The Synthesis, Characterization, and Reactivity of an Unusual, Amphoteric (Tetrahydroborato)ruthenium Hydride Complex of a Chelating Triphosphine, Ru(H)(η^2-BH_4)(ttp)[1]

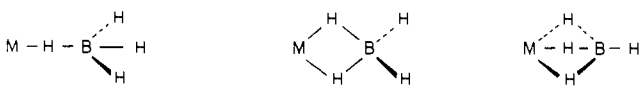
John B. Letts, Terry J. Mazanec, and Devon W. Meek*

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received September 4, 1981*

Abstract: Treatment of $[RuCl_2(ttp)]_x$ with excess sodium tetrahydroborate in refluxing tetrahydrofuran produces the yellow, microcrystalline complex RuH(η^2-BH_4)(ttp), **4**, which shows discrete proton NMR signals for the metal hydride, each of the two bridging protons, and the two terminal B-H protons at ambient temperature. A variable-temperature ^1H NMR study shows scrambling of the BH_4^- protons at two different temperatures, and the exchange process can be interpreted as a two-step process. Owing to the presence of both Ru-H and doubly bridged Ru-BH_4 linkages in **4**, addition of acid or base in the presence of neutral ligands L produces two different series of products, i.e., $[Ru(H)(L)_2(ttp)]^+$, L = CO, CH_3CN, and $P(OMe)_3$, and $RuH_2(L)(ttp)$, L = CO, PPh_3, and $P(OMe)_3$. In the case of $P(OMe)_3$, three different isomers (i.e., trans, cis-syn, and cis-anti) are obtained, depending on the sequence of addition of reagents, solvents, and reaction conditions. The cis-syn and cis-anti isomers of $[RuH(P(OMe)_3)_2(ttp)]^+$ are the first detected examples where the different structures are due to the fixed stereochemical orientation of the phenyl group on the central phosphorus atom of ttp. When $P(OPh)_3$ is used as the ligand L, the ortho-metalated product $\overline{RuH(P(OPh)_2OPh)(ttp)}$ is obtained instead of the target complex $RuH_2(P(OPh_3)ttp$, analogous to the $RuH_2(P(OMe)_3)(ttp)$ complex. The complexes have been characterized by elemental analyses, conductivity, infrared, proton, and phosphorus-31 NMR spectra, as well as an X-ray structure determination of complex **5d**. Complex **4** in the presence of NEt_3 catalytically hydrogenates 1-octene to octane at a rate comparable to that of $RhCl(PPh_3)_3$; in the presence of 1 equiv of $HBF_4 \cdot Et_2O$, **4** catalytically hydrogenates 1-octene at a rate ~0.75 that of $RhCl(PPh_3)_3$.

Introduction

Covalent bonding of the tetrahydroborate ion to transition metals, actinides, and lanthanides can occur via one, two, or three M-H-B bridges, e.g., **1**, **2**, and **3**.[2] Discrimination among the



1 **2** **3**

various bonding modes has previously been made primarily on the basis of infrared spectroscopy or from X-ray or neutron diffraction.[3,4] Nuclear magnetic resonance spectroscopy, which would appear to be a rapid and convenient method of determining the type of M-BH_4 bonding, has not generally proven useful, since the proton signals are degenerate in nearly all of these compounds due to rapid equilibration on the NMR time scale.[2] However, bulky tertiary phosphine ligands have been shown to be effective in stabilizing nonfluxional tetrahydroborate complexes of rhodium, ruthenium, and iridium.[5-7]

Herein we report the synthesis and characterization of Ru(H)(η^2-BH_4)(ttp), **4**, a complex which shows discrete proton NMR signals for the metal hydride, each of the two bridging protons, and the two terminal protons at ambient temperature. We also report the first example of magnetic coupling between phosphorus and a bridging proton of the tetrahydroborate ligand in a metal complex. Although the title complex is not an active hydrogenation catalyst in the absence of a cocatalyst, addition of 1 equiv of acid or of excess base generates a catalyst with activity comparable to that of $RhCl(PPh_3)_3$.

Experimental Section

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents employed were all reagent grade and were distilled from appropriate drying agents prior to use.

Infrared spectra were measured on a Perkin-Elmer 337 or 283B grating spectrophotometer from 400 to 4000 cm^{-1} and 200 to 4000 cm^{-1}, respectively, as Nujol mulls, pressed potassium bromide pellets or solutions. Sharp polystyrene absorptions at 1601 and 906.7 cm^{-1} were used for calibrations of the infrared spectra. Phosphorus-31 NMR spectra were collected on one or more of the Bruker Fourier transform instruments (HX 90, WP 200, or WM 300) which were operated at 36.43, 81.015, and 121.470 MHz, respectively. Ten-millimeter tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were used for the ^{31}P spectra. Phosphorus-31 chemical shifts are reported in parts per million from 85% H_3PO_4; positive chemical shifts are downfield from the external phosphorus standard. Proton magnetic resonance spectra were collected on the Bruker HX90 or WM300 instruments with Me_4Si or the residual protons in the deuterated solvents (referenced back to Me_4Si) as the internal standard. Conductivity data were obtained on approximately 10^{-3} M nitromethane solutions with a Lab-Line unbreakable beaker-type conductivity cell, Cat. No. 11200. The cell constant was approximately 0.11 cm^{-1}. An Industrial Instruments, Inc., conductivity bridge (Model RC16B2) was used to determine the cell resistance at 1000 Hz. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Hydrogenation Experiments. Catalytic hydrogenation experiments were carried out at a fixed hydrogen pressure (~1 atm) at room temperature using an automatic, gas-measuring instrument designed by Mr. Robert Fagan of the Department of Chemistry, The Ohio State University. A typical hydrogenation experiment used 1-octene (500:1 olefin to Ru ratio) with ~1.0 mmol of metal catalyst in a total volume of 50 mL (THF as the solvent). After each experiment, the volatile components were removed under vacuum and analyzed via gas chromatography on a Series 1200 Varian Aerograph instrument with β,β Chromosorb as the column support. Hydrogen uptake rates were compared to Wilkinson's catalyst $RhCl(PPh_3)_3$ at comparable conditions.

Ru(H)(η^2-BH_4)(ttp), 4. A mixture of 1.237 g of $[RuCl_2(ttp)]_x$[8] (1.683 mmol of Ru), 0.733 g of $NaBH_4$ (20 mmol), and 100 mL of THF was

(1) ttp = the chelating, triphosphine ligand $PhP(CH_2CH_2CH_2PPh_2)_2$.
(2) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263-293.
(3) (a) Bommer, J. C.; Morse, K. W. *J. Chem. Soc., Chem. Commun.* **1977**, 137. (b) *Inorg. Chem.* **1980**, *19*, 587. (c) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmidkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165.
(4) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558.
(5) (a) Empsall, H. D.; Mentzer, E.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 861-2. (b) Empsall, H. D.; Hyde, E. M.; Mentzer, E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 2069-74.
(6) (a) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 7154-62. (b) Marks, T. J.; Kennelly, W. J. *Ibid.* **1975**, *97*, 1439-43.
(7) Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem.* **1978**, *157*, 335.
(8) Mazanec, T. J. Ph.D. Dissertation, The Ohio State University, Columbus, OH, Dec 1978.

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heated to reflux for 2 h to give a bright yellow solution and a white solid. The solution was evaporated to dryness in vacuo and the precipitate extracted with 50 mL of benzene to give a clear yellow solution. This liquid was reduced in volume at ~50 °C to ~2 mL, allowed to cool, and diluted with 130 mL of diethyl ether. From the resulting solution a yellow solid crystallized; it was collected by filtration, washed with diethyl ether, and dried in vacuo: yield 0.85 g, 75%; mp 180 °C with decomp. Anal. Calcd for $C_{36}H_{42}BP_3Ru$: C, 63.62; H, 6.29; B, 1.59; Cl, 0.00. Found: C, 63.93; H, 6.29; B, 1.78; Cl, 0.00.

***cis*-[Ru(H)(CO)$_2$(ttp)][BF$_4$], 5a.** Carbon monoxide was bubbled through a solution of 0.182 g of Ru(H)(BH_4)(ttp) (0.268 mmol) in 20 mL of THF. Upon addition of 40 μL of HBF_4·Et_2O (1 equiv) the yellow color quickly dissipated. The volume was reduced to 3 mL, and just enough diethyl ether was added to cause the solution to become cloudy. The solution sat overnight and white, needle-like crystals formed; the crystals were collected by filtration, washed with 20 mL of ether, and dried in vacuo: yield 0.17 g, 79%; mp 130 °C with decomp. Anal. Calcd for $C_{38}H_{38}BF_4O_2P_3Ru$: C, 56.52; H, 4.74; F, 9.41. Found: C, 56.72; H, 4.96; F, 9.63.

