppe). This reaction and reactions of **2a** with other bases are not completely clean because of a side reaction (eq 10) which

$$[Ru(H_2)ClL_2]^+ + trans\text{-}RuHClL_2 \rightarrow trans\text{-}RuCl_2L_2 + [Ru(H_2)H(L)_2]^+ \quad (10)$$

produces small amounts of *trans*-$RuCl_2L_2$ and **3a**; these products must come from the reaction of *trans*-$RuHClL_2$ with HCl from **2a**. This should not alter the equilibrium constant for eq 9 because the reactants of eq 10 come from both sides of eq 9 and the products build up to only about 10% of the mixture over the time of equilibration. The pK_a of **2a** is estimated to be 6.0 ± 0.5 (on the pseudo-aqueous scale) on the basis of the pK_a of 4.9 for $[HPEtPh_2]^+$.[42] This pK_a value is consistent with the observation that **2a** is rapidly and completely deprotonated by *cis*-$RuH_2(dppe)_2$ in CD_2Cl_2 to give RuH(Cl)(dppe)$_2$ and **3a** (pK_a 15 in THF; see Table 9).[1] The complex RuCp*(dppm)H also reacts with **2a** in THF-d_8 to give $[RuCp^*(dppm)H_2]^+$ (pK_a 8.8 in THF)[43] and RuH(Cl)(dppe)$_2$ along with other products including **3a**.

Since protonated dppe should have a similar pK_a to $HPEtPh_2^+$, it is reasonable to propose that **2a** is in equilibrium with an unobserved isomer with a protonated, monodentate ligand, eq 11. This intermediate would have a Y-shaped equatorial plane

$$trans\text{-}[Ru(H_2)Cl(dppe)_2]^+ \rightleftharpoons RuH(Cl)(\eta^1\text{-}PPh_2CH_2CH_2PPh_2H^+)(dppe) \quad (11)$$

like **1**. It would explain the easy loss of HCl from **2a** where the H_2 and Cl are held trans to each other, since the free, protonated end of the ligand could swing around and protonate the chloride in the presence of a ligand, L′, to give HCl and *trans*-$[Ru(L')H(dppe)_2]^+$, L′ = CO and H_2, as in eqs 6 and 7, respectively. The analogous complex FeH(Cl)(η^1-$PPh_2CH_2CH_2PPh_2H^+$)(dppe) has been proposed as an intermediate in the reaction of *trans*-FeH(Cl)(dppe)$_2$ with HCl to give $FeCl_2$(dppe), dppe·HCl and H_2.[44] We find that the complex $[Fe(H_2)Cl(dppe)_2]^+$ does not exist, even at 193 K when FeHCl(dppe)$_2$ is protonated with HBF_4. Instead, protonated dppe and some $[Fe(H_2)H(dppe)_2]^+$ are formed. We would expect $[Fe(H_2)Cl(dppe)_2]^+$ to be even more acidic than **2a** because $[Fe(H_2)H(dppe)_2]^+$ is more acidic than $[Ru(H_2)H(dppe)_2]^+$;[1] therefore, $[Fe(H_2)Cl(dppe)_2]^+$ is very unstable because it adds a proton to its own dppe ligand.[45]

The pK_a values for complexes **2a** and **3a** can be combined with electrochemical potentials, $E°(MH^+/MH)$,[46] to calculate the dissociation energy of an H atom from the dihydrogen complexes in solution, $\Delta H_{BDE}\{MH_2^+\}$ (eq 12).[1] The electrochemical potential $E°(RuHCl(dppe)_2^+/RuHCl(dppe)_2)$ is −0.12 V vs $FeCp_2^+/FeCp_2$[1] and therefore $\Delta H_{BDE}\{RuH_2^+\}$ for **2a** is

$$\Delta H_{BDE}\{MH_2^+\} = 1.37\ pK_a\{MH_2^+\} + 23.1E°(MH^+/MH) + 66 \quad (12)$$

