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Syntheses and Characterization of Ruthenium(0) and Ruthenium(II) Complexes of Two Flexible Chelating Triphosphine Ligands

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Treatment of "RuCl₃·3H₂O" with the triphosphine ligands PhP(CH₂CH₂CH₂PR₂)₂ (ttp, R = Ph; Cyttp, R = *c*-C₆H₁₁) produces the complexes [RuCl₂(ttp)]₂, 1, and RuCl₂(Cyttp), 2, respectively. The ttp complex is polymeric whereas the Cyttp product is monomeric, presumably due to steric effects of the larger cyclohexyl (Cy) group. Treatment of 1 with carbon monoxide gives *cis* and *trans* carbonyl complexes, depending on the method of preparation; only a *trans*-dichloro carbonyl complex was obtained in the case of Cyttp. On the basis of infrared data (ν (S-O) 1280, 1112 cm⁻¹), the SO₂ adduct of 2 has a planar geometry around the sulfur atom. Both chloride ligands of 1 can readily be substituted with CH₃CN or CO by using TI⁺ as a halogen scavenger; the acetate ion replaces only one chloride in the absence of TI⁺. Treatment of 1 with NaBH₄ produces RuH(η^2 -BH₄)(ttp), which undergoes substitution reactions to yield the cationic hydrido ligand complexes [RuH(L)(L')(ttp)]Y (L = P(OCH₃)₃, PF₃, CO, NCCH₃; L' = P(OCH₃)₃, NCCH₃, CO; Y = BF₄) by treatment with HBF₄ and the appropriate ligands. If the ligand substitution reactions are performed in basic solutions, the ligand dihydrido complexes RuH₂(L)(ttp) result. The ruthenium(0) complexes Ru(CO)₂(ttp), 10, and Ru(CO)₂(Cyttp), 11, can be prepared by (i) Na/Hg reduction of 1 or 2, (ii) reduction of the dicarbonyl complexes [Ru(CO)₂(ttp)][BF₄]₂ or [RuH(CO)₂(ttp)]BF₄, or (iii) triphosphine substitution of Ru₃(CO)₁₂. The complex Ru(CO)₂(Cyttp), 11, undergoes oxidative addition reactions with halogens and acids to form the cationic, six-coordinate ruthenium(II) dicarbonyls [RuX(CO)₂(ttp)]Y (XY = HCl, HBr, HBF₄, Cl₂, Br₂) and with molecular oxygen to give Ru(CO)₃(CO)(Cyttp). The preparation and characterization of these new ruthenium(II) and ruthenium(0) triphosphine complexes are reported, and structures are proposed on the basis of their conductivity, elemental compositions, and infrared, ¹H, ³¹P, and ¹⁹F NMR spectroscopy.

Introduction

Since demonstration of the remarkable catalytic properties of RuHCl(PPh₃)₃ by Wilkinson et al.¹ an explosive growth in the chemistry of ruthenium phosphine compounds has occurred. The complex RuCl₂(PPh₃)₃ and its derivatives are capable of catalyzing olefin isomerization,² olefin dimerization,³ alkyl chloride addition to olefins,⁴ and asymmetric homogeneous hydrogenation.⁵ Small molecules such as N₂,⁶ SO₂,⁷ H₂,⁸ C₂H₄,^{7,8} O₂,^{8,9} and NO¹⁰ have

been activated by various ruthenium phosphine complexes. Recently, several ruthenium(0) phosphine complexes have also shown interesting chemistry and catalytic activity. For example, the hydroformylation of olefins is catalyzed by a number of mononuclear Ru(0) complexes (e.g., Ru(CO)₃(PPh₃)₂, Ru(CO)₃(diphos), and RuH(NO)(PPh₃)₃).¹¹ Diphosphine ligands also have been used to reduce the

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lability of the Ru-PR₃ bonds in five-, six-, and seven-coordinate ruthenium(II) compounds.¹²

Despite the commercial availability of several polydentate phosphine ligands, only a few reports of ruthenium complexes containing tri- or tetradentate phosphorus ligands have appeared in the chemical literature. In one report, Venanzi¹³ et al. prepared a series of five- and six-coordinate Ru(0) and Ru(II) complexes with the tridentate ligand TP (TP = PhP(C₆H₄-o-PPh₂)₂) and the rigid tetradentate ligand QP (QP = P(C₆H₄-o-PPh₂)₃). King,¹⁴ Khan,¹⁵ and Davies¹⁶ investigated ruthenium complexes of the more flexible ligands etp (PhP(CH₂CH₂PPh₂)₂) and PP₃ (P(CH₂CH₂PPh₂)₃), which have ethylene connecting chains between the phosphine groups. These previously reported compounds have been characterized primarily by infrared and ¹H NMR spectroscopy, although a ³¹P NMR chemical shift was reported for RuCl₂(QP).

The tridentate ligands PhP(CH₂CH₂CH₂PPh₂)₂ (ttp) and PhP(CH₂CH₂CH₂PCy₂)₂ (Cytpp) offer several advantages over monodentate phosphines containing similar phosphino groups. Such tridentate ligands provide (i) more control on the coordination number and stereochemistry of the resulting complex, (ii) an increased basicity (or nucleophilicity) at the metal, (iii) slower intra- and intermolecular exchange processes, and (iv) detailed structural and bonding information in the form of phosphorus chemical shifts and phosphorus-phosphorus and metal-phosphorus (where applicable) coupling constants.¹⁷

We report herein the synthesis and reactions of a series of Ru(0) and Ru(II) complexes of the chelating triphosphine ligands ttp and Cytpp. Structures are proposed for these compounds on the basis of their infrared and ¹H and ³¹P NMR spectra. Correlations between the metal oxidation state and the phosphorus-phosphorus coupling constants and between phosphorus chemical shifts and the nature of the trans ligands allow differentiation between several alternate structures.