The presence of BH_3·THF in the filtrate was confirmed by comparison of the infrared spectrum with that of an authentic sample.

***cis*-[Ru(H)(NCCH$_3$)$_2$(ttp)][BF$_4$], 5b.** One equivalent of HBF_4·Et_2O (55 μL) was added to a solution of 0.207 g of Ru(H)(BH_4)(ttp) (0.305 mmole in 10 mL of THF and 0.50 mL of CH_3CN; the yellow color disappeared rapidly and gas was evolved. The volume was reduced to 7 mL and cooled to 0 °C overnight. The following day very air-sensitive white crystals were isolated by filtration; they were washed with ether and dried in vacuo: yield 0.18 g, 73%; mp 50–90 °C with decomp. Anal. Calcd for $C_{40}H_{44}BF_4N_2P_3Ru$: C, 57.63; H, 5.32; N, 3.36. Found: C, 57.38; H, 5.38; N, 3.16.

***cis-syn*-[Ru(H)(P(OMe)$_3$)$_2$(ttp)][BF$_4$], 5c.** To a solution of 0.264 g of Ru(H)(BF_4)(ttp) (0.388 mmol) in 10 mL of THF was added 0.15 mL of $P(OMe)_3$. The solution was stirred for 10 min whereupon the yellow color began to fade. Then 63 μL of HBF_4·Et_2O (1 equiv) was added and the yellow color disappeared as gas was evolved. The volume was reduced to 3 mL, and just enough diethyl ether was added to cause cloudiness in the solution. White crystals formed overnight; they were isolated by filtration, washed with 20 mL of ether, and dried in vacuo: Yield 0.10 g, 27%; mp 150 °C with decomp. Anal. Calcd for $C_{42}H_{56}BF_4O_6P_5Ru$: C, 50.46; H, 5.64; P, 15.49. Found: C, 50.53, H, 5.72; P, 15.61. The second crop of crystals yielded the trans isomer **5e**.

***cis-anti*-[Ru(H)(P(OMe)$_3$)$_2$(ttp)][BF$_4$], 5d.** To a solution of 0.232 g of RuH(BH_4)(ttp) (0.342 mmol) in 10 mL of THF at 0 °C was added 0.15 mL of $P(OMe)_3$. After the solution was stirred for 10 min, 1 equiv of HBF_4·Et_2O was added; the solution rapidly became almost colorless. Enough hexane was added to cause cloudiness in the solution. After approximately 1 week at room temperature large, pale orange conglomerates of crystals were isolated; they were washed with hexane and dried in vacuo. Those crystals were recrystallized from acetone/hexane to give white crystals; yield 0.205 g, 60%; mp 185 °C with decomp. Anal. Calcd for $C_{42}H_{56}BF_4O_6P_5Ru$: C, 50.46; H, 5.64; P, 15.49. Found: C, 50.26; H, 5.67; P, 15.71.

***trans*-[Ru(H)(P(OMe)$_3$)$_2$(ttp)][BF$_4$], 5e.** To a solution of 0.17 g of Ru(H)(BH_4)(ttp) (0.259 mmol) in 10 mL of THF was added 0.15 mL of $P(OMe)_3$, and the solution was stirred overnight. To the resultant nearly colorless solution was added 42 μL of HBF_4·Et_2O; a gas was evolved. The volume was reduced to 2 mL, and 5 mL of diethyl ether was added; an orange oil separated. The oil was dissolved in 5 mL of acetone and diluted with 6 mL of hexane; pale orange crystals separated. The crystals were isolated by filtration and dried in vacuo: yield 0.176 g, 68%; mp 135 °C with decomp. Anal. Calcd for $C_{42}H_{56}BF_4O_6P_5Ru$: C, 50.46; H, 5.64; P, 15.49. Found: C, 50.70; H, 5.80; P, 15.28.

Ru(H)$_2$(CO)(ttp), 6a. (a) To a solution of 0.200 g of Ru(H)(BH_4)(ttp) (0.295 mmol) in 12 mL of THF was added 0.15 mL of NEt_3; carbon monoxide was bubbled through the solution overnight, and an additional 0.15 mL of NEt_3 was added. After the solution sat for several days, light tan crystals formed. These crystals were isolated by filtration, washed with hexane, and dried in vacuo: yield 0.155 g, 76%; mp 130 °C with decomp. Mass spectroscopy showed envelopes around *m/e* 692 and 664 corresponding to M − 2^+ and M − 2 − CO^+ ions.

(b) Carbon monoxide was bubbled through a solution of 0.180 g of Ru(H)(BH_4)(ttp) (0.265 mmol) in 2 mL of methanol and excess $NaOCH_3$ in 10 mL of THF for 2 h to give a pale yellow solution and a white solid. The mixture was filtered; the filtrate was reduced in volume, and hexane was added to give a tan soild. The solid was collected by filtration, washed with hexane, and dried in vacuo: yield 0.14 g, 81%; mp 130 °C with decomp; mass spectrum, *m/e* 692, 664.

***cis*-Ru(H)$_2$(P(OMe)$_3$)(ttp), 6b.** To a solution containing 0.114 g of Ru(H)(BH_4)(ttp) (0.164 mmol) in 10 mL of THF were added 0.10 mL of $P(OMe)_3$, and 0.10 mL of NEt_3 in sequence. After the solution was stirred for 2 h, it became colorless. The volume was reduced to 4 mL, and 2 mL of hexane was added; then the solution was allowed to stand overnight. The resulting white crystals were isolated by filtration, washed with hexane, and dried in vacuo: yield 0.35 g; 84% mp 140 °C with decomposition. The mass spectrum showed overlapping envelopes at *m/e* 790 and 788 corresponding to M^+ asnd M − 2^+. Anal. Calcd for $C_{39}H_{48}O_3P_4Ru$: C, 59.31; H, 6.12; P, 15.68. Found C, 58.98; H, 6.26; P, 15.36.

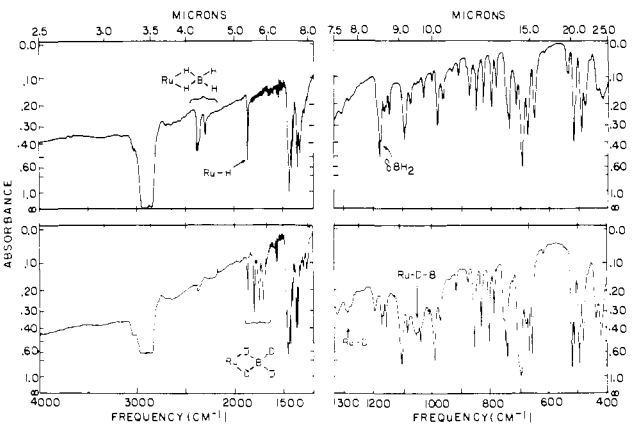


Figure 1. Top: infrared spectrum of RuH(η^2-BH_4)(ttp), **4** (Nujol mull). Bottom; infrared spectrum of RuD(η^2-BD_4)(ttp) (Nujol mull).

***trans*-Ru(H)$_2$(PPh$_3$)(ttp), 6c.** To a solution of 0.231 g of Ru(H)(BH_4)(ttp) (0.339 mmol) in 10 mL of THF was added 0.356 g of PPh_3 (1.356 mmol), and the mixture was stirred. After 1 h no apparent reaction had occurred, so 0.10 mL of NEt_3 was added and the solution was stirred overnight. The resulting pale yellow solution was reduced to 3 mL, and an equal volume of hexane was added to produce a cloudy solution and some flocculent material. Pale yellow crystals separated over a period of 5 h. The supernatant and a flocculent solid were removed by decantation; the yellow crystals were washed with hexane and dried in vacuo: yield 0.29 g, 95%; mp 120–125 °C with decomp. Anal. Calcd for $C_{54}H_{54}P_4Ru$: C, 69.89; H, 5.86; P, 13.35. Found: C, 70.00; H, 6.06; P, 13.44.

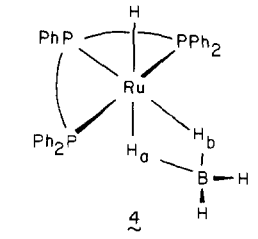
RuH(P(OPh)$_2$OPh)(ttp), 6d. To a solution of 0.210 g of RuH(BH_4)(ttp) (0.309 mmol) in 10 mL of THF was added 0.45 mL of $P(OPh)_3$ and 0.40 mL of NEt_3. The resultant solution became nearly colorless while it was stirred overnight; its volume was reduced to 2 mL, and 7 mL of hexane was added. The resultant solution became cloudy, and a small amount of brown solid separated after 1 h. The brown solid was removed by filtration, and hexane was added to the clear filtrate until it became cloudy. White crystals formed within 24 h; they were collected on a filter, washed with hexane, and dried in vacuo: yield 0.16 g, 56%; mp 100 °C with decomp. Anal. Calcd for $C_{54}H_{52}O_3P_4Ru$: C, 66.56; H, 5.38; P, 12.69. Found: C, 65.70; H, 5.54; P, 12.50.

