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Synthesis and Reactivity of Ruthenium Hydride Complexes of Chelating Triphosphines. 3. Synthesis and Characterization of New Ruthenium Hydride Complexes Containing $C_6H_5P(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$ (Cyttp)[1]

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The hydride complex $RuH(BH_4)$(Cyttp) was produced from the reaction of $RuCl_2$(Cyttp) with excess $NaBH_4$. A series of six-coordinate RuHCl(L)(Cyttp) complexes (L = CO, $P(OMe)_3$, CH_3CN) were synthesized from RuHCl(Cyttp), which was prepared from the reaction of $RuCl_2$(Cyttp) and excess lithium hydride in THF. Ruthenium dihydride complexes RuH_2(L)(Cyttp) (L = CO, N_2, $CNCH_2C_6H_5$, $P(OMe)_3$, and $P(OPh)_3$) were synthesized from $RuH_2(H_2)$(Cyttp), which was prepared from the reaction of $RuCl_2$(Cyttp) with NaH in THF under a H_2 atmosphere. The new compounds were characterized by microanalyses and infrared and ^1H and ^{31}P NMR spectroscopy. In addition, the single-crystal X-ray structure of *cis-mer*-$RuH_2(N_2)$(Cyttp) has been determined. $RuH_2(N_2)$(Cyttp) crystallizes in space group *Pnma* with cell parameters $a = 16.383$ (4) Å, $b = 20.659$ (4) Å, $c = 10.907$ (3) Å, $V = 3692$ Å^3, $Z = 4$, $R(F) = 0.040$, and $R_w(F) = 0.043$ for the 2442 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 211 variables.

Introduction

Ruthenium hydride tertiary phosphine complexes have been studied extensively because of their catalytic, chemical, and structural properties. They are active catalysts for a variety of processes such as hydrogenation,[2] hydrosilylation,[3] isomerization,[4] and polymerization[5] of olefins; hydrogenation[6] of aldehydes, ketones, and esters; hydrogenation of acetylenes[7] and polyaromatic hydrocarbons;[8] hydrogen transfer reactions;[9] formation of formic acid and formate esters from CO_2;[10] and carbon-carbon bond formation.[11]

A large number of ruthenium hydride complexes containing monophosphines and diphosphines are known.[12] However, little has been reported on ruthenium hydride complexes containing polyphosphine ligands,[13] although the advantages of chelating polydentate ligands have been discussed.[14] In order to make comparisons between the structural, chemical, and catalytic properties of transition-metal hydride complexes of monophosphines and those containing chelating triphosphines, we have recently synthesized several ruthenium hydride complexes containing Cyttp (Cyttp = $C_6H_5P(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$). The series of complexes includes RuHCl(Cyttp), an analogue to $RuHCl(PPh_3)_3$, the most active catalyst for hydrogenation of terminal olefins, and the molecular dihydrogen complex $RuH_2(H_2)$(Cyttp).

In a preliminary report, we briefly discussed the characterization of $RuH_2(H_2)$(Cyttp).[15] Herein, we report the detailed synthesis and characterization of these new compounds; the reactivity toward CO_2-like molecules, acetylenes, and olefins will be reported soon.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Air-sensitive solids were handled and transferred in a Vacuum Atmosphere HE43 inert-atmosphere box equipped with a Mo-40 catalyst system. Minute traces of oxygen and water were removed from commercially available argon by passing the gas through two columns packed with hot (180 °C) BASF active copper catalyst and Drierite, respectively.

Reagent-grade chemicals were used as purchased from Aldrich Chemical Co. Inc. unless stated otherwise. Sodium tetrahydroborate was obtained from Fisher Scientific Co. Ruthenium trichloride hydrate was loaned by Johnson Matthey Inc. $RuCl_2(PPh_3)_3$[16] was prepared as described in the literature. Cyttp[17] and $RuCl_2$(Cyttp)[13c] were prepared by modified literature methods.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1}, as pressed potassium bromide pellets, Nujol mulls, or in solution. Spectra were calibrated against the sharp 1601-cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz), phosphorus-31 (101.25 MHz), and carbon-13 (62.9 MHz) NMR spectra in 5-mm tubes.

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Table I. Spectral Characterization Data for the Ru(Cyttp) Hydride Complexes[a]

	^{31}P NMR[b]						
complex	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	$J_{P_1-P_2}$	$J_{P_1-P_3}$	$J_{P_2-P_3}$	^{1}H NMR features[c]
RuH(η^2-BH_4)(Cyttp) (**1**)	41.6	31.9		36.7			−17.18 (dt, 39.7, 21.3), −9.17 (br), −6.76 (br)[d]
RuHCl(Cyttp) (**2**)	57.9	25.9		36.8			−26.85 (dt, 49.7 19.0)[e]
$RuH_2(H_2)$(Cyttp) (**3**)	28.0	51.8		30.7			−8.2 (br, $\omega_{1/2}$ = 40 Hz)[d,f]
RuHCl(CO)(Cyttp) (**4**)	33.1	25.3		33.5			−5.76 (dt, 32.9, 22.2)
RuHCl(MeCN)(Cyttp) (**5**)	30.7	23.2		39.3			−16.38 (dt, 29.5, 20.5)
RuHCl(P(OMe)$_3$)(Cyttp) (**6A**)	43.7	17.2	133.9	39.7	27.3	20.7	−6.11 (dq, 186.0, 31.3)
RuHCl(P(OMe)$_3$)(Cyttp) (**6B**)	6.6	17.6	148.5	48.7	403.1	48.7	−18.76 (m, 28.6, 17.3, 14.0)
$RuH_2(N_2)$(Cyttp) (**7**)	14.1	45.2		29.4			−14.60 (qd, 22.5, 5.2), −8.04 (dtd, 77.1, 23.9, 5.2)
RuH_2(CO)(Cyttp) (**8**)	18.6	48.1		29.1			−9.37 (dtd, 71.3, 23.9, 4.0), −9.13 (qd, 24.9, 4.0)[e]
$RuH_2(CNCH_2Ph)$(Cyttp) (**9**)	19.7	50.1		30.9			−10.01 (qd, 24.1, 4.0), −8.86 (dtd, 67.0, 23.6, 4.0)
RuH_2(P(OPh)$_3$)(Cyttp) (**10A**)	12.1	43.5	127.7	29.7	27.4	28.2	−10.1 (m)
RuH_2(P(OPh)$_3$)(Cyttp) (**10B**)	15.9	35.9	119.0	33.9	22.0	28.3	−7.8 (m)
$RuH_2(P(OPh)_2OC_6H_4)$)(Cyttp)	12.6	22.1	159.1	39.5	22.7	22.7	−5.37 (dtd, 175.9, 23.6, 13.0)
RuH_2(P(OMe)$_3$)(Cyttp) (**11A**)	13.4	47.2	159.5	31.3	23.9	28.4	−10.5 (m)
RuH_2(P(OMe)$_3$)(Cyttp) (**11B**)	18.7	38.8	153.0	34.1	18.6	29.4	−8.3 (m)

[a] Solvents are C_6D_6 unless stated otherwise. [b] Chemical shifts are in δ with respect to external 85% H_3PO_4 (δ 0.0); positive values are downfield; coupling constants are in Hz. P_1 is the central phosphorus, and P_2 represents the two terminal phosphorus atoms in Cyttp with P_3 the corresponding phosphite in the complex. [c] Chemical shifts are in δ with respect to Me_4Si (δ 0.0); br = broad; d = doublet; m = multiplet; q = quartet; t = triplet; numbers in parentheses are coupling constants in Hz. [d] In toluene-d_8. [e] In CD_2Cl_2. [f] At room temperature; for other temperatures, see ref 15.

Residual solvent proton or carbon-13 resonances were used as internal standards for the ^{1}H or ^{13}C NMR spectra. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. $^{31}P\{^1H\}$ and selected ^{1}H NMR data for the new hydride complexes are collected in Table I. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

$RuCl_2$(Cyttp). A mixture of 3.61 g of Cyttp (6.08 mmol) and 5.50 g of $RuCl_2(PPh_3)_3$ (5.73 mmol) in ca. 40 mL of acetone was stirred at room temperature for 30 min to give a bright green solid. The solid was then collected on a filter frit, washed with acetone, and dried under vacuum overnight. Yield: 3.55 g, 81.6%.