Experimental Section

Bis(3-(diphenylphosphino)propyl)phenylphosphine (ttp) and bis(3-(dicyclohexylphosphino)propyl)phenylphosphine (Cytpp) were prepared according to our published procedures.¹⁸ All organic starting materials and solvents were reagent grade and were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. Commercial ruthenium trichloride trihydrate (RuCl₃·3H₂O) was obtained from either Matthey Bishop Co. or Engelhard Industries. An alcohol solution of RuCl₃·3H₂O was filtered prior to mixing with the phosphine ligands. The compounds RuCl₂(PPh₃)₃¹⁹ and Ru₃(CO)₁₂²⁰ were prepared according to the literature methods. The reagents Me₃O⁺PF₆⁻ and HBF₄·Et₂O were obtained from Cationics Inc.

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Infrared spectra were measured on either a Perkin-Elmer 337 or a Perkin-Elmer 283B grating spectrometer 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 calibration of the infrared spectra.

Conductivity data were obtained on ~10⁻³ M nitromethane solutions (except where specified otherwise) with a Lab Line unbreakable-type conductivity cell, catalogue no. 11200. An Industrial Instruments, Inc., conductivity bridge (Model RC16B2) was used to determine the resistance of solutions at 1000 Hz. In the experimental section, the molar conductance values, Λ_M, have the units ohm⁻¹ cm² mol⁻¹.

Phosphorus-31 NMR spectra were usually obtained on a Bruker HX-90 NMR spectrometer operating in the Fourier mode at 36.43 MHz with a Bruker BNC-12 data system. High-field phosphorus-31 NMR spectra were collected on either a Bruker WP-200 (81.615 MHz) or a Bruker WM-300 (121.470 MHz) spectrometer operating in the Fourier mode with quadrature phase detection and the Aspect-2000 data system. Ten-millimeter tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were generally used for the ³¹P NMR spectra. Positive phosphorus-31 chemical shifts are *downfield* from the external phosphorus standard.

Proton magnetic resonance spectra were collected on a Varian EM360 (with Me₄Si as the internal standard) or on the HX-90, WP-200, or WM-300 instruments with Me₄Si or the residual ¹H nuclei in the deuterated solvents (referenced to Me₄Si) as the internal standard. Selective decoupling experiments were performed on the HX-90 and WM-300 spectrometers. Fluorine-19 NMR spectra were collected on the HX-90 instrument at 84.66 MHz with CF₃COOH as the external standard.

Mass spectra were measured by C. R. Weisenberger at The Ohio State University on an AEI MS-902 mass spectrometer.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Preparation of the Metal Complexes. [RuCl₂(ttp)]₂ (1). A solution containing 0.514 g of RuCl₃·3H₂O (2.0 mmol) in 60 mL of methanol and 10.0 mL of stock ttp solution in benzene (3.70 mmol) was heated under reflux for 2 h. An orange crystalline solid formed; subsequently, the volume of the solution was reduced to 5 mL in vacuo. The resultant mixture was filtered; the solid was collected on a frit, washed with two 5-mL portions of methanol, and dried in vacuo; yield 0.765 g, 51%. Anal. Calcd for C₃₆H₃₇Cl₂P₃Ru: C, 58.85; H, 5.09; Cl, 9.65. Found: C, 58.67; H, 5.02; Cl, 9.81.

[RuBr₂(ttp)]₂. A solution of 0.787 g of RuCl₃·3H₂O (3.10 mmol) and 1.6 g of LiBr (18.4 mmol) in 250 mL of methanol was heated to reflux overnight. To the refluxing solution was added 9.0 mL of stock ttp solution in benzene (3.30 mmol), and a brown crystalline solid formed. The volume of the mixture was reduced to 50 mL in vacuo; the solid was collected by filtration, washed with two 10-mL portions of methanol and two 10-mL portions of ether, and then dried in vacuo; yield 2.42 g, 94%.

cis-[RuCl₂(CO)(ttp)] (3). Carbon monoxide was bubbled through a slurry of 0.268 g of [RuCl₂(ttp)]₂ (0.36 mmol of Ru) in 100 mL of CH₂Cl₂ for 90 min. The orange solid dissolved slowly to yield a gray precipitate and a yellow-orange solution. The mixture was filtered and the solid discarded; from the filtrate white crystals formed on the walls of the flask overnight. The volume of the solution was reduced to 20 mL in vacuo, and 50 mL of ether was added to ensure complete precipitation of the complex. The white solid was collected on a Schlenk filter, washed with two 10-mL portions of ether, and dried in vacuo; yield 0.152 g, 55%.

trans-[RuCl₂(CO)(ttp)] (5). Carbon monoxide was bubbled through a refluxing solution of 0.538 g of RuCl₃·3H₂O (2.12 mmol) in 250 mL of ethanol for 3 h to yield a characteristic cherry-red solution; then 8.0 mL (2.99 mmol) of the standardized benzene solution of ttp was added and a small amount of orange solid formed. The mixture was refluxed for 1 h, the solution was cooled, and the resulting light orange solid was separated by filtration. The volume of the filtrate was reduced to 100 mL and allowed to sit overnight; lemon-yellow crystals separated. These crystals were collected by filtration, washed with two 10-mL portions of ether, and dried in vacuo; yield 1.15 g, 71%. Anal. Calcd for C₃₇H₃₇Cl₂OP₃Ru: C, 58.27; H, 4.90; Cl, 9.30; P, 12.18. Found: C,

58.24; H, 4.87; Cl, 9.55; P, 12.86.

[RuCl(OAc)(ttp)] (4). A solution of 0.400 g of [RuCl₂(ttp)]_x (0.55 mmol) and 0.216 g of NaOAc·3H₂O (1.54 mmol) in 70 mL of THF was heated under reflux for 3 h; a yellow solid crystallized during the refluxing. The volume of the solution was reduced to 15 mL in vacuo, 10 mL of ether was added, and the resultant yellow solid was collected on a Schlenk filter and washed with 10-mL portions of water, ethanol, and ether. The solid was dried in vacuo; yield 0.364 g, 87%. Anal. Calcd for C₃₈H₄₀ClO₂P₃Ru: C, 60.19; H, 5.33; P, 12.25. Found: C, 59.08; H, 5.32; P, 12.99.