Reaction of Ru(H)(BH_4)(ttp) with HCl(aq). To a solution of 0.194 g of Ru(H)(BH_4)(ttp) (0.286 mmol) in 15 mL of THF was added 5.6 mL of 0.048 M aqueous HCl solution (1 equiv); a gas was evolved and an orange solid formed. The solution remained yellow so an additional equivalent of HCl was added, resulting in further crystallization and gas evolution. The orange solid was isolated by filtration, washed successively with 5-mL portions of methanol, water, methanol, and diethyl ether, and dried in vacuo. An infrared spectrum of the orange material was identical with that of an authentic sample of $[RuCl_2(ttp)]_x$.

Results and Discussion

Our successful preparation of catalytically active metal hydride complexes of the triphosphine ligand, $PhP(CH_2CH_2CH_2PPh_2)_2$, ttp, prompted us to investigated a series of its Ru(0) and Ru(II) complexes.[9,10] Thus, treatment of the rather insoluble, orange compound $[RuCl_2(ttp)]_x$ with an excess of sodium tetrahydroborate in refluxing tetrahydrofuran produced a yellow solution from which a yellow microcrystalline solid, **4**, could be isolated in good yield. The infrared spectrum of **4** suggested incorporation of the tetrahydroborate anion into the complex; this was supported by microanalysis. The infrared spectra, however (Figure 1), does not provide a definitive assignment concerning how the BH_4^- unit is attached to the metal. Absorptions at 2390, 2380, and 2330

(9) DuBois, D. L.; Meek D. W. *Inorg. Chim. Acta.* **1976**, *19*, L29.
(10) Niewahner, J.; Meek, D. W. *Adv. Chem. Ser.* **1981**, *No. 196*, 257.



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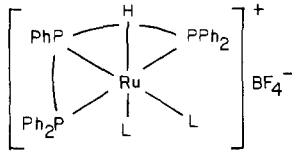


5a , L = CO
5b L = CH_3CN

cm^{-1} are assigned to the B–H_t (t = terminal) stretching mode, and the absorption at 1180 cm^{-1} is assigned to the B–H_t deformation. The B–H_b–Ru absorptions expected in the range 1650–2150 cm^{-1} either are very weak or are obscured by the overtone vibrations from the phenyl groups of the ligand. We have assigned the sharp, medium absorption at 1880 cm^{-1} to the ruthenium–hydride stretching frequency, due to its similarity with the other ν(Ru–H) absorptions reported herein rather than to the bridging Ru–H–B units. For comparison and verification of the assignment, the deuterated analogue of RuH(BH_4)ttp, RuD(BD_4)ttp, was prepared. The infrared spectrum of RuD(BD_4)ttp (Figure 1) shows sharp absorptions at 1805, 1755, and 1705 cm^{-1} due to ν(B–D_t), an absorption at 1280 cm^{-1} due to ν(Ru–D) and an absorption at 1060 cm^{-1} due to the Ru–D–B bridging frequency (obscured by the ttp ligand absorptions in RuH(BH_4)ttp); however, no absorption can be assigned definitively to the ν(B–D_t) deformation (expected at $\simeq$ 860 cm^{-1}). Other infrared absorptions due to the BH_4^- or BD_4^- groups are not distinguishable from those of the triphosphine ligand.

Infrared data reported for a number of similar compounds containing bidentate BH_4^- units (and one which was assigned as a monodentate BH_4^-) are collected in Table I. Compounds in which the M–BH_4 bonding is thought to be highly covalent (e.g., Ti(BH_4)(C_5H_5)$_2$) generally exhibit higher ν(B–H_t) values than those for which M–BH_4 bonding has considerable ionic character, i.e., Co(BH_4)[(Ph_2PCH_2)$_3$$CCH_3$].[11] On this infrared basis, the Ru–BH_4 bonding in **4** would appear to be fairly ionic; however the reactions (vida infra) and the solubility properties of **4** in nonpolar organic solvents suggest that the complex is a nonelectrolyte compound, as was found for RuH(BH_4)($PMePh_2$)$_3$.[7]

The proton NMR spectrum of **4** in C_6D_6 showed multiplet patterns typical of the ttp ligand[12] centered at δ 7.3 (25 H) and 1.8 (12 H) that are assigned to the phenyl and methylene protons, broad absorptions at δ 5.1 (2 H, $\nu_{1/2} \simeq$ 90 Hz), −5.8 (1 H, $\nu_{1/2} \simeq$ 85 Hz), and −7.9 (1 H, $\nu_{1/2} \simeq$ 90 Hz), and a sharp doublet of triplets at δ −15.6 (1 H, $^2J_{P_1-H}$ = 39 Hz, $^2J_{P_2-H}$ = 23 Hz). The high-field region of this spectrum is illustrated in Figure 2c. Broad-band decoupling of the boron nucleus causes the resonances at δ −5.8 and −7.9 to sharpen somewhat to a broad singlet ($\nu_{1/2} \simeq$ 25 Hz) and a doublet ($\nu_{1/2} \simeq$ 25 Hz, $^2J_{P-H}$ = 40 Hz), and the resonance at δ 5.1 ($\nu_{1/2} \simeq$ 25 Hz) to sharpen; boron coupling has little effect on the pattern at δ −15.6, as illustrated in Figure 2a. Moreover, phosphorus-31 decoupling (Figure 2b) causes the pattern at δ −15.6 to collapse to a sharp singlet and the absorptions at δ −5.8 ($\nu_{1/2} \simeq$ 40 Hz) and −7.9 ($\nu_{1/2} \simeq$ 35 Hz) to become broad singlets. We conclude from these observations that the resonance

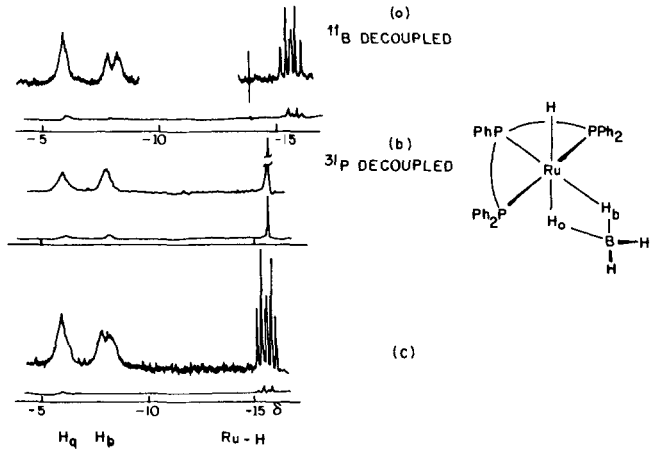


Figure 2. (a) Proton NMR spectrum of **4**, in C_6D_6 with ^{11}B decoupling. (b) Proton NMR spectrum of **4** in C_6D_6 with ^{31}P decoupling. (c) Proton NMR spectrum of RuH(η^2-BH_4)(ttp), **4**, in C_6D_6.

at δ 5.1 is due to two terminal B–H nuclei, and two resonances at δ −5.8 and −7.9 are due to the *nonequivalent* Ru–H–B bridges, the one at δ −7.9 being trans to the central phosphorus atom of the ttp ligand (indicated by the $^2J_{P-H_b}$ coupling). The observed 40-Hz coupling between phosphorus and a bridging hydrogen atom has precedent in the $^2J_{P-H_b}$ values reported for the compound $H_4Ru_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$, for which $^2J_{P-H_b}$(trans) $\simeq$ 28–30 Hz and $^2J_{P-H_b}$ (cis) $\simeq$ 9–18 Hz.[13] (The cis couplings in **4** are not resolved.)

The proton resonance at δ −15.6 is assigned to the hydrogen that is bonded directly to ruthenium; that hydrogen is cis to all three phosphorus atoms of the ttp ligand. This assignment is based on the magnitudes of the $^2J_{P-H}$ values (23 and 39 Hz), which are closer to the range of $^2J_{P-H}$ values reported[14] for a cis geometry (6–32 Hz) than for a trans geometry (73 Hz). The chemical shifts of the tetrahydroborate protons in **4** are consistent with the reported values, some of which are summarized in Table II.