RuH(η^2-BH_4)(Cyttp). A mixture of 0.60 g of $RuCl_2$(Cyttp) (0.79 mmol) and 0.3 g of $NaBH_4$ (9 mmol) in 10 mL of benzene and 30 mL of ethanol was refluxed for 45 min to give a bright yellow solid. After the reaction mixture was cooled to room temperature, the solid was collected on a filter frit; washed with ethanol, water, and ethanol; and dried under vacuum overnight. Yield: 0.50 g, 90%. Anal. Calcd for $C_{36}H_{66}BP_3Ru$: C, 61.14; H, 9.45. Found: C, 60.97; H, 9.39.

RuHCl(Cyttp). Method 1. A mixture of 1.00 g of $RuCl_2$(Cyttp) (1.32 mmol) and 0.40 g of LiH (10 mmol) in 40 mL of THF was stirred overnight at ca. 35 °C overnight to give a red solution. The solvent was then removed completely and ca. 40 mL of benzene was used to extract the soluble compounds. The volume of the extract was then reduced to ca. 2 mL, and 10 mL of MeOH was added to give a red powder. The powder was collected on a filter frit, washed with MeOH, and dried under vacuum. Yield: 0.75 g, 79%. Anal. Calcd for $C_{36}H_{62}ClP_3Ru$: C, 59.69; H, 8.63, Cl, 4.89. Found: C, 59.85; H, 8.50; Cl, 4.71.

Method 2. A mixture of 0.500 g of $RuCl_2$(Cyttp) (0.659 mmol) and 0.164 g of TlO_2CH (0.659 mmol) in 10 mL of MeOH and 30 mL of CH_2Cl_2 was stirred at room temperature for 30 min to give a deep red solution and a white precipitate (TlCl). The precipitate was removed by filtration through a filter frit containing ca. 4 cm of Celite. The solvent of the filtrate was then removed completely under vacuum. The red residue was washed with MeOH, collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.35 g, 73%.

RuH_4(Cyttp). A mixture of 0.30 g of $RuCl_2$(Cyttp) (0.40 mmol) and 0.20 g of NaH (8.3 mmol) in 30 mL of THF was stirred overnight at ca. 40–50 °C under H_2 atmosphere to give a light yellow solution. The solvent was then removed completely, and the residue was extracted with ca. 40 mL of benzene, which was removed subsequently to give a light yellow solid. The reactivity of the compound was studied by adding appropriate amounts of other reagents to the extract.

RuHCl(CO)(Cyttp). Method 1. Carbon monoxide gas was passed over a stirred solution of 0.20 g of RuHCl(Cyttp) in 30 mL of benzene for 10 min to give a colorless solution. The solvent was then removed completely under vacuum, and 6 mL of hexane was added to give a white powder. The powder was collected on a filter frit, washed with small amounts of hexane, and dried under vacuum overnight. Yield: 0.14 g, 67%. Anal. Calcd for $C_{37}H_{62}ClOP_3Ru$: C, 59.07; H, 8.31; Cl, 4.71. Found: C, 58.83; H, 8.49; Cl, 4.60.

Method 2. Carbon monoxide gas was passed slowly through a frit that contains solid RuHCl(Cyttp) overnight during which the color of the solid changed from red to white. The spectroscopic data of the white solid are identical with those of RuHCl(CO)(Cyttp), prepared as in method 1.

RuHCl(P(OMe)$_3$)(Cyttp). Isomer A. Trimethyl phosphite (0.10 mL, 0.85 mmol) was added to a solution of 0.10 g of RuHCl(Cyttp) (0.14 mmol) in 10 mL of benzene. Soon after the reagents were mixed, the liquids of the reaction mixture were removed completely under vacuum and then 3 mL of MeOH was added. After the reaction mixture was stirred for several hours, a light pink solid formed. The solid was collected on a filter frit, washed with a small amount of MeOH, and dried under vacuum overnight. Yield: 0.07 g, 60%. Anal. Calcd for $C_{39}H_{71}ClO_3P_4Ru$: C, 55.21; H, 8.44; Cl, 4.18. Found: C, 55.32; H, 8.35; Cl, 4.14.

RuHCl(P(OMe)$_3$)(Cyttp). Isomer B. Trimethyl phosphite (0.10 mL, 0.85 mmol) was added to a solution of 0.10 g of RuHCl(Cyttp) (0.14 mmol) in 20 mL of benzene. The mixture was stirred for 10 min to give a colorless solution. The liquids were then removed completely under vacuum, and 5 mL of MeOH was added. The mixture was stirred for 30 min to give a white powder, which was collected on a filter frit, washed with a small amount of MeOH, and dried under vacuum overnight. Yield: 0.08 g, 70%. Anal. Calcd for $C_{39}H_{71}ClO_3P_4Ru$: C, 55.21; H, 8.44; Cl, 4.18. Found: C, 55.27; H, 8.42; Cl, 4.15.

RuH_2(CO)(Cyttp). Carbon monoxide gas was passed over a stirred solution of RuH_4(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) in 30 mL of benzene for 10 min to give a colorless solution. The solvent was then removed completely under vacuum, and addition of 8 mL of hexane gave a white powder. The powder was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.16 g, 85%. Anal. Calcd for $C_{37}H_{63}OP_3Ru$: C, 61.90; H, 8.85. Found: C, 62.13; H, 8.81.

$RuH_2(N_2)$(Cyttp). Method 1. Dinitrogen gas was bubbled into 30 mL of a benzene solution of RuH_4(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) for 3 h. The volume of the solvent was reduced to ca. 5 mL, and then 10 mL of hexane was added to cause precipitation of a white powder. The powder was collected on a filter frit, washed with hexane, and dried under vacuum overnight.

Method 2. Dinitrogen gas was passed over a solution of RuH_4(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) in 15 mL of benzene for several days until the volume of the solution was reduced to ca. 1.5 mL to give pale yellow crystals. The crystals were

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washed with benzene, and dried under vacuum overnight. Some of these crystals were suitable for X-ray study. Yield: 0.15 g, 74%. Anal. Calcd for $C_{36}H_{63}N_2P_3Ru$: C, 60.23; H, 8.85; N, 3.90. Found: C, 60.44; H, 8.82; N, 3.87.

$RuH_2(CNCH_2Ph)(Cyttp)$. Benzyl isocyanide (0.05 mL, 0.4 mmol) was added to a solution of $RuH_4(Cyttp)$ (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2(Cyttp)$ with excess NaH) in 30 mL of benzene; a colorless solution resulted. The solvent of the reaction mixture was then removed completely under vacuum, and 15 mL of hexane was added to the reaction flask. The hexane solution was then transferred to a Schlenk tube, and argon was passed over the solution until the volume of the solution was decreased to ca. 0.5 mL. (The compound is very soluble in common organic solvents and is reactive with MeOH.) During this period, colorless needlelike crystals were formed. The crystals were collected on a filter frit, washed with a small amount of hexane, and dried under vacuum overnight. Yield: 0.12 g, 56%. Anal. Calcd for $C_{44}H_{70}NP_3Ru$: C, 65.48; H, 8.74; N, 1.74. Found: C, 65.33; H, 8.60; N, 1.70.

$RuH_2(P(OMe)_3)(Cyttp)$. Trimethyl phosphite (0.11 g, 0.85 mmol) was added to a solution of $RuH_4(Cyttp)$ (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2(Cyttp)$ with excess NaH) in 30 mL of benzene. After the mixture was stirred for 5 min, the solvent was removed completely under vacuum; then 7 mL of MeOH was added to the reaction flask and the mixture stirred for 15 min. The resultant white powder was collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.18 g, 84%. Anal. Calcd for $C_{39}H_{72}O_3P_4Ru$: C, 57.55; H, 8.92. Found: C, 57.33; H, 8.74.

$RuH_2(P(OPh)_3)(Cyttp)$. Triphenyl phosphite (0.24 g, 0.76 mmol) was added to a solution of $RuH_4(Cyttp)$ (ca. 0.40 mmol, prepared from 0.3 g of $RuCl_2(Cyttp)$ with excess NaH) in 30 mL of benzene. After the reaction mixture was stirred for 5 min, the solvent was removed completely under vacuum, 10 mL of acetone was added to the reaction flask, and the mixture was stirred for 30 min. The resultant white powder was collected by filtration, washed with acetone, and dried under vacuum overnight. Yield, 0.35 g, 89%. Anal. Calcd for $C_{54}H_{78}O_3P_4Ru$: C, 64.85; H, 7.86. Found: C, 64.68; H, 7.73.