[Ru(ttp)(NCMe)₂](AsF₆)₂. A slurry of 0.249 g of [RuCl₂(ttp)]_x (0.34 mmol) and 0.350 g of TlAsF₆ (0.70 mmol) in 100 mL of THF and 2 mL of MeCN was refluxed for 10 h. The solution became pale yellow within minutes, and a white solid started forming. After the mixture was cooled, the solid was allowed to settle and the supernatant was decanted. The volume of the supernatant was reduced in vacuo to 20 mL, and the remainder of the solvent was allowed to evaporate under a slow stream of nitrogen; a yellow oil resulted. A 10-mL portion of CH₂Cl₂ was added; then the solution was evaporated to dryness to give a yellow powder; yield 0.309 g, 81%. Anal. Calcd for C₄₀H₄₃As₂F₁₂N₂P₃Ru: C, 42.76; H, 3.86; N, 2.49; P, 8.29. Found: C, 39.61; H, 3.82; N, 2.61; P, 10.01.

[Ru(ttp)(CO)₂][BF₄]₂. Carbon monoxide was bubbled through a solution of 0.216 g of [RuCl₂(ttp)]_x (0.29 mmol) and 0.230 g of TlBF₄ (0.59 mmol) in 80 mL of CH₂Cl₂ for 4 h, whereupon the orange solid dissolved to give a cloudy grey solution. The solution was filtered through a 1-cm pad of Celite filter aid. The filtrate was evaporated to dryness to give a white solid, which was recrystallized from CH₂Cl₂-ether; yield 0.110 g, 42%. Anal. Calcd for C₃₈H₃₇B₂F₈O₂P₃Ru: C, 51.09; H, 4.18; P, 10.40. Found: C, 51.09; H, 4.41; P, 10.34.

[RuCl₂(Cyttp)] (2). A deep green solution resulted immediately upon addition of 6.0 mL of a stock solution of Cyttp (1.20 mmol) in benzene to 1.003 g of RuCl₂(PPh₃)₃ (1.04 mmol) in 30 mL of benzene. The solution was stirred for 1 h, and then the volume was reduced to 5 mL in vacuo. This concentrated solution was transferred to a 15-cm column of neutral alumina (10% H₂O treatment) and eluted with benzene. About 100 mL of deep green eluent was collected and concentrated to 5 mL. Addition of 50 mL of hexane caused precipitation of a bright green solid. The solution was collected on a frit, washed with 5 mL of hexane, and dried in vacuo; yield 0.627 g, 82%. Anal. Calcd for C₃₆H₆₁Cl₂P₃Ru: C, 56.97; H, 8.12; Cl, 9.34. Found: C, 56.97; H, 8.30; Cl, 9.29.

trans-[RuCl₂(CO)(Cyttp)] (6). Carbon monoxide gas was bubbled through a solution of 0.252 g of RuCl₂(Cyttp) (0.33 mmol) in 20 mL of benzene for 10 min. The green solution immediately turned a golden color. The solution was evaporated to dryness; the yellow solid was extracted with 20 mL of methanol, collected on a frit, washed with 5 mL of methanol, and dried in vacuo; yield 0.222 g, 85%. Anal. Calcd for C₃₇H₆₁Cl₂OP₃Ru: C, 56.47; H, 7.83; Cl, 9.01. Found: C, 56.69; H, 7.70; Cl, 8.89.

[RuCl₂(Cyttp)(SO₂)] (7). Sulfur dioxide was bubbled through a solution of 0.125 g of RuCl₂(Cyttp) (0.16 mmol) in 15 mL of toluene. The solution turned pink and a pink solid precipitated; addition of 30 mL of ether caused formation of more solid. The pink solid was collected on a Schlenk frit, washed with 5 mL of ether, and dried in vacuo. Anal. Calcd for C₃₆H₆₁Cl₂O₂P₃RuS: C, 52.55; H, 7.47; Cl, 8.62; S, 3.90. Found: C, 52.54; H, 7.34; Cl, 8.38; S, 4.15.

[Ru(ttp)(CO)₂] (10). **a. From RuCl₂(ttp).** To a well-stirred Na/Hg amalgam (0.5 g of Na, 20 mL of Hg) and 50 mL of THF was added 0.501 g of [RuCl₂(ttp)]_x (0.68 mmol). Carbon monoxide was bubbled through the resulting mixture overnight to yield a green cloudy solution. The THF layer was separated and filtered twice through 2-cm layers of Celite filter aid. The yellow-orange solution was reduced in volume to 5 mL in vacuo; then about 40 mL of ether was added. The resultant white solid was collected on a filter and discarded. The filtrate was concentrated to 2 mL in vacuo and a bright yellow solid separated. The solid was collected on a Schlenk filter, washed with two 10-mL portions of ether, and dried in vacuo; yield 0.271 g, 55%.

b. From Ru₃(CO)₁₂. A solution of 0.212 g of Ru₃(CO)₁₂ (1.0 mmol of Ru) and 4.0 mL of the ttp solution in 50 mL of benzene was refluxed overnight. The resulting red-orange solution was evaporated to dryness in vacuo, the residue extracted with hexane

(3 × 25 mL), and a yellow-orange solid collected on a filter frit; yield 0.456 g, 63%.

c. From cis-[RuH(CO)₂(ttp)]BF₄.²¹ To a solution of 0.211 g of cis-[RuH(CO)₂(ttp)]BF₄ (0.262 mmol) in 45 mL of THF was added 0.30 mL of a 1 M solution of LiHBEt₃, which caused evolution of a gas. The next day the yellow solution was reduced to dryness; 8 mL of benzene was added, and the resulting solution was filtered. Addition of 50 mL of hexane to the yellow filtrate caused precipitation of a yellow solid; this solid was isolated, washed with hexane, and dried in vacuo. The infrared and ³¹P{¹H} NMR spectra were identical with those of an authentic sample of Ru(CO)₂(ttp).

d. From [Ru(CO)₂(ttp)][BF₄]₂. To a mixture of 0.170 g of [Ru(CO)₂(ttp)][BF₄]₂ (0.191 mmol) in 50 mL of THF was added 1 equiv of LiHBEt₃ (0.20 mL of a 1 M solution); a clear, pale-yellow solution resulted. Addition of a second equivalent of LiHBEt₃ produced a dark yellow solution. This solution was reduced to dryness the next day; the resulting yellow solid was dissolved in 10 mL of benzene, and the solution was filtered. Enough hexane was added to the clear, yellow solution to precipitate a yellow solid; it was isolated, washed with hexane, and dried in vacuo. The infrared and ³¹P{¹H} NMR spectra of the yellow solid were identical with those of an authentic sample of Ru(CO)₂(ttp).