Our proposed structure for **4** is a distorted octahedral arrangement around ruthenium with a meridional arrangement of ttp and with the bidentate BH_4^- ligand spanning nonequivalent sites, i.e., **4**. The proposed C_s symmetry of **4** is supported by the ^{31}P{^{1}H} NMR spectrum, since we observe an AB_2 ^{31}P{^{1}H} NMR pattern in benzene ($\delta(P_1)$ 34.1, $\delta(P_2)$ 29.8 ($^2J_{P-P}$ = 40 Hz)). A very broad resonance centered at −14.2 ppm ($\nu_{1/2} \simeq$ 2000 Hz, referenced to BCl_3 at 47.0 ppm) was observed in the ^{11}B{^{1}H} NMR spectrum. The signal was invariant with broad-band decoupling of the phosphorus nuclei. The structure of **4** is similar to that proposed by Crabtree for Ru(H)(BH_4)($PMePh_2$)$_3$.[7]

The variable-temperature ^{1}H {^{11}B} NMR study of RuH(BH_4)ttp in benzene-d_6 (up to 350 K) and toluene-d_8 is shown in Figure 3 and reveals a high-temperature, unique fluxional behavior for the BH_4^- ligand. The room-temperature ($\sim$305 K) and 230 K spectra are identical; hence, the low-temperature limiting spectrum occurs even at room temperature. As the temperature is increased the resonances at −5.8 and 5.1 ppm begin to collapse first and both signals disappear into the base line at 348 K, whereas the signal that is assigned to H_b (bridging hydrogen of the BH_4^- ligand) remains as a doublet. The phosphorus coupling to H_b indicates that H_b remains trans to the central phosphorus atom of the ligand ttp. If the temperature is increased an additional 10 K, the resonance at −7.9 ppm also collapses; however, the ruthenium–hydride resonance remains a sharp doublet of triplets throughout the 230–378 K temperature range, indicating that it does not participate in the fluxional process of the BH_4^- ligand.

(11) (a) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768–74. (b) Marks, T. J.; Kolb, W. J.; Shimp, L. A. *Ibid.* **1972**, *11*, 2540–2546.

(12) (a) Uriarte, R. L.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79–85. (b) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266–274.

(13) Richter, S. I. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, 1977.

(14) (a) Holah, D. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* **1976**, *54*, 320–328. (b) Dewhirst, K. C.; Keim, W.; Reilly, C. A. *Inorg. Chem.* **1968**, *7*, 546. (c) Douglas, P. C.; Shaw, B. L. *J. Chem. Soc. A*, **1970**, 1556. (d) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 189–290.

Table I. Infrared Absorptions for Some Complexes Reported to Contain Bidentate Tetrahydroborate Ligands (in cm^{-1})[a]

compd	ν(B-H_t(D_t))	ν(B-H_b(D_b)-M)	other B-H(D)$_2$	ν(M-H(D))	ref
$IrH_2(BH_4)(P(t\text{-}Bu)_3)_2$	2460 s, 2367 m	2142 m, 1330 s	1196 s ($\delta(BH_2)$)	2253	5b
$IrH_2(BH_4)(PMe(t\text{-}Bu)_2)_2$	2458 s, 2425 s, 2347 m	2150 m, 1308 m	1188 s ($\delta(BH_2)$)	2249 m	5b
$IrHD(BD_4)(PMe(t\text{-}Bu)_2)_2$	1842 s, 1785 s, 1740 s	1612 w, 993	882 ($\delta(BD_2)$)	1542	5b
$Co(BH_4)(P_3)$[b]	2370 mw, 2330 m	2015 w			11a
$Cu(BH_4)(P_3)$[b]	2300 s	1980 w			11a
$CoH(BH_4)(P\text{-}c\text{-}Hx_3)_2$[c]	2390, 2368	1958, 1379			*d*
$RuH(BH_4)(PPh_3)_3$[e]	2382 s, 2340 sh		1119 m ($\delta(BH_2)$)	2080 w	14a
$RuH(BH_4)(PMePh_2)_3$	2395 s, 2375 sh, 2315 s	1945 s, 1370 s, br	1180 s ($\delta(BH_2)$)		7
$RuD(BD_4)(PMePh_2)_3$	1795 m, 1760 w, br, 1710 s	1405 m, 1032 s, br			7
$RuH(BH_4)$(ttp)	2390 m, 2380 m, 2330 m		1180 s ($\delta(BH_2)$)	1880 s	this work
$RuD(BD_4)$(ttp)	1805 s, 1755 s, 1705 s	1060 s		1280 m	this work
$Ti(BH_4)(C_5H_5)_2$	2438 s, 2400 vs	2050 m, 1940 s	1315 vs, 1155 sm		11b
$Mo(CO)_4BH_4^-$	2395 m, 2376 m	1925 s	1395 m, 1145 m		6a
$MoH(BH_4)(PMe_3)_4$	2340 s, 2290 s	1935 s, 1885 s	1360, 1165	1725 m	*f*

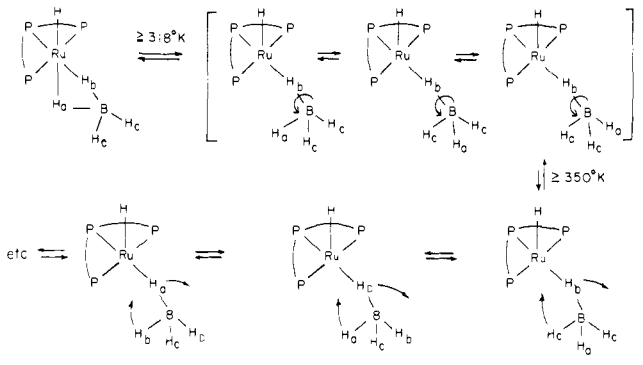
[a] Abbreviations: s = strong, m = medium, w = weak, d = doublet, and sh = shoulder. [b] $P_3 = CH_3C(CH_2PPh_2)_3$ ligand. [c] c-Hx = c-C_6H_{11}. [d] Nakajima, M.; Moriyama, H.; Kobayashi, A.; Saito, T.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* 1975, 80. [e] Reported to have monodentate BH_4^-, ref 14a. [f] Atwood, J. L.; Hunter, W. E.; Carmana-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1980, 467.

Table II. Proton NMR Data for Bidentate Tetrahydroborate Complexes

complex	solvent	*T*, K	$\delta(BH_t)$[b]	$\delta(BH_b)$[b]	δ(M-H)[b]	ref
$IrH_2(BH_4)(P(t\text{-}Bu)_3)_2$[a]	C_7D_8	300	6.17 (20)	−7.76 (21)	−21.0 (t)[d]	5b
$IrH_2(BH_4)(PMe(t\text{-}Bu)_2)_2$[a]	C_7D_8	300	6.86 (23)	−6.86 (23)	−19.5 (t)[e]	5b
$RhH_2(BH_4)(PMe(t\text{-}Bu)_2)_2$[a]			4.53	−3.9	−16.85 (m)	5b
$RuH(BH_4)(PPh_3)_3$	C_6D_6				−6.87 (br)	14a
$RuH(BH_4)(PMePh_2)_3$	C_6D_6	308		−5.1 −9.1	−14.09 (d of t)	7
$RuH(BH_4)$(ttp)[a]	C_6D_6	300	5.1 (40)	−5.8 (25) −7.9 (d, 25)[c]	−15.6 (d of t)[f]	this work

[a] ^{11}B-decoupled spectra. [b] Peak widths at half height are in parentheses: t = triplet; d = doublet; br = broad; m = multiplet. [c] $^2J_{P\text{-}H_b} \simeq$ 40 Hz. [d] $^2J_{P\text{-}H} = 11.8$ Hz. [e] $^2J_{P\text{-}H} = 12.7$ Hz. [f] $^2J_{P_1\text{-}H} = 39$ Hz and $^2J_{P_2\text{-}H} = 23$ Hz.

Scheme I



The calculated coalescence frequency at −0.8 ppm was not observed at 378 K; further increases in temperature were not tried, due to solvent limitations and safety considerations. This entire exchange process is reversible.

The variable-temperature NMR data indicate that the activation energy for the exchange of H_a is lower than that for H_b. The results can be interpreted in terms of a two-step process (Scheme I) which causes scrambling of the bridging and terminal BH_4^- protons. For the lower temperature step (<348 K), one exchange possibility would involve breaking the Ru-H_a bond; then H_a could scramble on the NMR time scale with the two terminal hydrogen atoms (H_c), while H_b remains static. Note that H_b retains its stereochemical integrity in this first step as evidenced by maintenance of the trans ^{31}P-^1H coupling in the range 338–348 K. Thus, the fluxional behavior of the BH_4^- ligand at ≲348 K can be viewed as a bidentate to monodentate rearrangement, with subsequent rotations around the Ru-H_b-B linkage (Scheme I). The second step equilibrates H_b with H_a and H_c, either by Ru-H_b bond breaking to form the ion pair $[RuH(ttp)]^+[BH_4]^-$ or by a fluxional process in which the Ru-H_b-B bridge breaks, interconverting H_a, H_b, and H_c by rotation (Scheme I) about the appropriate Ru-H-B bridge. A sequence of these two steps results in complete scrambling of the BH_4^- protons. The slightly lower energy required to break the Ru-H_a bond may reflect the higher trans influence of hydride compared to tertiary phosphines.