$RuH(P(OPh)_2OC_6H_4)(Cyttp)$. A 0.10-g sample of $RuH_2(P(OPh)_3)(Cyttp)$ in 30 mL of toluene was refluxed overnight to give a light yellow solution. The solvent was removed completely, and 6 mL of acetone was added to the flask. After the mixture was stirred for 1 h, the resultant gray-white solid was collected on a filter frit, washed with small amount of acetone, and dried under vacuum overnight. Yield: 0.06 g, 60%.

Crystallographic Analysis of $RuH_2(N_2)(Cyttp)$. The crystal used for data collection was a pale yellow rhombuslike plate, which had been coated with a thin layer of epoxy as a precaution against possible air sensitivity. The crystal system is orthorhombic with the following systematic absences: $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$. The space group possibilities are restricted to *Pnma* or $Pn2_1a$ (nonstandard setting for $Pna2_1$). The cell constants were determined at room temperature by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 26–29° and with Mo Kα radiation (λ(Kα) = 0.71073 Å).

Intensities were measured by the ω–2θ scan method. Six standard reflections were measured after every 150 reflections during data collection and indicated that the crystal was stable. Data reduction and all subsequent calculations were done with the TEXSAN package of crystallographic programs.[18]

The structure was solved and refined in *Pnma*. With $Z = 4$, the molecule is required to contain a crystallographic mirror plane. The position of the ruthenium atom was located by Patterson methods. By phasing on the ruthenium atom in the DIRDIF procedure,[19] we located the remainder of the unique atoms in the asymmetric unit on an electron density map. Full-matrix least-squares isotropic refinement of this model converged at a R value of 0.072 for those reflections with $F_o^2 > 3\sigma(F_o^2)$. After a cycle of anisotropic refinement, all of the hydrogen atoms, including the two hydrogen atoms bonded to ruthenium, were located on a difference electron density map. The hydrogen atoms bonded to carbon atoms were included in the model as fixed contributions in their calculated positions with C–H = 0.98 Å and $B_H = 1.2B_{C(eq)}$. Initially, the two hydrogen atoms bonded to ruthenium were fixed at their positions from the difference map, but in the final stages of refinement, they were refined isotropically. The final refinement cycle yielded agreement indices of $R(F) = 0.040$ and $R_w(F) = 0.043$ for the 2441 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 211 variables. Four reflections were removed from the data set because of uneven backgrounds: (260), (280), (1,20,1), and (5,20,1). The maximum and minimum peaks in the final difference electron density map are 0.48 and –0.50 e/Å^3. Scattering factors for neutral atoms, including terms for anomalous scattering, are from the usual sources.[20] All full-matrix least-squares refinements were based on

Table II. Crystallographic Details for $RuH_2(N_2)(Cyttp)$

$C_{36}H_{63}N_2P_3Ru$	fw = 717.90
a = 16.383 (4) Å	space group: *Pnma*
b = 20.659 (4) Å	T = 22 °C
c = 10.907 (3) Å	λ = 0.71073 Å (Mo Kα)
V = 3692 Å^3	ρ_{calcd} = 1.29 g cm^{-3}
Z = 4	μ = 5.69 cm^{-1}
$R(F)^a$ = 0.040	$R_w(F)^b$ = 0.043

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Table III. Final Positional Parameters for $RuH_2(N_2)(Cyttp)^a$

atom	x	y	z	B(eq), Å^2
Ru	0.085739 (33)	1/4	0.940848 (45)	2.03 (2)
P(1)	0.071763 (69)	0.360811 (54)	0.963582 (94)	2.24 (5)
P(2)	0.05569 (10)	1/4	0.73367 (15)	2.32 (7)
N(1)	0.20721 (38)	1/4	0.96337 (56)	3.2 (3)
N(2)	0.27256 (45)	1/4	0.98361 (75)	5.7 (4)
C(1)	0.01503 (31)	0.40596 (23)	0.84430 (41)	3.0 (2)
C(2)	0.02543 (29)	0.38434 (23)	0.71016 (40)	2.8 (2)
C(3)	–0.00929 (28)	0.31750 (24)	0.68394 (38)	2.8 (2)
C(4)	0.01512 (29)	0.38815 (22)	1.10262 (38)	2.4 (2)
C(5)	–0.07040 (30)	0.35838 (24)	1.10999 (43)	3.3 (2)
C(6)	–0.11599 (33)	0.38134 (27)	1.22475 (51)	4.2 (3)
C(7)	–0.06881 (41)	0.36539 (29)	1.33985 (48)	4.9 (3)
C(8)	0.01550 (38)	0.39560 (28)	1.33488 (44)	4.2 (3)
C(9)	0.06154 (30)	0.37296 (23)	1.21998 (39)	3.0 (2)
C(10)	0.16913 (27)	0.40760 (22)	0.97578 (39)	2.6 (2)
C(11)	0.16400 (31)	0.47744 (23)	1.02258 (44)	3.3 (2)
C(12)	0.24886 (37)	0.50725 (27)	1.03515 (53)	4.5 (3)
C(13)	0.29856 (35)	0.50295 (33)	0.91598 (56)	5.2 (3)
C(14)	0.30054 (32)	0.43480 (32)	0.86662 (48)	4.3 (3)
C(15)	0.21567 (31)	0.40658 (24)	0.85278 (44)	3.2 (2)
C(16)	0.13557 (43)	1/4	0.61245 (59)	2.7 (3)
C(17)	0.21611 (46)	1/4	0.64707 (64)	3.4 (3)
C(18)	0.27859 (45)	1/4	0.55998 (80)	4.3 (4)
C(19)	0.25853 (46)	1/4	0.43759 (77)	4.1 (4)
C(20)	0.17862 (49)	1/4	0.40070 (63)	4.0 (4)
C(21)	0.11754 (43)	1/4	0.48795 (64)	3.3 (3)
H(1)	–0.0122 (40)	1/4	0.9409 (60)	5 (2)^b
H(2)	0.0734 (51)	1/4	1.0875 (77)	8 (2)^b

[a] $B(eq) = (8/3)\pi^2\sum_i\sum_j U_{ij}ai^*aj^*\mathbf{ai}\cdot\mathbf{aj}$. [b] Atoms were refined isotropically.

Table IV. Selected Bond Lengths and Angles for $RuH_2(N_2)(Cyttp)^a$

		Bond Lengths (Å)			
Ru–N(1)	2.005 (6)	Ru–P(1)	2.314 (1)	Ru–P(2)	2.313 (2)
Ru–H(1)	1.60 (7)	Ru–H(2)	1.61 (8)	N(1)–N(2)	1.093 (8)
		Bond Angles (deg)			
N(1)–Ru–P(2)	109.3 (2)	N(1)–Ru–P(1)	94.88 (4)		
H(1)–Ru–H(2)	83 (4)	H(1)–Ru–P(2)	78 (2)		
H(1)–Ru–N(1)	173 (2)	H(1)–Ru–P(1)	84.3 (3)		
P(2)–Ru–P(1)	94.80 (3)	P(1)–Ru–P(1)′	163.23 (6)		
H(2)–Ru–N(1)	90 (3)	H(2)–Ru–P(1)	83.2 (3)		
H(2)–Ru–P(2)	160 (3)				

[a] Estimated standard deviations in the least significant figure are given in parentheses. Primed atoms are related to the corresponding unprimed atoms by the crystallographic mirror plane, with the symmetry operation x, $1/2 - y$, z.

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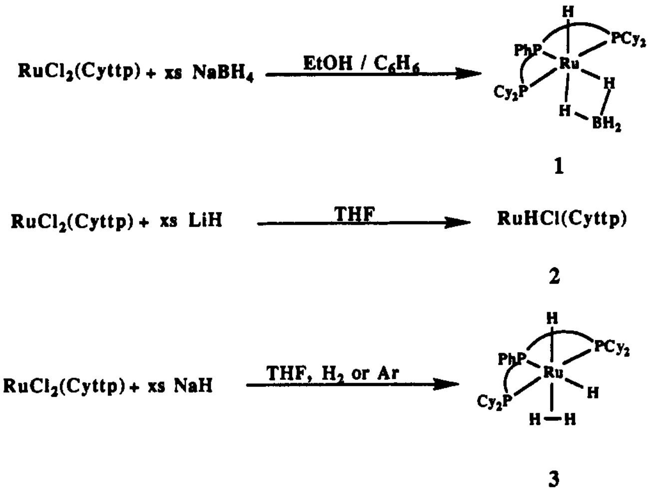
(18) TEXSAN, TEXRAY Structure Analysis Package, Version 2.1. Molecular Structure Corporation, College Station, TX, 1987.