71 kcal mol^{-1} (Table 9). This is much smaller than the value of about 82 kcal mol^{-1} for **3a** but it is comparable to the value observed for the dihydride $[RuCp(PPh_3)_2(H)_2]^+$ of 72 ± 2 kcal mol^{-1} or the the dihydrogen and dihydride tautomers of $[RuCp^*(dppm)H_2]^+$ (Table 9).[1] It is larger than the $\Delta H_{BDE}\{RuH^+\}$ of about 58 kcal mol^{-1} determined for the related trihydride $[Ru(H)_3(dppf)_2]^+$ (see below). The high $\Delta H_{BDE}\{RuH_2^+\}$ value for **3a** has been attributed to the strong H–H bonding (d(H–H) 0.88 Å, J(H,D) 32 Hz). Therefore these energies suggest that complex **2a** (d(H–H) 0.92 or 1.16 Å, J(H,D) 26 Hz) has acidity properties closer to that of a dihydride than of a dihydrogen complex. The spectroscopic properties of **2a** could be interpreted to indicate that, like $[RuCp^*(dppm)(H\cdot\cdot H)]^+$ (see Table 9), it is close in energy to a dihydride tautomeric form or, in other words, the energy of homolysis, ΔH_{hom}, of the H–H bond is small. These ideas are shown graphically in Figure 6. This diagram shows that the reason that **3a** is 9 pK_a units less acidic than **2a** is because **3a** has a stronger H–H bond and is therefore further in energy from a dihydride tautomeric form.

The only related acidity study is the one by Rottink and Angelici[47] where the enthalpies of protonation of complexes $Os(Cp)X(PPh_3)_2$ in CH_2ClCH_2Cl were measured (eq 13). The

$$Os(Cp)X(PPh_3)_2 + CF_3SO_3H \rightarrow [Os(Cp)(X)(H)(PPh_3)_2]^+ + CF_3SO_3^- \quad (13)$$

ΔH values were −19.7 kcal mol^{-1} when X = Cl and −37.3 kcal mol^{-1} when X = H. Here again the hydride substituted acid $[Os(Cp)(H)_2(PPh_3)_2]^+$ is much less acidic than the chloride substituted acid $[Os(Cp)(H)(Cl)(PPh_3)_2]^+$. This might be a steric effect since reaction 13 involves an increase in coordination number at osmium which would be disfavored by the larger chloride ligand. In the case of our acid–base reactions (eq 9) there is no change in coordination number of ruthenium.

Acidity and Electrochemistry of $[Ru(H)_3(dppf)_2]^+$. This complex is the only established trihydride of Ru with bidentate phosphine ligands. Therefore it is interesting to see what effect the lack of an H–H bond has on the acidity as noted earlier.[1] When we tried to prepare the complex $[RuH(dppf)_2]^+$ by the