A result similar to that obtained by procedure d was obtained when methylolithium in diethyl ether was used instead of LiHBEt₃.

[Ru(Cyttp)(CO)₂] (11). A solution of 0.158 g of Ru₃(CO)₁₂ (0.74 mmol of Ru) and 4.20 mL of the stock solution of Cyttp (0.81 mmol) in 50 mL of benzene was refluxed for 16 h. The progress of the reaction was followed by monitoring the disappearance of the infrared carbonyl absorptions of Ru₃(CO)₁₂ and the appearance of new absorptions at 1880 and 1820 cm⁻¹. The solution turned from orange to purple and finally to yellow-orange. The liquid was evaporated to dryness to give a yellow solid, which was extracted with three 30-mL portions of hexane and collected on a Schlenk frit; yield 0.35 g, 65%. Anal. Calcd for C₃₈H₆₁O₂P₃Ru: C, 61.35; H, 8.27; P, 12.49. Found: C, 60.83; H, 8.08; P, 13.01.

[RuBr(CO)₂(Cyttp)]AsF₆ (12). To a solution of 0.171 g of Ru(CO)₂(Cyttp) (0.228 mmol) in 10 mL of benzene was added 1 equiv (13.1 μL) of Br₂. A clear yellow solution was produced within a few minutes after the addition of Br₂. A copious quantity of pale yellow microcrystals was attached to the sides of the flask the next day. The crystals were isolated, washed with benzene, and dried in vacuo; they were then recrystallized from acetone and diethyl ether-hexane to give a white solid. The white solid was dissolved in ethanol (20 mL) and added to a solution containing 0.12 g (0.5 mmol) of NaAsF₆ in 5 mL of ethanol. White microcrystals of [RuBr(CO)₂(Cyttp)]AsF₆ formed gradually; they were isolated, washed in succession with ethanol, water, ethanol, and diethyl ether, and then dried in vacuo; yield 0.15 g, 65%; mp >280 °C; Δ_M = 92. Anal. Calcd for C₃₈H₆₁AsBrF₆O₂P₃Ru: C, 45.06; H, 6.07; Br, 7.89. Found: C, 44.69; H, 5.97; Br, 8.03.

[RuI(CO)₂(Cyttp)]I (13). A solution of 0.11 g of iodine (0.45 mmol) in 5 mL of benzene was added dropwise to a solution of 0.340 g of Ru(CO)₂(Cyttp) (0.453 mmol) in 20 mL of benzene until the bright yellow color disappeared. Pale yellow crystals formed overnight; these crystals were isolated, washed with diethyl ether, and dried in vacuo; yield 0.41 g, 91%, mp 175 °C dec; Δ_M = 94. Anal. Calcd for C₃₈H₆₁I₂O₂P₃Ru: C, 45.74; H, 6.16; I, 25.43. Found: C, 45.51; H, 6.34; I, 25.61.

[RuH(CO)₂(Cyttp)]BF₄ (14). To a solution of 0.18 g of Ru(CO)₂(Cyttp) (0.24 mmol) in 11 mL of benzene was added HBF₄·Et₂O (≈100 μL, more than a 2:1 molar ratio), which caused the yellow solution to become a pale pink. The resultant white crystals were isolated the next day; they were washed with diethyl ether and dried in vacuo; yield 0.17 g, 85%; mp 200 °C dec; Δ_M = 95. Anal. Calcd for C₃₈H₆₂BF₄O₂P₃Ru: C, 54.87; H, 7.51; F, 9.13. Found: C, 55.00; H, 7.37; F, 9.31.

[RuH(CO)₂(Cyttp)]AsF₆ (15). **a. From HCl(aq).** To a solution of 0.206 g of Ru(CO)₂(Cyttp) (0.333 mmol) in 15 mL of benzene was added 12 mL of a 0.048 M HCl(aq) solution. After the solution was stirred for several hours, the stirring was stopped and a clear organic phase and a milky aqueous phase resulted.

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The solution (both phases) was reduced to dryness, and the resulting white solid was collected on a filter and then dissolved in ethanol (20 mL). The ethanol solution was filtered and then combined with an ethanol solution of NaAsF_6 (0.11 g, 0.5 mmol in 4 mL of ethanol). A white solid began to precipitate within minutes; this solid was isolated, washed in succession with ethanol, water, ethanol, and diethyl ether, and dried in vacuo: yield 0.27 g, 87%; mp 180 °C dec; $\Lambda_M = 91$. Anal. Calcd for $\text{C}_{38}\text{H}_{62}\text{AsF}_6\text{O}_2\text{P}_3\text{Ru}$: C, 48.87; H, 6.69; F, 12.20; Cl, 0.00. Found: C, 48.81; H, 6.65; F, 12.36; Cl, 0.00.

b. From HBr(aq) . Replacing HCl(aq) with concentrated HBr(aq) (48.2%, $d = 1.49$ g/mL) and then replacing the bromide anion with ionic AsF_6^- gave the same product, $[\text{RuH}(\text{CO})_2(\text{Cytpp})]\text{AsF}_6$; yield 0.193 g, 82%.

$\text{Ru}(\text{CO})_3(\text{CO})(\text{Cytpp})$ (16). a. Approximately 0.200 g of $\text{Ru}(\text{CO})_2(\text{Cytpp})$ (0.266 mmol) was deliberately exposed to air for 1 week; the initial yellow solid became almost colorless during this time. The white solid was washed with benzene in air to remove any unreacted starting material, and then it was washed with diethyl ether; the solid was finally dried with an air stream: yield 0.19 g, 95%; mp 150 °C dec. Anal. Calcd for $\text{C}_{38}\text{H}_{61}\text{O}_4\text{P}_3\text{Ru}$: C, 58.37; H, 7.86. Found: C, 58.73; H, 8.06.

b. A solution of 0.231 g of $\text{Ru}(\text{CO})_2(\text{Cytpp})$ (0.308 mmol) in 10 mL of benzene was prepared, and oxygen was bubbled through it for 0.5 h; a white solid, which was isolated from a pale yellow solution, was washed with benzene and diethyl ether and dried in vacuo; yield 0.11 g, 48%. An infrared spectrum was identical with that of an authentic sample of $\text{Ru}(\text{CO})_3(\text{CO})(\text{Cytpp})$ prepared by procedure a.