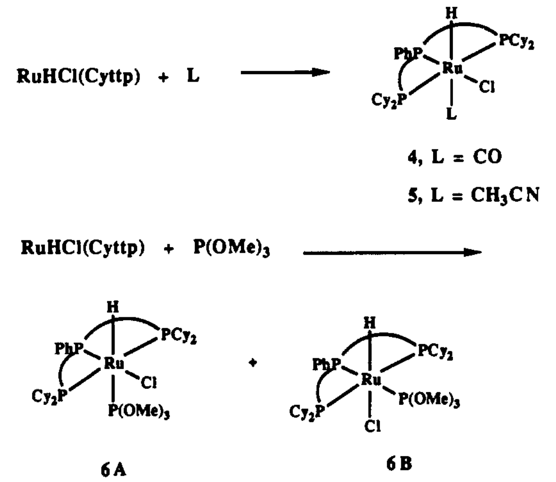
(19) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van der Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Haltiwanger, R. C.; Bruins Slot, H. J. DIRDIF: Direct Methods for Difference Structures—an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands.

(20) Scattering factors for the non-hydrogen atoms and anomalous dispersion terms are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 148. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Scheme I. Synthesis of Ruthenium Hydride Complexes from $RuCl_2$(Cyttp)



Scheme II. Reactions of RuHCl(Cyttp) with Neutral Ligand



F so that the function minimized in least-squares is $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Further crystallographic details are given in Table II. Final atomic coordinates and selected bond lengths and bond angles are presented in Tables III and IV, respectively.

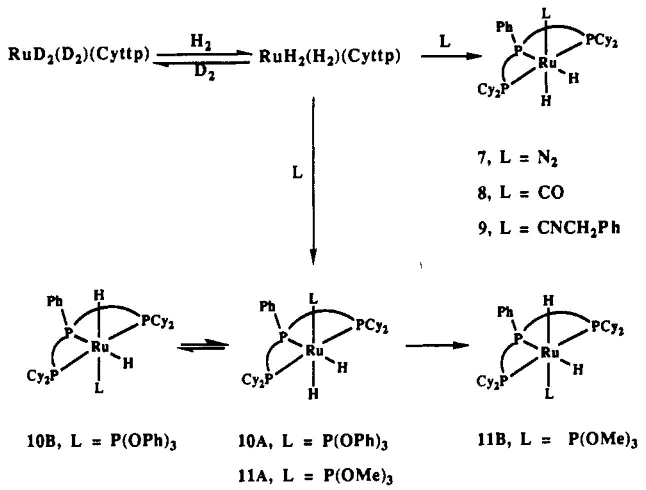
Results

Three different ruthenium hydride complexes $RuH(\eta^2\text{-}BH_4)$(Cyttp) (**1**), RuHCl(Cyttp) (**2**), and $RuH_2(H_2)$(Cyttp) (**3**) were synthesized from $RuCl_2$(Cyttp) by use of different reducing agents as shown in Scheme I. The 16-electron complex RuHCl(Cyttp) is reactive toward small ligands such as CO, CH_3CN, and $P(OMe)_3$ to form 18-electron complexes RuHCl(L)(Cyttp) (**4**, L = CO; **5**, L = CH_3CN; **6**, L = $P(OMe)_3$) as illustrated in Scheme II. As summarized in Scheme III, $RuH_2(H_2)$(Cyttp) reacts reversibly with N_2 to form *cis-mer*-$RuH_2(N_2)$(Cyttp) (**7**), and it reacts instantaneously with neutral ligands L to form *cis-mer*-RuH_2(L)(Cyttp) complexes (**8**, L = CO; **9**, L = $PhCH_2NC$; **10**, L = $P(OPh)_3$; **11**, L = $P(OMe)_3$. An X-ray diffraction study was undertaken for *cis-mer*-$RuH_2(N_2)$(Cyttp), whose results are presented in Figure 1 and Tables II–IV. The structures and properties of the new ruthenium hydride complexes will be discussed below.

Discussion

Ruthenium Hydride Complexes from $RuCl_2$(Cyttp). Reaction of excess $NaBH_4$ and $RuCl_2$(Cyttp) in $EtOH/C_6H_6$ produces $RuH(\eta^2\text{-}BH_4)$(Cyttp) (**1**). Its analogue $RuH(\eta^2\text{-}BH_4)$(ttp)[13a] can also be prepared in the same way. The spectroscopic data for $RuH(\eta^2\text{-}BH_4)$(Cyttp) are very similar to those of $RuH(\eta^2\text{-}BH_4)$(ttp).[13a] In the room-temperature ^1H NMR spectrum the Ru–H resonance was observed at −17.18 ppm as a doublet of

Scheme III. Substitution Reactions of $RuH_2(H_2)$(Cyttp)



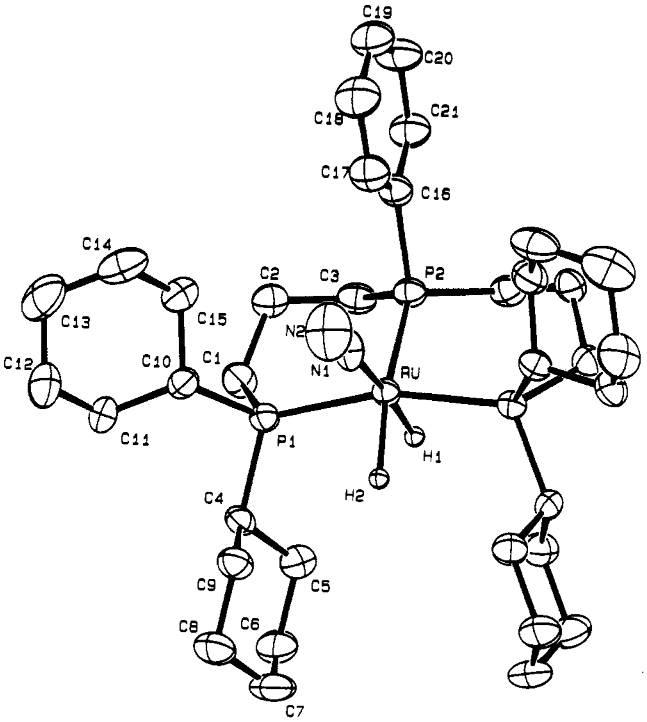


Figure 1. ORTEP drawing of $RuH_2(N_2)$(Cyttp); hydrogen atoms are not shown except for the metal hydrides, H(1) and H(2), which are drawn with an arbitrary radius. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids.

triplets (^2J(PH) = 39.7, 21.3 Hz). The broad signals at −9.2, −6.8, and 4.8 ppm were assignable to the two bridging hydrides and the terminal BH_2, respectively. The structure is also consistent with its infrared spectrum, in which terminal B–H and Ru–H stretching frequencies were observed at 2395 and 2330 cm^{-1} and at 1960 cm^{-1}, respectively. The similar ruthenium complexes $RuH(\eta^2\text{-}BH_4)$(tripod) (tripod = $MeC(CH_2PPh_2)_3$,[13d,e] $RuH(\eta^2\text{-}BH_4)(PR_3)_3$ (PR_3 = PMe_3,[21] PMe_2Ph[22]) have been reported previously. However, in these complexes the ^1H NMR signals for the terminal BH hydrogen are usually too broad to be observed at room temperature.[13e,22] In contrast to the η^2 nature of the BH_4 ligand in the above complexes, the BH_4 group functions as a η^1 ligand in $RuH(BH_4)(PPh_3)_3$.[23]

$RuHCl(PPh_3)_3$ has been prepared by treating $RuCl_2(PPh_3)_3$ with $NaBH_4$ in refluxing aqueous benzene solution[2a] or by