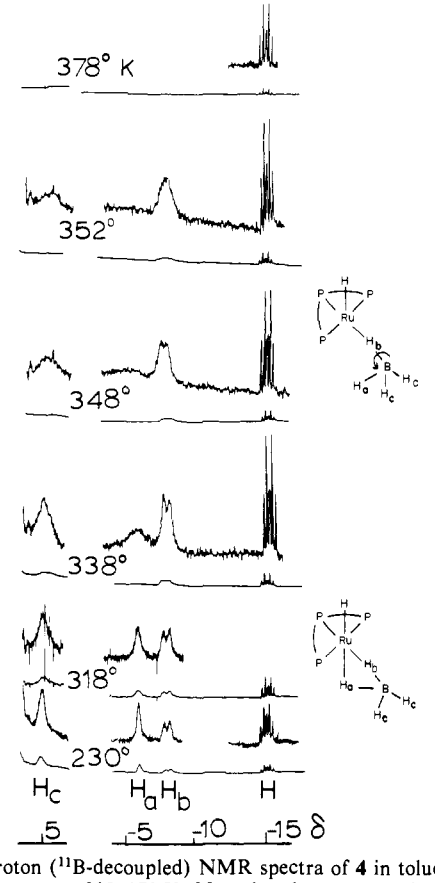


Figure 3. Proton (^{11}B-decoupled) NMR spectra of **4** in toluene-d_8 for the temperature range 230–378 K. Note that the resonance for H_a begins to collapse in the temperature range 338–348 K, whereas the resonance of H_b remains. Both H_a and H_b resonances collapse by 378 K.

An alternative explanation involves a process in which a terminal hydrogen (H_c) moves into a bridging position as the bridging

Table III. Reactions of $Ru(H)(BH_4)(ttp)$ with Selected Acids and Bases[a]

reagents	products
excess HCl(aq)	$[RuCl_2(ttp)]_x$
1 equiv of HBF_4, excess CO	5a, *cis*-$[Ru(H)(CO)_2(ttp)][BF_4]$
1 equiv of HBF_4, excess CH_3CN	5b, *cis*-$[Ru(H)(NCCH_3)_2(ttp)][BF_4]$
1 equiv of HBF_4, excess $P(OMe)_3$	5c, *cis-syn*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$
1 equiv of HBF_4, excess $P(OMe)_3$	5d, *cis-anti*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$
excess $P(OCH)_3$, then HBF_4 (1 equiv)	5e, *trans*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$
excess NEt_3, excess CO	6a, *cis*-$RuH_2(CO)(ttp)$
excess $NaOCH_3$, excess CO	6a, *cis*-$RuH_2(CO)(ttp)$
excess $P(OMe)_3$ + excess NEt_3	6b, *cis*-$RuH_2(P(OMe)_3)(ttp)$ + $BH_3{\cdot}NEt_3$
excess $(P(OMe)_3$	6b, *cis*-$RuH_2(P(OMe)_3)(ttp)$ + $BH_3{\cdot}P(OMe)_3$
excess PPh_3 + excess NEt_3	6c, *trans*-$RuH_2(PPh_3)(ttp)$
excess $P(OPh)_3$ + excess NEt_3	6d, $RuH(P(OPh)_2OPh)(ttp)$

[a] All reactions were performed at 25 °C in THF except 5d which was done at 0 °C.

Table IV. Characterization Data for the Ru(ttp) Complexes

complex	^1H NMR[a]	^{31}P NMR[b] $\delta(P_1)$	$\delta(P_2)$	J_{P-P}	IR[c]	other
4, $Ru(H)(BH_4)(ttp)$[d]	−15.6 d of t (RuH) (39, 23)	34.1	29.8	40	ν(RuH) 1880 s	MS, M − 4+
5a, *cis*-$[Ru(H)(CO)_2(ttp)][BF_4]$	−6.4 d of t (27, 19)	−3.1	17.8	40	ν(CO) 2045, 2005 s ν(RuH) 1920 s	Λ_M = 99
5b, *cis*-$[Ru(H)(NCCH_3)_2(ttp)][BF_4]$[e]	−6.9 q (19, 19)	34.5	27.7	45	ν(CN) 2275 w, 2250 w ν(RuH) 2025 s	
5c, *cis-syn*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$[f]	−8.1 m (16, 20)	−7.4	25.0	40	ν(RuH) 1930 s	Λ_M = 90.5
5d, *cis-anti*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$[g]	−7.9 m (15, 19)	2.5	21.9	47	ν(RuH) 2045 s	
5e, *trans*-$[Ru(H)(P(OMe)_3)_2(ttp)][BF_4]$[h]	−9.2 m (57, 13)	−9.6	19.3	44	ν(RuH) 1940 s	Λ_M = 90
6a, *cis*-$Ru(H)_2(CO)(ttp)$		14.4	40.1	28	ν(CO) 1965 s ν(RuH) 1950 s, 1795 s	MS, M − 2+, M − 30+
6b, *cis*-$Ru(H)_2(P(OMe)_3)(ttp)$[i]	−6.21 m (14, 21) (H_A) −6.75 m (61, 21) (H_B)	16.4	38.0	36	ν(RuH) 1925 s, 1860 s	MS, M+, M − 2+
6c, *trans*-$Ru(H)_2(PPh_3)(ttp)$[j]	−8.79 m	23.0	27.1	29	ν(RuH) 1930 s, 1895 s	
6d, $RuH(P(OPh)_2OPh)(ttp)$[k]	−5.00 d of d of t (14, 20)	8.8	30.9	41	ν(RuH) 1895 s	

[a] Chemical shifts are in δ with respect to Me_4Si = 0.00; d = doublet, t = triplet, q = quartet, m = multiplet; numbers in parentheses are $^2J_{H-P_1}$ and $^2J_{H-P_2}$ in Hz, resonances due to the ttp ligand are not included. [b] Chemical shifts are in δ with respect to external H_3PO_4 = 0.0; positive values are downfield; coupling constants are in Hz; P_1 is the central phosphorus and P_2 the two terminal phosphorus atoms in the ttp ligand. [c] Absorptions are in cm^{-1}; s = strong, w = weak. [d] Further data are contained in Tables I and II. [e] ^1H NMR CH_3CN δ 2.7 and 1.3. [f] ^1H NMR $^2J_{H-P_2}$ = 16, $^2J_{H-P_4}$ = 122 Hz, $\delta(P(OCH_3)_3)$ 3.37 ($^3J_{P-H}$ = 11 Hz), $\delta(P(OCH_3)_3)$ 3.31 ($^3J_{P-H}$ = 10 Hz). ^{31}P NMR $\delta(P_3$(trans to P_1)) 139.5, $\delta(P_4)$ 137.8 ($^2J_{P_1-P_4}$ = −35, $^2J_{P_2-P_3}$ = −46, $^2J_{P_2-P_4}$ = −32, $J_{P_3-P_4}$ = −39, $^2J_{P_1-P_3}$ = 346 Hz). [g] The ^1H NMR showed an unexplainable asymmetric multiplet which seemed to depend on decoupling power when ^{31}P decoupled. The following $^2J_{H-P}$'s are approximate: $^2J_{H-P_4}$ = 124 Hz, $^2J_{H-P_3}$ = 25 Hz. $\delta(P(OCH_3)_3)$ 3.98 ($^3J_{P-H}$ = 9.5 Hz), $\delta(P(OCH_3)_3)$ 3.06 ($^3J_{P-H}$ = 10 Hz). ^{31}P NMR $\delta(P_3$(trans to P_1)) 138.0, $\delta(P_4)$ 137.8 ($^2J_{P_1-P_3}$ = 324, $^2J_{P_1-P_4}$ = −33, $^2J_{P_2-P_3}$ = −47, $^2J_{P_2-P_4}$ = −30, $^2J_{P_3-P_4}$ = −38 Hz). [h] ^1H NMR $^2J_{H-P_3}$ = 34, $^2J_{H-P_4}$ = 18, $\delta(P(OCH_3)_3)$ 3.14 ($^3J_{P-H}$ = 10 Hz), $\delta(P(OCH_3)_3)$ 3.21 ($^3J_{P-H}$ = 10 Hz). ^{31}P NMR $\delta(P_3)$ 135.6, $\delta(P_4)$ 137.3 ($^2J_{P_1-P_3}$ = −25, $^2J_{P_1-P_4}$ = −22, $^2J_{P_2-P_3}$ = −50, $^2J_{P_2-P_4}$ = −47, $^2J_{P_3-P_4}$ = +575 Hz). [i] ^1H NMR $^2J_{H_A-P_3}$ = 134, $^2J_{H_B-P_3}$ = 18, $^2J_{H_A-H_B}$ = 5 Hz, $\delta(P(OCH_3)_3)$ 3.12 ($^3J_{P-H}$ = 9.5 Hz). ^{31}P NMR $\delta(P_3)$ 153.3 ($^2J_{P_1-P_3}$ = 17, $^2J_{P_2-P_3}$ = 33 Hz). [j] The ^1H NMR shows a very complex multiplet at δ −8.79 which gives a 2:40 integrated intensity with respect to the phenyl protons; ^{31}P NMR $\delta(P_3)$ 59.4 ($^2J_{P_1-P_3}$ = 218, $^2J_{P_2-P_3}$ = 26 Hz). [k] ^1H NMR $^2J_{H-P_3}$ = 163 Hz. ^{31}P NMR $\delta(P_3)$ 159.36 ($^2J_{P_1-P_3}$ = 20, $^2J_{P_2-P_3}$ = 24 Hz).