$[\text{RuH}(\text{CH}_3\text{CN})(\text{PF}_3)(\text{ttp})]\text{BF}_4$ (17). One equivalent of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (45 μL) was added to a solution of $\text{RuH}(\text{BH}_4)(\text{ttp})^{21}$ (0.269 mmol) in 15 mL of THF and 0.5 mL (12.1 mmol) of MeCN ; the yellow color faded rapidly and a gas was evolved. Then PF_3 was bubbled through the solution for 5 min followed by N_2 purging for 5 min; the resulting solution was pale red. Enough diethyl ether was added to cause initial cloudiness in the solution; it was placed in the freezer overnight. A small amount of a fine, red precipitate was filtered from the solution the next day; then the solution was placed in a dry ice/2-propanol bath (-78 °C) overnight. A white microcrystalline solid was isolated the next day from the -78 °C solution; the solid was washed with diethyl ether and dried in vacuo; yield 0.15 g, 65%; mp 130 °C dec. Anal. Calcd for $\text{C}_{38}\text{H}_{41}\text{BF}_7\text{NP}_4\text{Ru} \cdot 0.5\text{H}_2\text{O}$: C, 51.30; H, 4.75; N, 1.57; P, 13.92. Found: C, 51.63; H, 4.78; N, 1.39; P, 13.76.

***trans*- $[\text{RuH}(\text{P}(\text{OCH}_3)_3)_2(\text{ttp})]\text{BF}_4$ (18).** a. **From *cis*- $[\text{RuH}(\text{CH}_3\text{CN})_2(\text{ttp})]\text{BF}_4$.** One equivalent of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (65 μL) was added to a solution of 0.222 g of $\text{RuH}(\text{BH}_4)(\text{ttp})^{21}$ (0.327 mmol) in 10 mL of THF and 0.35 mL (8.5 mmol) of CH_3CN ; the yellow color faded, and a gas was evolved. The solution was filtered, and the filtrate was reduced to dryness; the remaining white solid was dissolved in 10 mL of acetone, and 0.20 mL (1.6 mmol) of $\text{P}(\text{OMe})_3$ was added; the ^{31}P NMR spectrum of this solution showed that >95% of the complex present in solution was *trans*- $[\text{RuH}(\text{P}(\text{OMe})_3)_2(\text{ttp})]\text{BF}_4$. Hexane was added to the solution to the point of cloudiness; white crystals were isolated the next day. The crystals were washed with hexane and dried in vacuo; yield 0.29 g, 90%. A ^{31}P NMR spectrum of the crystals in acetone confirmed the presence of *trans*- $[\text{RuH}(\text{P}(\text{OMe})_3)_2(\text{ttp})]\text{BF}_4$.

b. From *cis*- $\text{RuH}_2(\text{P}(\text{OMe})_3)(\text{ttp})$. To a solution of 0.133 g of *cis*- $\text{RuH}_2(\text{P}(\text{OMe})_3)(\text{ttp})^{21}$ (0.168 mmol) in 9 mL of THF was added 0.10 mL (0.8 mmol) of $\text{P}(\text{OMe})_3$. Upon addition of 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (27 μL) a gas was evolved and the solution became nearly colorless. When the solvent was evaporated, a pale orange oil remained; it was washed with hexane and dissolved in 4 mL of acetone. To the acetone solution was added 6 mL of hexane; and white crystals formed over a period of 1 week; these crystals were isolated, washed with hexane, and dried in vacuo; yield 0.15 g, 90%. The white crystals proved to be pure *trans*- $[\text{RuH}(\text{P}(\text{OMe})_3)_2(\text{ttp})]\text{BF}_4$ (cf. ^{31}P NMR spectroscopy). A ^{31}P NMR spectrum of the filtrate showed mostly the *trans* isomer, with less than 5% of the *cis* isomers, *cis*-syn and *cis*-anti.²¹

Reaction of *cis*- $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. To a solution of 0.127 g of *cis*- $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4^{21}$ (0.157 mmol) in 15 mL of chloroform was added 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (26 μL); there was no visible change. After several hours, diethyl ether

was added to the solution to the point of cloudiness. White crystals were isolated the next day; they were washed with diethyl ether and dried in vacuo; yield 0.12 g, 95%. An infrared spectrum of these crystals was identical with that of an authentic sample of *cis*- $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4$.

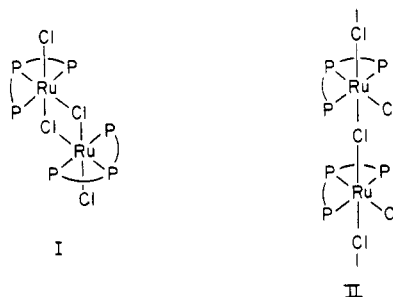
Addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to $\text{Ru}(\text{CO})_2(\text{ttp})$. To a solution of 0.10 g of $\text{Ru}(\text{CO})_2(\text{ttp})$ (0.14 mmol) in 15 mL of THF was added 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, and the yellow color faded. The solution was reduced to dryness, and the white residue was dissolved in approximately 1 mL of acetone- d_6 . The ^1H NMR spectrum showed the presence of *cis*- $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4^{21}$.

$[\text{RuH}(\text{CH}_3\text{CN})(\text{P}(\text{OMe})_3)(\text{ttp})]\text{BF}_4$. To a solution of 0.202 g of *cis*- $\text{RuH}_2(\text{P}(\text{OMe})_3)(\text{ttp})^{21}$ (0.256 mmol) in 10 mL of THF was added 0.30 mL (7.0 mmol) of acetonitrile. On addition of 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (55 μL) a gas was evolved and the solution became cloudy. A white solid precipitated from the solution during a 2-h period; it was isolated, washed successively with 2 mL of THF and 6 mL of hexane, and dried in vacuo; yield 0.206 g, 86%.