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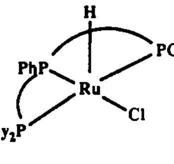
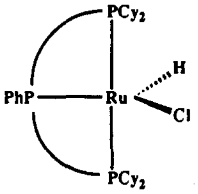
treatment of $RuCl_2(PPh_3)_3$ with H_2 in the presence of NEt_3.[2a,24] However, the analogous compound RuHCl(Cyttp) (**2**) could not be prepared by these methods. When 1 equiv of $NaBH_4$ was used, a mixture of $RuH(BH_4)$(Cyttp) and RuHCl(Cyttp) in low yield and mostly unreduced ruthenium chloride complex usually resulted. Treatment of $RuCl_2$(Cyttp) with H_2 in the presence of NEt_3 gives intractable products. Thus, two alternate methods were developed for the preparation of RuHCl(Cyttp). The first method involved treating $RuCl_2$(Cyttp) with 1 equiv of thallium formate in either of the mixed solvents CH_2Cl_2/MeOH or C_6H_6/MeOH. The thallium formate reaction probably involves a formate intermediate such as $RuCl(O_2CH)$(Cyttp), which extrudes CO_2 to give the hydride complex. Although the intermediate was not detected in this study, the general instability of formate complexes to give metal hydrides is well documented.[25] The isolated product RuHCl(Cyttp) is usually contaminated with trace amounts of RuH_2(CO)(Cyttp). By the second method, RuHCl(Cyttp) was isolated in good yield by treating $RuCl_2$(Cyttp) with excess LiH in THF. It was noted that an unknown ruthenium compound, probably another isomer of RuHCl(Cyttp), was also produced in a small amount by the LiH reaction in at least two experiments although we were unable to consistently reproduce this observation.

RuHCl(Cyttp) is an air-sensitive red solid. The Ru–H stretching frequency was observed at 2020 cm^{-1}. The ^{13}C resonances for the cyclohexyl carbon atoms attached to the terminal phosphorus atoms appeared as virtual triplets at 37.2 ppm (t, $J(PC)$ = 11.6 Hz) and 33.1 ppm (t, $J(PC)$ = 8.0 Hz); thus, the triphosphate must be meridional around ruthenium so that the terminal phosphorus atoms are trans to each other.[26] The hydride resonance was observed at −26.85 ppm in the ^1H NMR spectrum. The $^2J(PH)$ coupling constant between the hydride and the terminal phosphorus nuclei is 19.0 Hz, while that between the hydride and the central phosphorus atom is 49.7 Hz. The ^{31}P NMR spectrum showed a doublet at 25.9 ppm for the terminal phosphorus atoms and a triplet at 57.9 ppm for the central phosphorus atom. The ^{31}P NMR pattern implies that a weak trans influence ligand (e.g., chloride) is trans to the central phosphorus atom of the triphosphine.[27] Thus, the most likely structure of the compound is square-pyramidal **2A** or trigonal-bipyramidal **2B**; **2A** is preferred, on the basis of the ^{31}P NMR spectral pattern and some of the chemical reactions described above.

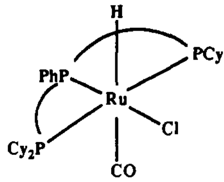


2A

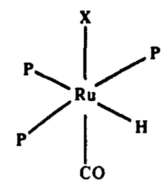


2B

Reactions of RuHCl(Cyttp). As expected, the 16-electron complex RuHCl(Cyttp) is reactive toward small ligands to form 18-electron complexes RuHCl(L)(Cyttp). Carbon monoxide reacted with RuHCl(Cyttp) either in the solid state or in solution to form RuHCl(CO)(Cyttp) (**4**). On the basis of the spectroscopic data, its geometry should be represented as **4A**. The hydride resonance appeared at −5.76 ppm as a doublet of triplets ($^2J(PH)$ = 32.9, 22.2 Hz). The similar magnitude observed for the coupling between phosphorus and the hydride is consistent with the hydride being cis to all three phosphorus atoms of the triphosphate ligand.[12] The downfield resonance for the hydride implies that this hydride is trans to a strong trans influence ligand (e.g., CO rather than chloride). Thus, the CO ligand is also cis to the three phosphorus atoms of the ligand. This structure was confirmed by the ^{13}C NMR spectrum, in which the CO resonance appeared at 207.1 ppm as a quartet ($^2J(PC)$ = 7.2 Hz). The coupling constant magnitude is typical for cis phosphorus–^{13}CO coupling in ruthenium carbonyl complexes (typical range = 6–13 Hz). Trans phosphorus–^{13}CO coupling constants are generally larger than 70 Hz in ruthenium carbonyl complexes.[28] A triplet at 33.1 ppm ($^2J(PP)$ = 33.5 Hz) and a doublet at 25.3 ppm were observed for the central and terminal phosphorus atoms, respectively, in the ^{31}P NMR spectrum of RuHCl(CO)(Cyttp); this pattern is consistent with a weak trans-influence ligand (e.g., chloride) located trans to the central phosphorus atom.[27] The CO stretching frequency is at 1955 cm^{-1}; the Ru–H vibration was not observed. The geometry of this complex is unusual; to our knowledge, all of the monophosphine complexes of the formula $RuHX(CO)(PR_3)_3$ (X = halide; PR_3 = phosphines or phosphites) possess geometry **4B**.[29] The geometry of RuHCl(CO)(Cyttp) might suggest that the precursor RuHCl(Cyttp) has a square-pyramidal structure (i.e., **2A**), in which the hydride is cis to the three phosphorus atoms of the triphosphine.



4A



4B

Acetonitrile also reacted with RuHCl(Cyttp) to form $RuHCl(CH_3CN)$(Cyttp) (**5**). The acetonitrile ligand is weakly bonded to the ruthenium, and it can be removed by pumping at 0.1 Torr. Since the ^{31}P NMR parameters and the $^2J(PH)$ coupling constants of this compound are similar to those for RuHCl(CO)(Cyttp) (Table I), it is likely that the acetonitrile complex has the same geometry as RuHCl(CO)(Cyttp), i.e., like **4A**.

Two isomers of formula $RuHCl(P(OMe)_3)$(Cyttp) (**6**) were isolated when RuHCl(Cyttp) was treated with $P(OMe)_3$ under different reaction conditions. If the reaction time is very short, isomer **6A** is isolated; if the reaction time is longer, isomer **6B** is isolated. After the two isomers were isolated, no subsequent isomerization was observed in benzene or dichloromethane solution.

In isomer **6A**, $P(OMe)_3$ is trans to the hydride and cis to the three phosphorus atoms of the triphosphine ligand, which is similar to the structure of RuHCl(CO)(Cyttp). In its ^{31}P NMR spectrum the $P(OMe)_3$ resonance appeared at 133.9 ppm (dt, $^2J(PP)$ = 27.3, 20.7 Hz); these small phosphorus–phosphorus coupling constants suggest that $P(OMe)_3$ is cis to the three phosphorus atoms of the triphosphine ligand.[30] The signals for the central and terminal phosphorus atoms were observed at 43.7 ppm (td, $^2J(PP)$ = 39.7, 27.3 Hz) and 17.2 ppm (dd, $^2J(PP)$ = 39.7, 20.7 Hz), which indicate that the central phosphorus atom is trans to a weak trans influence ligand, namely chloride.[27] Thus, the hydride is trans to $P(OMe)_3$; this structural assignment is consistent with the ^1H NMR spectrum (hydride resonance occurred at −6.11 ppm (dq, $^2J(PH)$ = 186.0, 20.1 Hz)).