hydrogen (H_a) moves out.[15] Such a concerted process is permutationally indistinguishable from the monodentate mechanism discussed in the above paragraph. However, in the case of $RuH(BH_4)(ttp)$, such an η^3-BH_4 transition state would be a pseudo 20-electron complex, which would violate the "effective atomic number" concept. According to a recent theoretical paper,[16] the η^3-BH_4–M transition state, **3**, appears to be favored over the η^1-BH_4–M transition state for exchange of the hydrogen atom positions of covalent BH_4 metal complexes. Marks et al. have used a concerted mechanism to explain the fluxionality of the bidentate BH_4^- ligand(s) in $Hf(CH_3C_5H_4)_2(BH_4)_2$[17] and [(PPN)Mo$(BH_4)(CO)_4$],[6a] which occurs significantly below room temperature.

The structure of **4** suggests that there may be both acidic and hydridic proton sites, e.g., Ru–H–B and Ru–H, respectively. In order to determine whether the chemical reactivity of **4** would exhibit two different types of acid–base behavior, we treated **4** with a variety of acids and bases. A summary of the results is presented in Table III.

Treatment of **4** with 1 equiv of a protonic acid containing a noncoordinating anion in the presence of an excess of a neutral ligand liberates H_2 and yields the appropriate cationic metal hydride, $[Ru(H)(L)_2(ttp)][BF_4]$. When HCl was used as the acid, the hydride generated is apparently unstable to further protonation (or else disproportionation) and gives the rather insoluble compound $[RuCl_2(ttp)]_x$. A similar result was obtained by Crabtree and Pearman in the reaction of $Ru(H)(BH_4)(PMePh_2)_3$ with a carboxylic acid, although in their case the carboxylate anion functioned as a bidentate ligand to give an isolable six-coordinate complex.[7] The reaction can be summarized by eq 1. Carbon monoxide or acetonitrile by themselves cause no reaction.

$$RuH(\eta^2\text{-}BH_4)(ttp) + HBF_4{\cdot}Et_2O + 2L \xrightarrow{THF} [RuH(L)_2(ttp)][BF_4] + H_2 + THF{\cdot}BH_3 \text{ or } (MeO)_3P{\cdot}BH_3 \quad (1)$$

$$L = CO, CH_3CN, P(OMe)_3$$

(15) We thank Professor T. J. Marks and a reviewer for suggesting the alternate concerted process for interconversion of the different hydrogen atoms of the η^2-BH_4 group.

(16) Barone, V.; Dolcetti, G.; Lelj, F.; Russo, N. *Inorg. Chem.* **1981**, *20*, 1687–1691.

(17) Johnson, P. L.; Cohen, S. A.; Marks, T. J. Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709.

Whereas **4** reacts rapidly with acids to give cationic hydrides, the complex reacts more slowly with bases to yield neutral dihydride compounds according to eq 2. In each case neutral

$$RuH(\eta^2\text{-}BH_4)(ttp) + B + L \xrightarrow{THF} RuH_2(L)(ttp) + B{\cdot}BH_3 \quad (2)$$

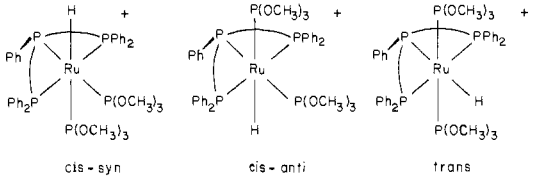
$$B = NEt_3,\ P(OMe)_3,\ NaOCH_3;\ L = CO,\ P(OMe)_3,\ PPh_3$$

ligands fill the remaining coordination sites. In the case of $P(OMe)_3$ it can act both as a base and a neutral ligand. Addition of excess NEt_3 alone causes formation of an uncharacterizable brown solid which has no infrared absorptions in the region 1600–2500 cm^{-1}. Characterization data for the isolated complexes appear in Table IV.

The stereochemistry of the cationic complexes varies with the neutral ligand, L. When L = CO or CH_3CN, the two neutral ligands are cis to each other. The structural assignments of **5a** and **5b** are based on a combination of infrared and NMR spectra. For example, the proton NMR spectra of both $[RuH(CO)_2(ttp)][BF_4]$ and $[RuH(CH_3CN)_2(ttp)][BF_4]$ show that the magnitudes of the $^2J_{P_1-H}$ and $^2J_{P_2-H}$ coupling constants are similar; thus, the hydride ligand must be cis to all three phosphorus atoms rather than trans to P_1.[14] Two strong infrared absorptions (ν_{CO}) at 2045 and 2005 cm^{-1} also indicate the cis stereochemistry for $[RuH(CO)_2(ttp)][BF_4]$.

The structure of **5a** and **5b** are also supported by the $^{31}P\{^1H\}$ NMR spectra which show that the relative chemical shifts for resonances P_1 and P_2 are reversed for the carbonyl and acetonitrile complexes; i.e., P_1 is more shielded than P_2 in the $[RuH(CO)_2(ttp)][BF_4]$ complexes, whereas P_1 is less shielded than P_2 in the $[RuH(CH_3CN)_2(ttp)][BF_4]$ case. This structural assignment illustrates the sensitivity of ^{31}P NMR spectra and the usefulness of an empiricism concerning the effect of different trans ligands on the chemical shifts of the phosphorus resonances.[12b] We, and others, have observed that in planar and octahedral complexes the ligand trans to a phosphorus atom has a strong influence on its ^{31}P chemical shift.[12b,18-20] Particularly, for second-row transition metals, strong-field ligands (e.g. CO) cause the ^{31}P resonance to appear at higher chemical shifts relative to a comparable complex with halide (or acetonitrile) trans to the phosphine. The relative trans influence series Cl ≃ CH_3CN < PR_3 < CO < C < H seems to hold for a wide variety of metals. The relatively weak-field effect (and the low trans influence) of CH_3CN is also indicated by the fact that the acetonitrile ligands in $[RuH(CH_3CN)_2(ttp)]^+$ are labile (i.e., undergo exchange) in solution at room temperature.

Some insight into the possible sequence of acid and base attack on Ru(H)(BH_4)(ttp) can be gained from consideration of the reactions (eq 1), where L = $P(OMe)_3$. In this case the stereochemistry of the product depends on the sequence of addition of the reagents. The cis products (**5c** or **5d**) are obtained when HBF_4



5c **5d** **5e**

and the phosphite are added together; however, when both $P(OMe)_3$ and Ru(H)(BH_4)(ttp) are in solution overnight before the acid is added, the trans isomer **5e** is isolated. These isomers can be distinguished readily on the basis of their ^1H and ^{31}P NMR spectra; $^2J_{H-P_1}$ is larger (57 Hz) when the hydride is trans to P_1 (**5e**) than when the two atoms are in the cis configuration (16 Hz in **5c** and 15 Hz in **5d**). Similarly the phosphite–phosphite coupling is large and positive in the trans isomer ($J_{P_3-P_4}$ = 575 Hz in **5e**) but small and negative in the cis isomers ($J_{P_3-P_4}$ = −39 and −38 in **5c** and **5d**, respectively. Figure 4 shows the $^{31}P\{^1H\}$ NMR spectra for all three isomers. The two cis isomers result from the fact that the stereochemistry about P_1 is fixed; i.e., the barrier to inversion for coordinated phosphine is quite high.[21] Therefore, if the phenyl group is oriented downward (as shown in **5c–e**), the complex cation has two different axial sites; the phenyl and tri-