$[\text{RuH}(\text{CO})(\text{P}(\text{OMe})_3)(\text{ttp})]\text{BF}_4$ (22). Carbon monoxide was bubbled through a solution of $\text{RuH}_2(\text{P}(\text{OMe})_3)(\text{ttp})^{21}$ (0.305 mmol) in 15 mL of THF; on addition of 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (50 μL) a gas was evolved and the solution remained clear. A white solid precipitated over a period of 30 min as carbon monoxide was bubbled through the solution. Then nitrogen was bubbled through the solution for 10 min to remove excess CO. The resulting white solid was isolated, washed with 15 mL of diethyl ether, and dried in vacuo; yield 0.23 g, 85%; mp 210 °C dec; $\Lambda_M = 91$. Anal. Calcd for $\text{C}_{40}\text{H}_{47}\text{BF}_4\text{O}_4\text{P}_4\text{Ru}$: C, 53.17; H, 5.24; P, 13.71. Found: C, 53.07; H, 5.21; P, 13.56.

Results and Discussion

A. Synthesis of the $\text{RuX}_2(\text{ttp})$ and $\text{RuCl}_2(\text{Cytpp})$ Complexes. Soon after addition of $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (ttp) to a refluxing methanol solution of " $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ", a microcrystalline orange compound separates from the brown solution. The elemental composition of the orange compound agrees with the formulation $\text{RuCl}_2(\text{ttp})$; however, its low solubility prevents its characterization by ^{31}P or ^1H NMR spectroscopy or by cryoscopic measurements. The corresponding bromide complex also was very insoluble in common organic solvents. Thus, the complexes are probably dimeric or polymeric in the solid state (e.g., I or II, respectively).



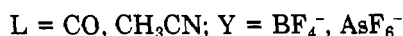
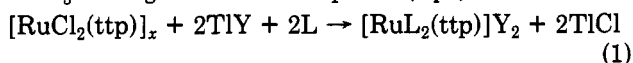
Structure I has also been proposed for the analogous complex $[\text{RuCl}_2(\text{etp})]_2$.¹⁴ The stoichiometrically corresponding complex of a monodentate phosphine, $\text{RuCl}_2(\text{PPh}_3)_3$, has a monomeric distorted square-pyramidal structure with *trans* chlorides and an apical phosphine.²² The far-infrared spectrum (250–600 cm^{-1}) of $[\text{RuCl}_2(\text{ttp})]_x$ has an absorption at 291 cm^{-1} , which is absent in the bromide complex; thus, it is assigned to the Ru–Cl stretching frequency. The reported $\nu(\text{Ru}-\text{Cl})$ values for the dimeric and monomeric forms of $\text{RuCl}_2(\text{etp})$ are at 284 and 332 cm^{-1} , respectively.^{14,15}

In the case of the cyclohexyl (Cy) ligand $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$ (Cytpp), the corresponding bright

green complex RuCl₂(Cyttp) is quite soluble even in non-polar solvents; it is formulated as a monomeric five-coordinate complex. The ³¹P{¹H} NMR spectrum of RuCl₂(Cyttp) in toluene is an A₂X pattern. Spectral characterization data for several ttp and Cyttp complexes are presented in Table I.

B. Ligand Substitution Reactions. Attempts to prepare a tridentate precise analogue to the catalytically active RuH(Cl)(PPh₃)₃ complex were unsuccessful; [RuCl₂(ttp)]_x either failed to give any characterizable products with most reducing agents (i.e., LiAlH₄, H₂/NEt₃) or reacted with excess NaBH₄ to give RuH(BH₄)(ttp),²¹ which contains a unique type of η²-BH₄ ligand; i.e., it is static and coupled to phosphorus at room temperature. Likewise, RuCl₂(Cyttp) failed in our hands to give any characterizable products with several reducing agents (e.g., LiAlH₄, H₂/NEt₃, NaBH₄).

Despite the insolubility of [RuCl₂(ttp)]_x, it proved to be amenable to ligand substitution. In the presence of thallose salts, the chloride ligand can be replaced by CO or CH₃CN to give cationic complexes (eq 1). Both the CO



and CH₃CN complexes were characterized by ³¹P NMR and infrared spectroscopy (Table I). Vector analysis of the ν(CO) absorptions for [Ru(CO)₂(ttp)]²⁺ gives an intraligand OC-Ru-CO angle of 97°.

Recently, Cole-Hamilton et al.²³ have shown that RuCl₂(L-L)₂ (L-L = Ph₂PCH₂PPh₂ or Ph₂PCH₂CH₂PPh₂) can be reacted with CO and silver salts of noncoordinating anions to produce [Ru(CO)₂(L-L)₂]_xY₂ complexes, which are stable to loss of CO. Venanzi^{13b} has also replaced the chloride ions in RuCl₂(QP) via a metathesis reaction; in this case, neutral RuX₂P₄ complexes were prepared, i.e., Ru(NCS)₂(QP) and Ru(CN)₂(QP). Presumably, if Venanzi's QP complexes were treated in the presence of Ag⁺ or TI⁺, [Ru(CO)₂(QP)]²⁺ cations, analogous to Cole-Hamilton's [Ru(CO)₂(L-L)₂]²⁺ and our [Ru(CO)₂(ttp)]²⁺ dicarbonyl cations, could be prepared.

Attempts to substitute acetate for chloride by treatment of RuCl₂(ttp) with excess sodium acetate resulted in the isolation of the mixed six-coordinate complex RuCl(O₂CCH₃)(ttp), 4. The infrared spectrum of 4 shows the carboxylate absorptions at 1530 and 1470 cm⁻¹, indicative of bidentate coordination by the acetate group.²⁴ Since the triphosphine is bound strongly to ruthenium, replacement of the second chloride by acetate would require the second acetate ligand to be monodentate in a six-coordinate Ru(II), d⁶, complex. Evidently a monodentate acetate group does not compete with chloride for the sixth coordination site.