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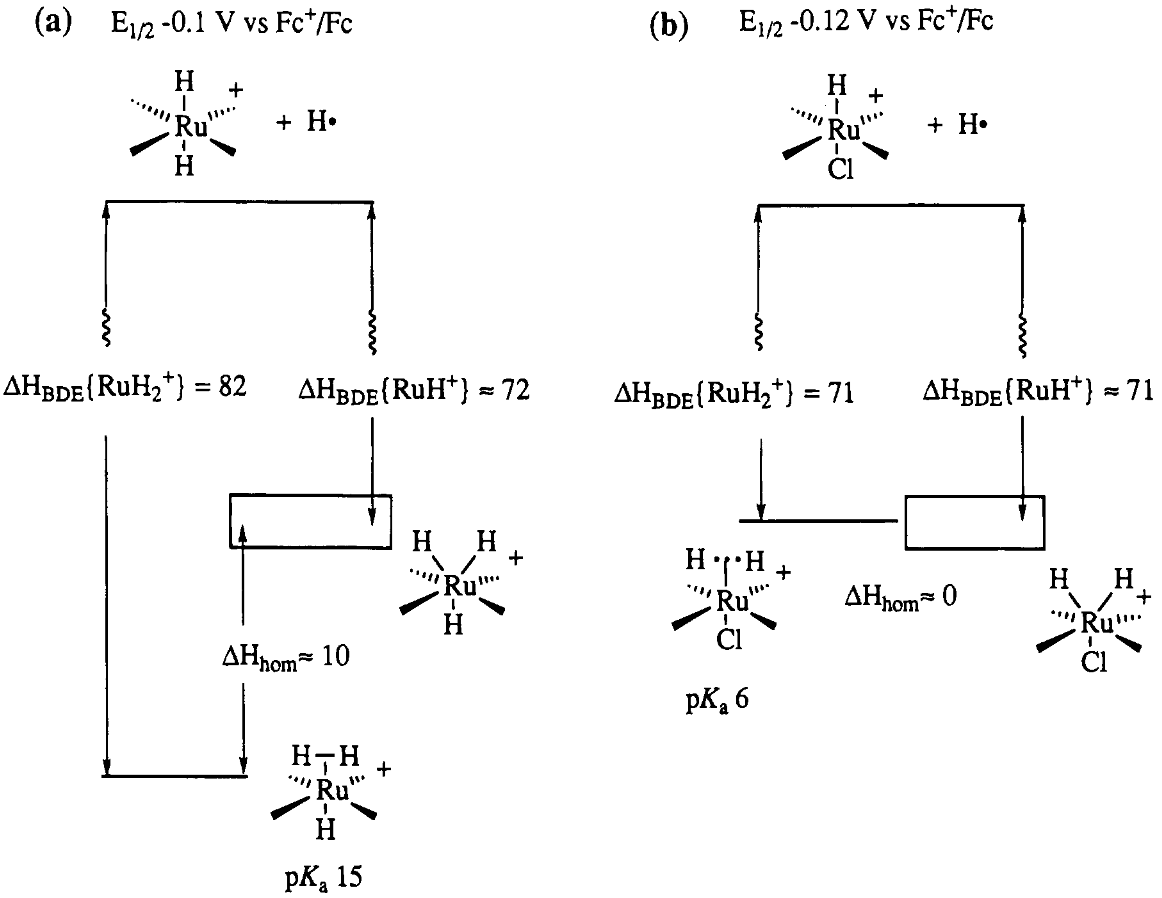

Figure 6. (a) Energy level diagram adapted from ref 1 for the dissociation of an H atom from *trans*-$[Ru(H_2)H(dppe)_2]^+$ (**3a**) and its postulated trihydride form $[Ru(H)_3(dppe)_2]^+$. (b) Energy level diagram for the dissociation of an H atom from *trans*-$[Ru(H_2)Cl(dppe)_2]^+$ (**2a**) and its postulated dihydride form $[Ru(H)_2Cl(dppe)_2]^+$. The energies $\Delta H_{BDE}\{RuH_2^+\}$ were calculated by use of the pK_a and $E_{1/2}$ values and eq 12. The ruthenium−hydride energy $\Delta H_{BDE}\{RuH^+\}$ is estimated (see Discussion).

reported route[6] we obtained instead the yellow dihydride complex *cis*-$RuH_2(dppf)_2$ (eq 14, dppf = 1,1′-bis(diphenylphosphino)ferrocene).

$$[RuH(cod)(NH_2NMe_2)_3]^+ + 2dppf + H_2 \rightarrow cis\text{-}RuH_2(dppf)_2 + cod + 2NH_2NMe_2 + NH_3NMe_2^+ \quad (14)$$