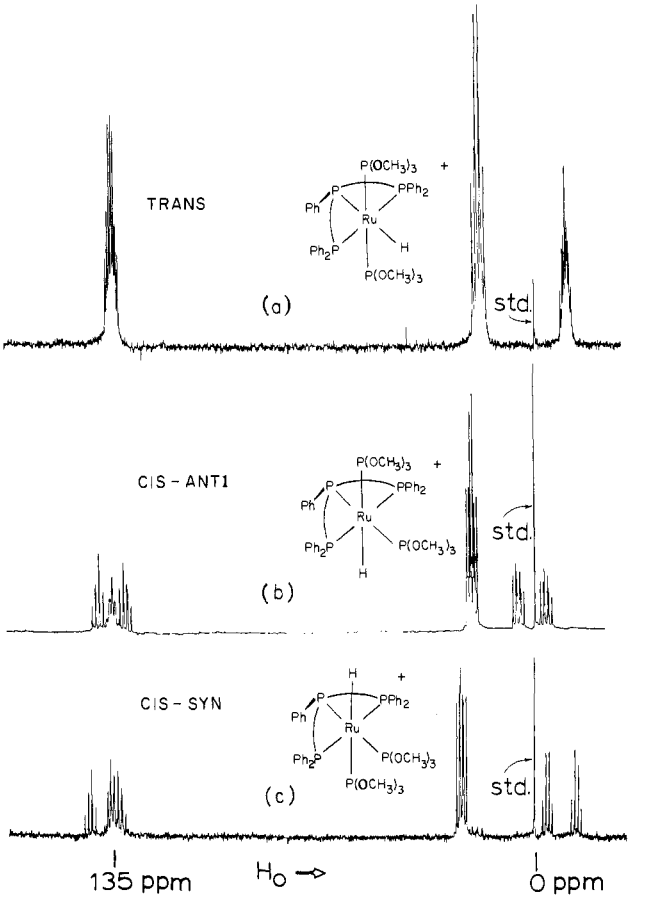


Figure 4. The 36.43-MHz $^{31}P\{^1H\}$ NMR spectra in acetone-d_6 of (a) *trans*-$[RuH(P(OMe)_3)_2(ttp)]^+$, (b) *cis-anti*-$[RuH(P(OMe)_3)_2(ttp)]^+$, and (c) *cis-syn*-$[RuH(P(OMe)_3)_2(ttp)]^+$. The secondary standard $(MeO)_3PO$ was calibrated with 85% H_3PO_4 at 0.00 ppm.

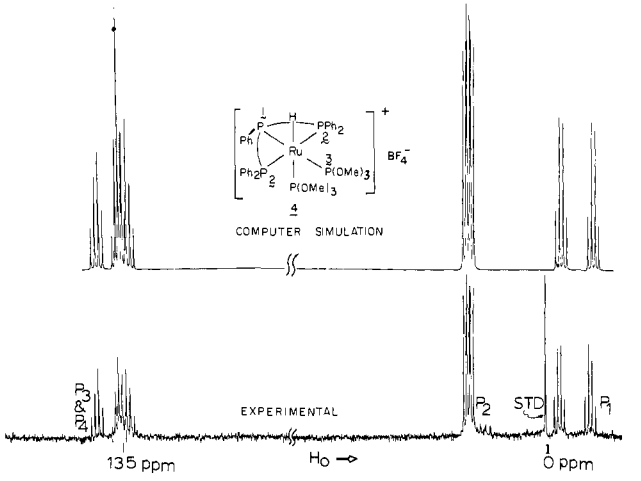


Figure 5. Comparison of the experimental 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of the cis-syn isomer of $[RuH(P(OMe)_3)_2(ttp)]^+$ with that of the computer simulation, using the parameters in Table IV.

(18) Baliman, G.; Pregosin, P. S. *J. Magn. Reson.* **1976**, *22*, 235.
(19) Blum, P. R. Ph.D. Dissertation, The Ohio State University, Columbus, OH, Dec 1977.
(20) Arpac, E.; Dahlenburg, L. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 672.
(21) Lehn, J. M.; Munschi, B. *J. Chem. Soc. D* **1969**, 1327.

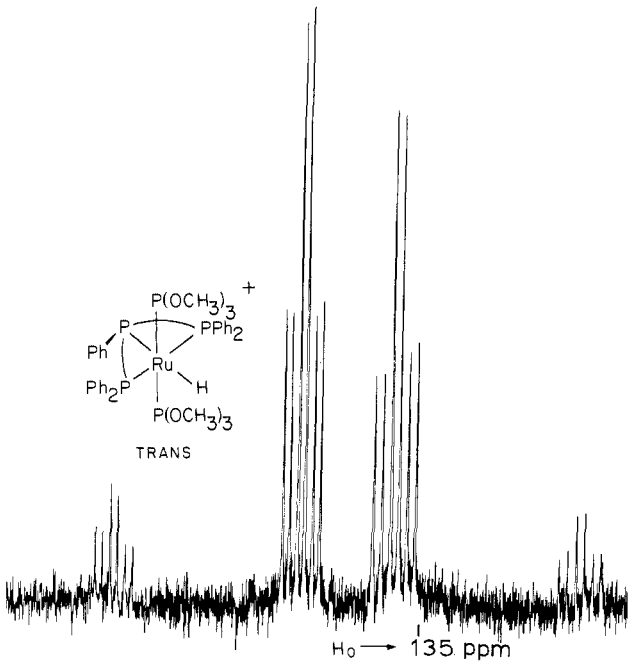


Figure 6. The 121.47-MHz $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[RuH(P(OMe)_3)_2(ttp)]^+$ in acetone-d_6, which shows an AB NMR pattern for the two trimethyl phosphite ligands.

methyl phosphite groups are syn and anti with respect to the Ru–P_1 bond.[22] These two *cis*-$[RuH(P(OMe)_3)_2(ttp)]^+$ complexes provide the first definitive evidence for the stereochemical effect of the substituent on P_1 with the ttp-like ligands. Figure 5 shows the good agreement between the experimental and the computer-simulated spectrum of the cis-syn isomer **5c**. Simulated spectra were run also for most of the complexes listed in Table IV, and good agreement with the appropriate experimental spectrum was obtained.

At 36.43 MHz both phosphite ligands in *trans*-$[RuH(P(OMe)_3)_2(ttp)]^+$ appear equivalent, which suggests a minimal stereochemical effect of the fixed phenyl orientation on P_1. However, a $^{31}P\{^1H\}$ spectrum of the compound at 121.47 MHz clearly shows an AB NMR pattern ($\Delta\delta << J_{P-P}$) for the ^{31}P resonances of the two phosphite ligands (Figure 6). The two phosphites also display different P–P coupling constants to the other phosphorus atoms, i.e., 25 and 50 Hz vs. 22 and 47 Hz. In addition, the phosphite–hydride couplings observed in the $^1H\{^{31}P\}$ spectrum are significantly different, being 18 and 34 Hz.

Predominantly the trans isomers can be obtained by treating $HBF_4 \cdot Et_2O$, $P(OMe)_3$, and $RuH(\eta^2\text{-}BH_4)(ttp)$ at −78 °C. To date, we have not found the proper reaction conditions to produce exclusively one isomer. However, we have determined the solvent and crystallization conditions that separate one isomer cleanly (>99% purity by ^{31}P NMR) from another. There is no NMR evidence for isomerization in solution at room temperature. It is somewhat puzzling why $P(OMe)_3$ gives the two different cis isomers (and a trans isomer) whereas CO and CH_3CN apparently form only cis isomers. Perhaps the differentiation is due to the fact that $P(OMe)_3$ by itself can react slowly with $RuH(BH_4)(ttp)$ to produce the neutral dihydride *cis*-$RuH_2(P(OMe)_3)(ttp)$ as an intermediate, whereas CO and CH_3CN do not produce analogous compounds.[23]

(22) A single-crystal X-ray structure determination of the cis-anti isomer has been completed (Professor L. Pignolet, University of Minnesota, personal communication, 1981). The complex has structure **5d**; thus, the other cis isomer must be the cis-syn isomer **5c**.

(23) After this manuscript was submitted, we discovered that the reaction of $HBF_4 \cdot Et_2O$, $RuH(\eta^2\text{-}BH_4)(ttp)$, and CO in THF at 25 °C produces two cis isomers, analogous to the syn and anti isomers of the $P(OMe)_3$ complex. The ^{31}P and ^1H NMR data for the second cis isomer are as follows: $\delta(P_1)$ 0.9, $\delta(P_2)$ 16.6 (J_{PP} = 42 Hz), δ(Ru–H) −5.8 (d of t). In contrast to the $P(OMe)_3$ reactions however, we have not found a *trans*-$[RuH(CO)_2(ttp)]^+$ complex.