The complex RuH(η²-BH₄)(ttp), 19, undergoes substitution to produce either *cis*-RuH₂(P(OMe)₃)(ttp), 20, or *cis*-[RuH(CH₃CN)₂(ttp)]BF₄, 21, depending on whether the reaction is done in the presence of a base or an acid, respectively.²¹ Addition of 1 equiv of HBF₄·Et₂O to 20 in the presence of CO produces [RuH(CO)(P(OMe)₃)(ttp)]BF₄, 22. The infrared spectrum of 22 shows a strong carbonyl absorption at 1995 cm⁻¹ and a strong ruthenium hydride absorption at 1900 cm⁻¹. Examination of the ³¹P{¹H} NMR spectrum of 22 (Figure 1) reveals that the chemical shift of P₁, the central phosphorus atom of ttp,

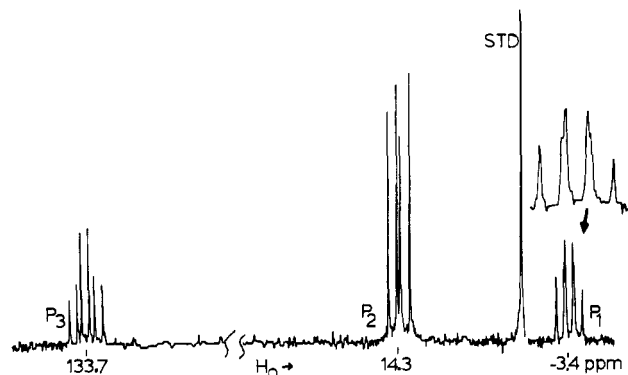
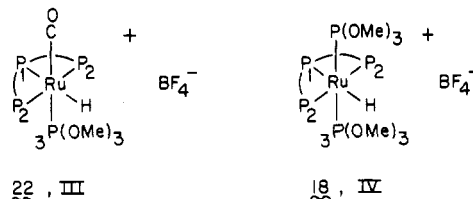


Figure 1. The ³¹P{¹H} NMR spectrum of [RuH(CO)(P(OMe)₃(ttp)]BF₄ at 36.43 MHz in acetone.

is located upfield from that of the wing phosphorus atoms of ttp, P₂. The relative shielding of P₁ and P₂ implies that the ligand trans to P₁ is a strong trans-influence ligand, i.e., either the carbonyl or the hydride.¹⁷ The observed small phosphorus-phosphorus coupling constants are only consistent with the P(OMe)₃ ligand being *cis* to P₁; i.e., the small P-P coupling precludes P(OMe)₃ from being trans to P₁. Also, the fairly large ²J_{H-P} coupling constant (57 Hz) observed in the ¹H NMR spectrum of [RuH(CO)(P(OMe)₃(ttp)]BF₄ is consistent with the hydride being trans to P₁ as shown in III.²⁵ The reaction of 20 with 1 equiv of HBF₄·OEt₂ in the presence of P(OMe)₃ yields the known complex *trans*-[RuH(P(OMe)₃)₂(ttp)]BF₄,²¹ 18 (IV).

The isolated products are consistent with the apical hydride in *cis*-RuH₂(P(OMe)₃)(ttp), 20, being removed preferentially, leading to cationic complexes with structures III and IV, respectively. Addition of a second equivalent



of HBF₄·OEt₂ to either structure III or IV fails to remove the remaining hydride. Apparently, the apical hydrogen of 20 is the most hydridic or at least the most reactive; perhaps it is the most accessible sterically. However, we can not rule out indiscriminate hydride loss from 20, followed by rearrangement to a common five-coordinate intermediate and then subsequent attack by CO or P(OMe)₃.

The lability of the acetonitrile ligands in 21 is demonstrated by the synthesis of [RuH(CH₃CN)(PF₃)(ttp)]BF₄, 17, when PF₃ was bubbled through a solution of 21, which was generated in situ. The infrared spectrum of 17 showed the presence of both CH₃CN (2305 (w) cm⁻¹) and PF₃ (820 (s) cm⁻¹), in addition to the ν(Ru-H) absorption at 2005 cm⁻¹. The ³¹P{¹H} NMR spectrum of 17 (Figure 2) confirms the presence of a PF₃ ligand; its ³¹P{¹H} resonance is centered at 126.0 ppm. Since the multiplet due to the P₁ nucleus is downfield from the P₂ multiplet of ttp, the ligand trans to P₁ must be toward the weak end of the trans-influence series; thus, it can be assigned to acetonitrile. In the Ru-H region, the proton NMR spectrum of 17 shows a beautiful 32-line multiplet (which can be viewed as a doublet of quartet of quartets) at δ -3.6 (Figure 3). The accidental equivalence of the magnetic coupling

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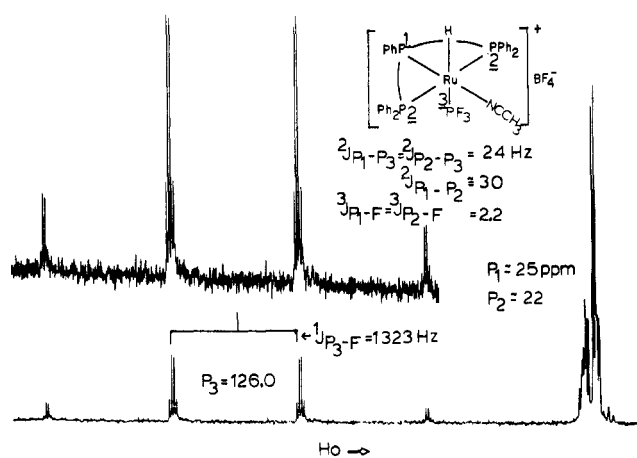


Figure 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{RuH}(\text{MeCN})(\text{PF}_3)(\text{ttp})][\text{BF}_4]$ at 36.43 MHz in acetone.