The reaction occurs under Ar so that the H_2 is generated from the hydrazine or the MeOH. The reaction also goes under an H_2 atmosphere. The complex $[RuH(dppf)_2]^+$ may form but, in the presence of H_2, would be converted rapidly into the trihydride, $[Ru(H)_3(dppf)_2]^+$ (**4**) as reported.[6] However, complex **4** is very acidic (see below) and would be quickly deprotonated by the hydrazine base to give the dihydride product of eq 14. The ^1H NMR spectrum of the dihydride has a multiplet at −10.4 ppm and the ^{31}P NMR spectrum has two broad singlets; the broadening is indicative of the exchange process observed for such *cis*-dihydrides.[48]

The dihydride reacts with $[PPh_3H]BF_4$ (pK_a 2.7) but not $[PCy_3H]^+$ (pK_a 9.7) to give the trihydride $[Ru(H)_3(dppf)_2]^+$ (**4**) (eq 15) that has properties as reported.[6] The strong acid

$$cis\text{-}RuH_2(dppf)_2 + HPPh_3^+ \rightarrow \underset{\mathbf{4}}{[Ru(H)_3(dppf)_2]^+} + PPh_3 \quad (15)$$

$HBF_4{\cdot}Et_2O$ is too oxidizing; its use in eq 15 results in the formation of a paramagnetic product.

The dihydride reacts with $[HPCy_2Ph]^+$ (pK_a ≈ 6 ± 1)[49] in CD_2Cl_2 to give an equilibrium with $K = 0.008 \pm 0.004$ (eq 16,

$$cis\text{-}RuH_2(dppf)_2 + [HPR_2R']^+ \rightleftharpoons [Ru(H)_3(dppf)_2]^+ + PR_2R' \quad (16)$$

R = Cy, R′ = Ph). The dihydride reacts with $[HPPh_2Et]^+$ (pK_a ≈ 4.9) in CD_2Cl_2 to give an equilibrium as in eq 16 with $K = 0.34 \pm 0.10$. Therefore, the pK_a of $[Ru(H)_3(dppf)_2]^+$ on the pseudo-aqueous scale is 4.4 ± 0.1. The dihydride in CH_2Cl_2 has a reversible $E_{1/2}\{Ru^{3+}/Ru^{2+}\}$ electrochemical potential at −0.63 V vs Fc^+/Fc. Therefore, the Ru−H bond dissociation energy of the trihydride, $\Delta H_{BDE}\{RuH^+\}$, is approximately 58 kcal mol^{-1}. However, more work is needed to see if pK_a and $E_{1/2}$ values for some complexes can be determined in CH_3CN solution so that a direct comparison can be made with other metal−hydride bond energies determined by Tilset and Parker.[50−52] It is interesting that the dppf ligand is more electron donating than the dppe ligand as judged on the basis of the electrochemical potentials of the corresponding dihydride complexes: −0.63 V for $RuH_2(dppf)_2$ versus approximately −0.2 V for $RuH_2(dppe)_2$.[1] It is paradoxical that the more electron-donating ligand produces a more acidic $[RuH_3L_2]^+$ complex; the paradox is explained by the absence and presence of H−H bonding in the dppf and dppe complexes, respectively.

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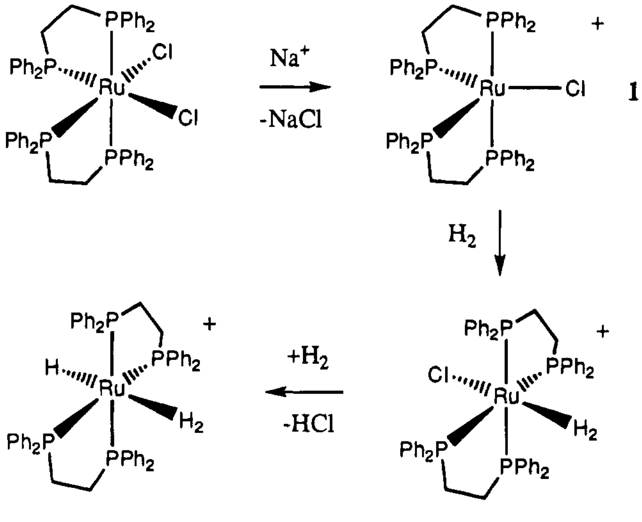
Scheme 1. Steps in the Synthesis of **3a** from the Reaction of *cis*-$RuCl_2(dppe)_2$ with $NaBPh_4$ and H_2 in THF