In isomer **6B**, $P(OMe)_3$ is trans to the central phosphorus atom as indicated clearly by its ^{31}P NMR spectrum in which the coupling constant between $P(OMe)_3$ and the central phosphorus is 403.1 Hz. It is interesting to note that the chemical shifts for the $-PCy_2$ groups are almost identical in both isomer **6A** (17.2 ppm) and isomer **6B** (17.6 ppm), whereas the $P(OMe)_3$ resonance shifted 14.6 ppm downfield and the –PPh resonance shifted 37.1

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ppm upfield in isomer **6B** compared with isomer **6A**, owing to a change in the trans ligands. In the proton NMR spectrum of **6B**, the Ru–H resonance was observed at −18.76 ppm as a complicated multiplet, owing to coupling of the Ru–H with four cis phosphorus atoms. Triphenylphosphine failed to react with RuHCl(Cyttp), presumably owing to its large cone angle.[31]

$RuH_2(H_2)$(Cyttp) and Its Reactions. $RuH_4(PR_3)_3$ has aroused great interest in terms of its chemical, catalytic, and structural properties. Owing to the easy formation of $RuH(BH_4)$(Cyttp), the hydride complex RuH_4(Cyttp) (**3**) could not be prepared from the reaction of $RuCl_2$(Cyttp) with $NaBH_4$. Treatment of $RuCl_2$(Cyttp) with other "Super-Hydrides" (Aldrich) such as $LiBHEt_3$, and $KBH(O(i\text{-}Pr))_3$ gives mixtures of RuH_4(Cyttp) and uncharacterized compounds. It was found that the most efficient method to synthesize RuH_4(Cyttp) is to treat $RuCl_2$(Cyttp) with excess NaH. Excess NaH is necessary, since the reaction rate is slow and the intermediate RuHCl(Cyttp) seems resistant to conversion into RuH_4(Cyttp) when smaller ratios of NaH are used. Interestingly, under similar conditions, treatment of $RuCl_2$(Cyttp) with LiH produces only RuHCl(Cyttp). The different products may be related to the different solubilities of LiCl and NaCl in THF. The reaction is best done under a hydrogen atmosphere; however, RuH_4(Cyttp) is formed even under an argon atmosphere. Under argon, the product formed is less pure than that formed under a hydrogen atmosphere, and it is usually contaminated by a small amount of RuH_2(CO)(Cyttp). Under argon, the source of the $Ru(H_2)$ hydrogen atoms has not been determined; they could come from either the NaH or THF. THF has been reported as a hydrogen donor in ruthenium-catalyzed hydrogen transfer reactions.[9a,b]

Isolated RuH_4(Cyttp) is a light yellow solid. The purity is dependent on the $RuCl_2$(Cyttp) sample used. It is very air-sensitive, turning dark immediately if exposed to air. It is very soluble in aromatic solvents and fairly soluble in THF, hexane and ether; it reacts with dichloromethane and methanol to form RuHCl(Cyttp) and RuH_2(CO)(Cyttp), respectively.

We have formulated the compound RuH_4(Cyttp) as the ruthenium η^2-dihydrogen complex *cis-mer*-$RuH_2(H_2)$(Cyttp) based on its spectroscopic properties, especially T_1 values, and other experiments.[15] The chemical properties are also consistent with this formulation. Since the η^2-H_2 ligand is usually weakly bound to a metal center, it is expected that the η^2-H_2 ligand in RuH_4(Cyttp) could be easily replaced by other simple ligands. In fact $RuH_2(H_2)$(Cyttp) behaves chemically as if it was RuH_2(Cyttp).

In addition to exchange with D_2 gas as reported previously,[15] RuH_4(Cyttp) reacts instantaneously with CO, $PhCH_2NC$, $P(OMe)_3$, and $P(OPh)_3$ to form *cis-mer*-RuH_2(L)(Cyttp) complexes. It also reacts with N_2 reversibly to form *cis-mer*-$RuH_2(N_2)$(Cyttp).

The isolated complex $RuH_2(N_2)$(Cyttp) (**7**) is obtained as an air-sensitive, white powder or as pale yellow crystals, which turn black when exposed to air for prolonged period. It is only sparingly soluble in benzene or toluene. It is fairly stable under vacuum, and it reacts with hydrogen gas in solution to form RuH_4(Cyttp).

In its infrared spectrum, the $\nu(N\equiv N)$ stretching frequency is observed at 2100 cm^{-1} and the ν(Ru–H) stretching frequencies at 1920 and 1960 cm^{-1}. The $\nu(N\equiv N)$ frequency is slightly lower than that in other ruthenium phosphine dinitrogen complexes, e.g., 2163 cm^{-1} in $[RuH(N_2)(depe)_2]BPh_4$,[32] 2147 cm^{-1} in $RuH_2(N_2)(PPh_3)_3$,[33] and 2130 cm^{-1} in $RuH_2(N_2)(P(p\text{-tolyl})_3)_3$.[33] This shift could be attributed to the fact that the triphosphine is more basic than the phosphines in the three examples above; thus one could expect more effective back-donation of electron density to the antibonding orbitals of the dinitrogen ligand. On the basis of correlations between spectrosopic and chemical properties of complexes, Morris et al. proposed that when the $N\equiv N$ triple-bond stretching frequency is in the 2060–2150-cm^{-1} range in a d^6 metal complex, the corresponding dihydrogen complex should be stable, with respect to homolytic cleavage or irreversible loss of H_2 at 25 °C.[34] The $\nu(N\equiv N)$ stretching frequency of 2100 cm^{-1} for $RuH_2(N_2)$(Cyttp) thus suggests that the dihydrogen complex $RuH_2(H_2)$(Cyttp) is stable. Our data here are consistent with this proposal. The hydride cis to the three phosphorus atoms has a ^1H resonance at −14.60 ppm (qd, $^2J(PH) = 22.5$ Hz, $^2J(HH) = 5$ Hz) and the one trans to the central phosphorus at −8.04 ppm (dtd, $^2J(PH) = 77.1, 23.9$ Hz; $J(HH) = 5$ Hz). The spectral data of this compound in solution agree with the results of the X-ray diffraction study.

The ORTEP drawing of $RuH_2(N_2)$(Cyttp) is shown in Figure 1. The geometry of the coordination sphere of the compound is roughly octahedral. The triphosphine ligand is meridional around ruthenium. The hydrides are cis to each other and the dinitrogen ligand is bound "end-on" to ruthenium. There is a crystallographic mirror plane that contains the following atoms: ruthenium, the two hydrides H(1) and H(2), N(1), N(2), P(2), and the phenyl ring. The phenyl group on the central phosphorus atom is oriented toward the dinitrogen molecule. Due to the reduced steric requirement of the hydride ligand, the phosphines are bent toward the H(1). The ruthenium atom is displaced 0.25 Å from the least-squares plane H(2), P(1), P(2), and P(1)′ atoms, and this displacement is in the direction toward the N(1) atom. It is difficult to say if this displacement is the result or the cause of the phosphines being bent toward H(1). The phosphines are also bent toward H(2), since the P(1)–Ru–H(2) angle is 83.2 (3)°. The angle N(1)–Ru–P(2) (109.3 (2)°) is larger than that for N(1)–Ru–P(1) (94.88 (4)°), which is probably due to the steric interactions between the dinitrogen ligand and the phenyl group on the central phosphorus atom of the triphosphine ligand. The distances between Ru and P(1) and P(2) are comparable at 2.314 (1) and 2.314 (2) Å. These comparable Ru–P distances contrast with those of the other meridional ruthenium complexes such as $Ru(CCPh)(\eta^3\text{-}PhC_3CHPh)$(Cyttp),[1] $RuH(O_2CH)(PPh_3)_3$,[35] $RuH(O_2CMe)(PPh_3)_3$,[36] $RuHCl(PPh_3)_3$,[37] and $RuCl_2(PPh_3)_3$,[38] in which the mutually trans Ru–P bonds are longer than the unique Ru–P bond. For example, in $Ru(C\equiv CPh)(\eta^3\text{-}PhC_3CHPh)$(Cyttp) the mutually trans Ru–P bond distances are 2.405 (1) and 2.417 (1) Å, whereas the unique Ru–P distance is 2.290 (1) Å. The similar trans and cis Ru–P bond lengths in $RuH_2(N_2)$(Cyttp) are probably due to the fact that both phosphine and hydride ligands are good trans-influence ligands. The unique Ru–P bond is longer than the trans Ru–P bonds in *mer*-$RuH(CH{=}C(Me)CO_2C_4H_9)(PPh_3)_3$, where the unique phosphorus atom is trans to a vinyl carbon atom.[39] The bond distances between ruthenium and H(1) and H(2) are 1.60 (7) and 1.61 (8) Å, which are comparable with the values of 1.58 (15) Å in *cis*-$RuH_2(dppe)_2$,[40] and 1.46 (4)–1.60 (3) Å in $Cp^*RuH_3(PPh_3)$.[41] The Ru–N bond is 2.005 (6) Å and is in the range for Ru–N bond distances in other ruthenium dinitrogen complexes (ranged from 1.822 (13) to 2.10 (1) Å).[42] The $N\equiv N$ triple bond is 1.093 (8) Å and is comparable to $N\equiv N$ distances observed in other ruthenium–dinitrogen complexes.[42] As in other "end-on" dinitrogen

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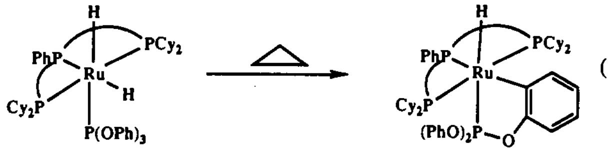
complexes,[42] the Ru–N–N linkage is nearly linear; the angle Ru–N(1)–N(2) is 175.4 (7)°.