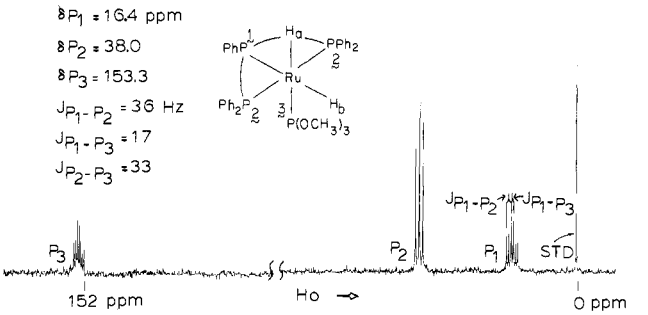


Figure 7. $^{31}P\{^1H\}$ NMR spectrum of *cis*-$[RuH_2(P(OMe)_3)(ttp)]$ in C_6D_6. Note that all of the J_{P-P} couplings are relatively small, in contrast to the $^2J_{P-P}$ values of 300–500 Hz observed for trans $^2J_{P-P}$ couplings in similar complexes.

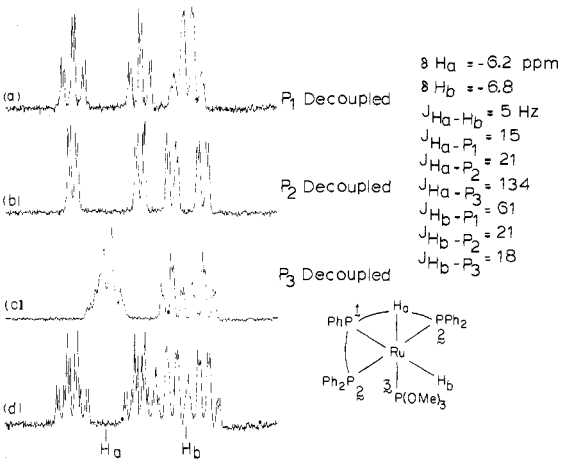


Figure 8. (d) The 300-MHz proton NMR spectrum of *cis*-$[RuH_2(P(OMe)_3)(ttp)]$ in the Ru–H region. Parts a, b, and c show the effect of decoupling P_1, P_2, and P_3 selectively.

A plausible reaction sequence for the formation of either *cis*-$[RuH(CO)_2(ttp)][BF_4]$ or *cis*-$[RuH(CH_3CN)_2(ttp)][BF_4]$ would first involve attack by the acid, $HBF_4 \cdot Et_2O$, at the most basic hydrogen, which is thought to be the metal hydride, to generate the observed H_2 gas. The next step may involve coordination of a neutral ligand (1 equiv of CO) to give an 18-electron species, $[Ru(\eta^2\text{-}BH_4)(CO)(ttp)]BF_4$, which is apparently unstable to loss of BH_3 as $THF \cdot BH_3$. A second ligand molecule then adds to the resultant 16-electron complex to give the observed six-coordinate cations.

In contrast, base attack is expected to occur at the Ru–H–B hydrogen bridges, which are relatively acidic. The bridge-splitting reaction is a common one in covalent borohydride chemistry and has precedent in the reaction of $Cp_2Zr(BH_4)_2$ with 1 equiv of NEt_3 to give $Cp_2Zr(BH_4)H$ or 2 equiv of NEt_3 to give $[Cp_2ZrH_2]_x$.[24] The postulated intermediate, $RuH_2(ttp)$, is a 16-electron complex that has never been characterized; in the presence of even a weak ligand it should react to form an 18-electron, six-coordinate complex. In the presence of CO, we obtain the dihydride carbonyl complex $RuH_2(CO)(ttp)$. Once the complex is isolated from the mother solution it does not redissolve in common organic solvents; therefore, we were unable to obtain a satisfactory proton NMR spectrum of this complex. To circumvent the solubility problem, we used $P(OMe)_3$, which generally gives more soluble metal complexes. A $^{31}P\{^1H\}$ NMR spectrum of *cis*-$RuH_2P(OMe)_3(ttp)$ (Figure 7) shows no large phosphorus–phosphorus couplings; all of the $^2J_{P-P}$ values are small and consistent with the $P(OMe)_3$ ligand being cis to the other phosphorus atoms. The cis structure is confirmed unequivocally by the 300-MHz proton NMR spectra in which we were able to decouple the different phosphorus atoms selectively (Figure 8). The *cis*-$RuH_2P(OMe)_3(ttp)$ complex reacts

(24) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979.

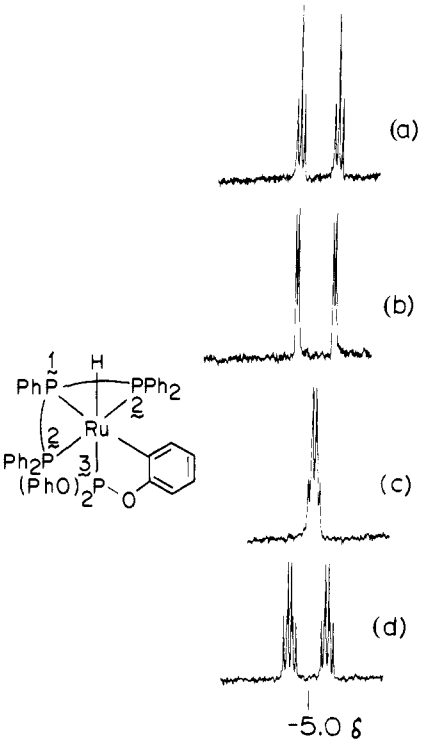
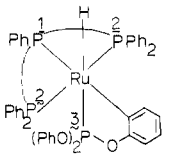


Figure 9. (d) The Ru–H region of the 300-MHz proton NMR spectrum of the orthometalated compound RuH(P(OPh)₂OPh)(ttp), **6d**, in THF-d_8. Parts a, b, and c show the effect of selective decoupling on phosphorus atoms P_1, P_2, and P_3, respectively.

readily with 1 equiv of $HBF_4 \cdot Et_2O$ and excess $P(OMe)_3$ in THF at room temperature to give predominantly the trans isomer of $[RuH(P(OMe)_3)_2(ttp)]^+$. Interestingly, PPh_3 reacts with $RuH(BH_4)(ttp)$ in the presence of NEt_3 to give *trans*-$RuH_2(PPh_3)(ttp)$. The trans isomer may be formed due to the steric requirements of PPh_3 (cone angle = 145°).[25]

In contrast to the reaction of $P(OMe)_3$, $P(OPh)_3$ produces the orthometalated complex RuH(P(OPh)₂OPh)(ttp), **6d**, even at room temperature. The phosphorus-31 NMR spectrum shows a doublet of triplets centered at 159.36 ppm downfield from 85% H_3PO_4; this resonance corresponds to the phosphorus atom in the five-membered ring of the orthometalated triphenyl phosphite



6d

ligand.[26] Both the infrared and proton NMR spectra of **6d** show only one type of Ru–H moiety. The proton NMR spectrum, without ^{31}P decoupling, has a resonance pattern of a doublet of doublet of triplets centered at −5.0 ppm (Figure 9). Structure **6d** is confirmed by the proton NMR spectra in Figure 9 in which the different phosphorus nuclei are decoupled selectively.

Catalytic Hydrogenation. Hydrogenation of 1-octene was attempted with $RuH(BH_4)(ttp)$ as a catalyst. At room temperature under 1 atm of H_2, **4** was inactive as a catalyst. However, on addition of 1 equiv of $HBF_4 \cdot Et_2O$, catalytic hydrogenation commenced immediately at a rate ~0.75 times that of $RhCl(PPh_3)_3$ in THF; the hydrogenation gave only *n*-octane. Similarly, an excess of NEt_3 produced complete hydrogenation of 1-octene to octane at a rate comparable to that of $RhCl(PPh_3)_3$, with no isomerization. When NEt_3 was used as the cocatalyst, an induction period of about 10 min was needed before the maximum rate was obtained; the slow step seems to be the RuHBH bridge cleavage reaction. It may be inferred that $RuH_2(ttp)$ is the active catalyst in the presence of base. In the presence of acid, the catalytic species is probably cationic, e.g., $[RuH(solvent)_x(ttp)]^+$. However, the 18-electron cationic complexes $[RuH(CH_3CN)_2(ttp)]BF_4$ and $[RuH(P(OMe)_3)_2(ttp)]BF_4$ are not effective catalysts, which may reflect the need for ligand dissociation to occur to generate a vacant coordination site before the ruthenium complex can function as a mild hydrogenation catalyst.

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Registry No. 4, 81624-51-3; **5a**, 81616-36-6; **5b**, 81616-38-8; **5c**, 81616-40-2; **5d**, 81654-86-6; **5e**, 81654-88-8; **6e**, 81624-52-4; **6b**, 81616-41-3; **6c**, 81616-42-4; **6d**, 81616-43-5; $[RuCl_2(ttp)]_x$, 81616-72-0.

(25) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(26) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.