3a **2a**

Conclusion

The complex $[RuCl(dppe)_2]^+$ (**1**) has an interesting distorted trigonal bipyramidal structure with a Y-shaped equatorial plane and is quite stable. It reacts with most ligands to give *cis*-[Ru(Cl)(L or X^-)$(dppe)_2]^+$ complexes but it reacts with H_2 to give exclusively *trans*-$[Ru(H_2)Cl(dppe)_2]^+$ (**2a**). The position of complexes **1** and **2a** in the route to *trans*-$[Ru(H_2)H(dppe)_2]^+$ from *cis*-$RuCl_2(dppe)_2$ has been firmly established (Scheme 1).

There are some striking differences in the chemistry of dihydrogen complexes *trans*-$[Ru(H_2)Cl(L)_2]^+$ (**2**) and *trans*-$[Ru(H_2)H(L)_2]^+$ (**3**). The T_1(min) and ^1J(H,D) NMR data indicate that the H−H distance is longer in the former complexes. It has not been established yet whether complexes **2** have fast-spinning H_2 ligands with d(H−H) of about 0.9 Å or slow-spinning H••H ligands with d(H−H) of about 1.2 Å. We hope that a future neutron diffraction study will resolve this question. The H−H lengthening by a trans chloride can be explained by $p\pi(Cl)-d\pi(Ru)$ repulsions which enhance $d\pi(Ru)\rightarrow\sigma^*(H_2)$ back-bonding. In addition, a $RuCl^+$ fragment is expected to be more Lewis-acidic than a RuH^+ fragment, so that depletion of σ electrons from the H_2 ligand would be greater for **2** than for **3**. Other dihydrogen complexes with H_2 trans to terminal Cl ligands such as $[Os(H\cdot\cdot H)(en)_2Cl]^+$,[9] $Ir(H\cdot\cdot H)H(Cl)_2(P^iPr_3)_2$[12] and $Re(H\cdot\cdot H)Cl(PMePh_2)_4$[53] have elongated H_2 ligands. The characterization of other complexes *trans*-$[M(H_2)XL_2]^+$, M = Ru, Os, is in progress.

The pK_a values of **2a** (6) and **3a** (15) are very different. The lower value (greater acidity) for **2a** is attributed to a lower H−H bond strength in this complex. The high acidity of the trihydride complex $[Ru(H)_3(dppf)_2]^+$ is also in accord with this idea. Therefore, the measurement of pK_a and electrochemical data for such complexes can be used to estimate the strength of H−H bonding in the complex. It has been suggested that complexes containing an elongated H−H bond are less acidic than those which have an H_2 ligand with a short H−H bond.[54] This work demonstrates that this is not always the case. An increase in electron density at the metal can paradoxically make the H_2 ligand more acidic by weakening the H−H bond.

The acidic nature of **2a** is apparent from its reactivity. It eliminates HCl and reacts with ligands L to give complexes *trans*-$[Ru(L)H(dppe)_2]^+$, L = H_2, CO.

Acknowledgment. This research was supported by grants to R.H.M. from the Natural Sciences and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a loan of ruthenium and osmium salts from Johnson Matthey Co. We thank Alex Young for measuring the FAB mass spectra, Nick Plavac for running some NMR spectra, Prof. Peter MacDonald for running the CP MAS ^{31}P NMR spectra, and Adina Petroff, Tina Fong, and Marcel Schlaf for some experimental work. We are grateful to Prof. M. Saburi for providing some synthetic details.

Supplementary Material Available: Tables giving structure determination summaries, atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for complexes **1** and **2a** and an electron density difference map for **2a** (19 pages). Ordering information is given on any current masthead page.

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