The reactions of RuH_4(Cyttp) with CO and $PhCH_2NC$ give RuH_2(CO)(Cyttp) (**8**) and $RuH_2(CNCH_2Ph)$(Cyttp) (**9**), respectively. On the basis of their spectroscopic data, the structures of these compounds are similar to that of $RuH_2(N_2)$(Cyttp). Their ^{31}P NMR parameters are similar to those of $RuH_2(N_2)$(Cyttp) (Table I). In the ^1H NMR spectrum of $RuH_2(CNCH_2Ph)$(Cyttp), the resonance at −10.05 ppm (qd, $^2J(PH)$ = 24.7 Hz, $^2J(HH)$ = 4.0 Hz) is assigned to a hydride that is located cis to three phosphorus atoms. The signal at −8.86 ppm (dqd, $^2J(PH)$ = 67.0, 24.7 Hz; $^2J(HH)$ = 4.0 Hz) is assigned to the hydride trans to the central phosphorus atom. In the ^1H NMR spectrum of RuH_2(CO)(Cyttp) in CD_2Cl_2, the chemical shift for the hydride trans to the central phosphorus atom is −9.37 ppm, while that for the hydride trans to CO is −9.13 ppm. In C_6D_6, the resonances for the two hydrides in RuH_2(CO)(Cyttp) overlapped to give a complicated multiplet around −8.9 ppm. In the infrared spectrum of RuH_2(CO)(Cyttp), a strong absorption at 1920 cm^{-1} assignable to ν(CO) was observed; however the ν(Ru–H) frequency was not observed. It may be obscured by the CO absorption. In addition, no sharp, strong absorption above 2000 cm^{-1} in the infrared spectrum of $RuH_2(CNCH_2Ph)$(Cyttp), which could be assigned to a CN stretching frequency, was observed; only a fairly strong and very broad absorption between 1850 and 1950 cm^{-1} was observed. As in $RuH_2(N_2)$(Cyttp), the phenyl group on the central phosphorus atom is on the same side as the CO and $CNCH_2Ph$ in RuH_2(CO)(Cyttp) and $RuH_2(CNCH_2Ph)$(Cyttp), respectively. This orientation was determined by proton NOE difference spectra.

When RuH_4(Cyttp) was treated with $P(OPh)_3$ at room temperature, two isomers of formula $RuH_2(P(OPh)_3)$(Cyttp) (**10**) were observed in solution. The initially isolated white solid consists essentially of isomer **10A** and trace amounts of isomer **10B**. Isomer **10A** would slowly undergo partial isomerization into isomer **10B** in benzene solution at room temperature. Both the isomers have *mer* and cis geometry around the ruthenium center. The isomers result from the relative orientation of the phenyl group on the central phosphorus atom of the triphosphine due to a high barrier for inversion of coordinated phosphines. In isomer **10A**, the phenyl group on the central phosphorus atom is on the same side as $P(OPh)_3$, whereas in isomer **10B**, one of the hydrides is on the same side as the phenyl group of the central phosphorus atom. The stereochemical effect of the phenyl group on the central phosphorus atom in ttp ($PhP(CH_2CH_2CH_2PPh_2)_2$) has been noted before.[13a]

In the ^{31}P NMR spectrum of $RuH_2(P(OPh)_3)$(Cyttp), for isomer **10A**, the resonance for $P(OPh)_3$ was observed at 127.7 ppm ("q", $^2J(PP)$ = 28.2, 27.4 Hz), and the resonances at 43.5 ppm (dd, $^2J(PP)$ = 29.7, 28.2 Hz) and 12.1 ppm (td, $^2J(PP)$ = 29.7, 27.4 Hz) were assigned to the terminal phosphorus and the central phosphorus atoms of the triphosphine. The lack of large phosphorus–phosphorus coupling suggests that all the phosphorus atoms are located cis to one another. For isomer, **10B**, the resonances for $P(OPh)_3$ and the central phosphorus atom of the triphosphine are shifted slightly to higher field (119.0 ppm ("q", $^2J(PP)$ = 22.0, 28.3 Hz) and 35.9 ppm (td, $^2J(PP)$ = 33.9, 28.3 Hz), respectively), while the resonance for the terminal phosphorus atoms of the triphosphine is shifted slightly to lower field to 15.9 ppm (dd, $^2J(PP)$ = 33.9, 22.0 Hz) compared with that of isomer **10A**. In the hydride region of their ^1H NMR spectra the resonances for the hydrides appear as complicated multiplets at ca. −10.1 ppm for isomer **10A** and ca. −7.8 ppm for isomer **10B** due to overlap of the resonances of the two hydrides coupled with four phosphorus atoms. The phenyl group on the central phosphorus is not on the same side as the hydride in isomer **10A**, since no NOE difference effect was observed for the resonance of the ortho proton of the phenyl group when its hydride resonance was irradiated. In contrast, a NOE difference effect was observed for the resonance of the ortho proton of the phenyl group when the hydride resonance of isomer **10B** was irradiated. Thus the isomer formed initially has the same geometry as its N_2, CO, and $CNCH_2Ph$ analogues.

It has been reported that $P(OPh)_3$ reacts with $RuH(\eta^2\text{-}BH_4)$(ttp) to form an orthometalated complex in the presence of NEt_3 at room temperature.[13a] Interestingly, no detectable orthometalated products were produced during the reaction of $P(OPh)_3$ with RuH_4(Cyttp) at room temperature. The isolated $RuH_2(P(OPh)_3)$(Cyttp) does not undergo orthometalation in benzene solution at room temperature either. However, when $RuH_2(P(OPh)_3)$(Cyttp) in benzene or toluene was refluxed overnight, or the solid $RuH_2(P(OPh)_3)$(Cyttp) was pumped at ca. 35 °C overnight, the orthometalated compound $RuH(P(OPh)_2OC_6H_4)$(Cyttp) was obtained (eq 1). In the ^{31}P NMR spectrum, the resonance for the orthometalated triphenyl phosphite was observed at 159.1 ppm (q, $^2J(PP)$ = 22.7 Hz) compared to the values of 127.7 ppm in isomer **10A** and 119.0 ppm in isomer **10B** of $RuH_2(P(OPh)_3)$(Cyttp). The chemical shift differences are consistent with the presence of an orthometalated triphenyl phosphite in this compound.[43] The phosphite ligand is cis to the three phosphorus atoms of the triphosphine ligand, since only small phosphorus–phosphorus coupling was observed. In the ^1H NMR spectrum the resonance for the hydride appeared at −5.37 ppm (dtd, $^2J(PH)$ = 175.9, 23.6, 13.0 Hz).



(1)

The reaction between $P(OMe)_3$ and RuH_4(Cyttp) at room temperature resembles that of $P(OPh)_3$. When RuH_4(Cyttp) is treated with $P(OMe)_3$, two isomers of the formula $RuH_2(P(OMe)_3)$(Cyttp) (**11**) were also observed in solution. In the initially isolated product, mainly isomer **11A** was present. When the isolated product was redissolved in benzene or dichloromethane, essentially all of the isomer **11A** converted into isomer **11B** over a period of 2 days. Both isomers have *mer* and cis geometry around the ruthenium center. As in the case of $P(OPh)_3$, the phenyl group on the central phosphorus atom in the initially formed isomer **11A** is on the same side as $P(OMe)_3$, whereas in isomer **11B** one of the hydrides is on the same side as the phenyl group as confirmed by proton NOE difference spectra. The spectroscopic data for $RuH_2(P(OMe)_3)$(Cyttp) are also comparable with those for its $P(OPh)_3$ analogues as shown in Table I.

As in the case of RuHCl(Cyttp), PPh_3 failed to react with RuH_4(Cyttp) presumably owing to steric factors. It is interesting to note that *trans*-$RuH_2(PPh_3)$(ttp) has been isolated from the reaction of $RuH(\eta^2\text{-}BH_4)$(ttp) with PPh_3 in the presence of NEt_3.[13a] This is consistent with the fact that Cyttp is a larger ligand than ttp.[31]

Thus, when RuH_4(Cyttp) is treated with monodentate ligands all the initial complexes have the *cis-mer-syn*-RuH_2(L)(Cyttp) geometry. The term "syn" refers to a stereoisomer in which the phenyl group of the central phosphorus atom is on the same side as a larger group L, and the term "anti" refers to a stereoisomer in which the phenyl group is on the opposite side of the larger group L. In the cases of CO, N_2, $PhCH_2NC$, which are linear ligands, only syn isomers were observed, and no isomerization was observed at room temperature. In the cases of $P(OPh)_3$ and $P(OMe)_3$, which are much bulkier than the linear ligands,[31] the initially formed syn isomers converted into the anti isomers. The results can be rationalized on the basis of steric interactions between the ligand and the phenyl group on the central phosphorus atom of the triphosphine. Thus, bulkier ligands tend to form anti isomers to avoid the steric interaction.

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Registry No. **1**, 129215-67-4; **2A**, 130611-13-1; **3**, 118575-30-7; **4**, 130574-84-4; **5**, 130574-88-8; **6A**, 130574-85-5; **6B**, 130694-29-0; **7**, 118575-35-2; **8**, 118575-32-9; **9**, 130574-86-6; **10A**, 130694-31-4; **10B**, 130694-32-5; **11A**, 130694-30-3; **11B**, 130790-16-8; $RuCl_2(PPh_3)_3$, 34076-51-2; $RuCl_2$(Cyttp), 84623-42-7; $RuH(P(OPh)_2OC_6H_4)$(Cyttp), 130574-87-7.

Supplementary Material Available: Tables (SUP-1–SUP-4 and SUP-6) of complete bond distances and angles, calculated positional parameters and *B* values for hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, and complete crystallographic data (7 pages); a table (SUP-5) of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Isomer Preference of Oxidation States. Chemistry of the $Os(xanthate)_2(PPh_3)_2^z$ (z = 0, +) Family

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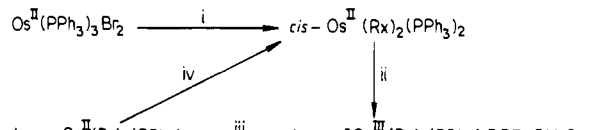
The title family consist of cis isomers of osmium(II) (z = 0; **1**) and osmium(III) (z = +; $\mathbf{1}^+$) and the corresponding trans isomers (**2**, $\mathbf{2}^+$). Four xanthates, $ROC(S)S^-$ (Rx^-), have been used: R = Me, Et, *i*-Pr, $PhCH_2$. All complexes except $\mathbf{1}^+$ have been isolated in pure state in excellent yields: **1** by the reaction of $Os(PPh_3)_3Br_2$ with KRx, $\mathbf{2}^+$ via oxidation of **1** with cerium(IV), and **2** by the reduction of $\mathbf{2}^+$ by hydrazine hydrate. The formal potentials, $E°$(cis) and $E°$(trans), of the redox couples $\mathbf{1}^+$–**1** and $\mathbf{2}^+$–**2** are respectively ~0.4 and ~0.1 V vs SCE; the equilibrium constants K^{II} and K^{III} of the isomerization reactions $\mathbf{2} \rightleftharpoons \mathbf{1}$ and $\mathbf{1}^+ \rightleftharpoons \mathbf{2}^+$ are ~10 and ~10^4, respectively (CH_2Cl_2, 303 K). The metal oxidation states strongly differentiate the isomeric coordination spheres. The matched combinations are cis-Os^{II} (**1**) and trans-Os^{III} ($\mathbf{2}^+$). The mismatched species $\mathbf{1}^+$ and **2** are unstable and isomerize spontaneously in solution. To establish isomer structures and to probe the origin of the differentiation process, the X-ray structures of *cis*-$Os(Mex)_2(PPh_3)_2$ (**1a**), *trans*-$Os(Mex)_2(PPh_3)_2$ (**2a**), and *trans*-$[Os(Mex)_2(PPh_3)_2]PF_6{\cdot}2H_2O$ ($\mathbf{2a}^+$) have been determined. **1a**: space group *Pbca*, $Z = 8$, a = 10.774 (3) Å, b = 18.580 (7) Å, c = 38.043 (6) Å, and V = 7616 (4) Å^3. **2a**: space group $P\bar{1}$, $Z = 1$, a = 9.231 (4) Å, b = 10.466 (5) Å, c = 11.149 (5) Å, α = 101.33 (3)°, β = 108.66 (3)°, γ = 108.02 (3)°, and V = 916.8 (7) Å^3. $\mathbf{2a}^+$: space group $P\bar{1}$, $Z = 1$, a = 9.766 (4) Å, b = 11.363 (5) Å, c = 11.677 (5) Å, α = 112.19 (4)°, β = 105.13 (4)°, γ = 97.17 (4)°, and V = 1121.6 (9) Å^3. The binding in the OsS_4 fragment is primarily σ in nature. The mean Os–S distance *decreases* upon metal oxidation: **1a**, 2.424 (5) Å; **2a**, 2.410 (2) Å; $\mathbf{2a}^+$, 2.378 (2) Å. The OsP_2 fragment is subject to $5d\pi$–$3d\pi$ back-bonding, which decreases rapidly in the order **1a** > **2a** > $\mathbf{2a}^+$, leading to a large and progressive increase in mean Os–P length: **1a**, 2.317 (4) Å; **2a**, 2.365 (4) Å; $\mathbf{2a}^+$, 2.439 (3) Å. The stability order **1** > **2** as well as the redox potential order $E°$(cis) > $E°$(trans) arises primarily from the superior Os–P back-bonding in **1** compared to **2**. Due to the poor back-bonding ability of osmium(III), steric factors become controlling and this explains the stability of $\mathbf{2}^+$ over $\mathbf{1}^+$. Paramagnetic ($S = {}^1/_2$) $\mathbf{2}^+$ affords strongly rhombic EPR spectra—the axial and rhombic distortion parameters being ~7000 and ~2000 cm^{-1}, respectively. A weak optical transition within the Kramers doublets is observable near 7600 cm^{-1}.

Introduction

This work stems from our interest in the differentiation of isomeric coordination spheres by unequal oxidation states of the same metal ion.[1-4] Herein we describe examples of this phenomenon in osmium(II,III) chemistry using a family of OsS_4P_2 complexes assembled from xanthates and triphenylphosphine. The synthesis and characterization of geometrical isomers are described. The preferred geometries are cis for osmium(II) and trans for osmium(III). Mismatched combinations of oxidation state and geometrical configuration can be imposed by rapid redox, but these relax via spontaneous isomerization. Such processes have been thermodynamically and kinetically quantitated by using voltammetric and spectroscopic techniques. The origin of isomer preference of oxidation states is probed by X-ray structure determination of three complexes differing in geometry and/or oxidation state. Osmium–phosphine back-bonding is shown to play a pivotal role.

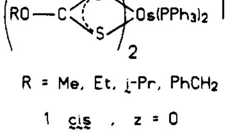
Scheme I[a]



[a] Legend: (i) KRx, EtOH, boil; (ii) CH_2Cl_2–CH_3CN(1:10), $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$–$H_2O$, stir, NH_4PF_6–H_2O; (iii) CH_3CN, $NH_2NH_2{\cdot}H_2O$, stir under N_2 atm., 273K; (iv) CH_2Cl_2, warm.

Results

A. Complexes and Their Synthesis. The four subgroups of the $Os(Rx)_2(PPh_3)_2^z$ (Rx^- = $ROC(S)S^-$; z = 0, +) family correspond to cis-osmium(II) (**1**), cis-osmium(III) ($\mathbf{1}^+$), trans-osmium(II) (**2**), and trans-osmium(III) ($\mathbf{2}^+$). All but $\mathbf{1}^+$ have been isolated



R = Me, Et, *i*-Pr, $PhCH_2$

1 cis, z = 0
1^+ cis, z = +
2 trans, z = 0
2^+ trans, z = +

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