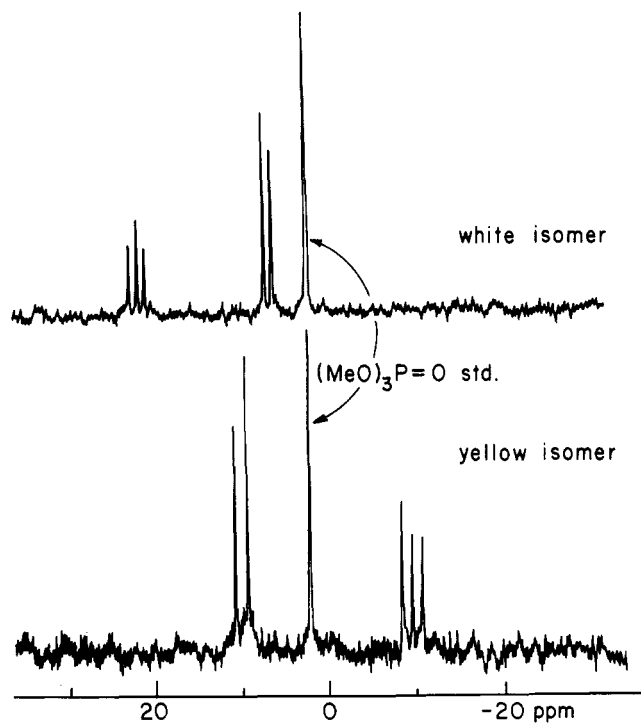


Figure 4. Phosphorus-31 $\{^1\text{H}\}$ NMR spectra of *cis*- $\text{RuCl}_2(\text{ttp})\text{CO}$ (white isomer) and *trans*- $\text{RuCl}_2(\text{ttp})\text{CO}$ (yellow isomer) in THF.

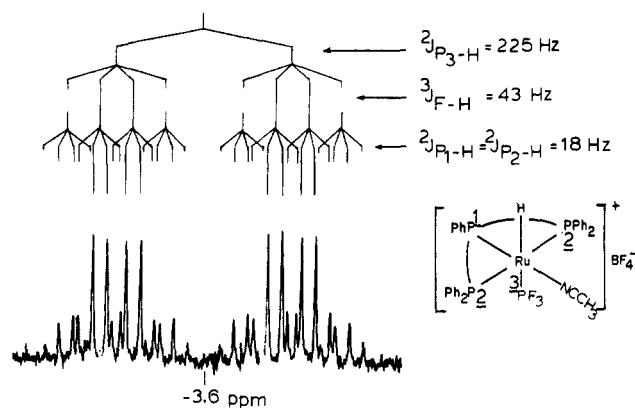
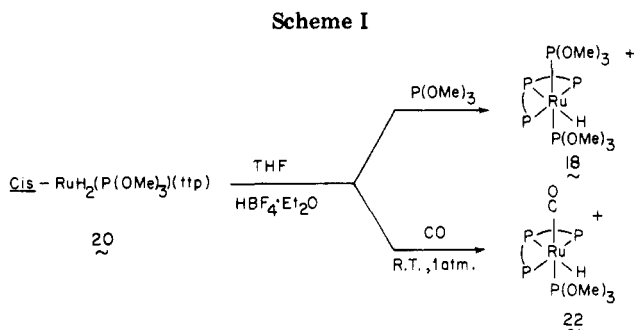
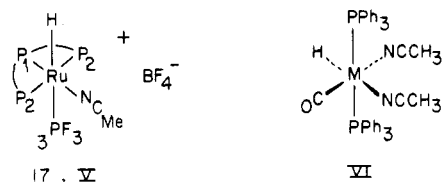


Figure 3. The Ru-H region of the 90-MHz proton NMR spectrum of $[\text{RuH}(\text{MeCN})(\text{PF}_3)(\text{ttp})][\text{BF}_4]$ in acetone- d_6 .

of P_1 and P_2 to P_3 (PF_3) and the hydride is verified in the ^{31}P NMR ($^2J_{\text{P}_1-\text{P}_3} = ^2J_{\text{P}_2-\text{P}_3} = 24$ Hz), the ^{19}F NMR ($^3J_{\text{F}-\text{P}_1} = ^3J_{\text{F}-\text{P}_2} = 22$ Hz), and the ^1H NMR ($^2J_{\text{H}-\text{P}_1} = ^2J_{\text{H}-\text{P}_2} = 18$ Hz) spectra. The large $^2J_{\text{H}-\text{P}_3}$ coupling constant of 225 Hz confirms the assigned stereochemistry around ruthenium, i.e., structure V.

Precedence for the very different lability of the acetonitrile ligands in 21 has been observed in the chemistry of $[\text{MH}(\text{CO})(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2]\text{ClO}_4$, VI ($\text{M} = \text{Ru}, \text{Os}$),⁸ which react rapidly with CO to replace one acetonitrile and much slower with phosphines to replace the second acetonitrile. In our case, treatment of *cis*- $[\text{RuH}(\text{MeCN})_2$



$(\text{ttp})\text{BF}_4$, 21, with excess $\text{P}(\text{O}(\text{Me})_3)$ yields predominantly *trans*- $[\text{RuH}(\text{P}(\text{O}(\text{Me})_3)_2)(\text{ttp})]\text{BF}_4$, 18. The *trans* isomer, i.e., 18, which is the kinetic product,²⁶ is probably formed via a 16-electron, five-coordinate cationic intermediate. This intermediate probably rearranges prior to substitution by the second $\text{P}(\text{O}(\text{Me})_3)$ ligand, since the *trans* isomer is formed rather than the *cis* isomer, which would be the direct substitution product expected from the starting material (i.e., from 21). On the other hand, if $\text{P}(\text{O}(\text{Me})_3)$ is

added to 21 in the presence of excess CH_3CN , complex 18 is not formed cleanly; instead, a white solid is obtained, and it appears to be a mixed $\text{CH}_3\text{CN-P}(\text{O}(\text{Me})_3)$ complex. However, we have been unable to obtain consistent analytical and spectroscopic data on the white solid. It is interesting that a similar white solid can be obtained from the reaction of 20 with CH_3CN and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. The exact role of CH_3CN as a competing ligand in these PF_3 and $\text{P}(\text{O}(\text{Me})_3)$ reactions has not been evaluated adequately; however, excess CH_3CN does compete with the PX_3 ligands. The substitution chemistry of complexes 20 and 21 is summarized in Schemes I and II, respectively.

C. Adduct Formation with the $\text{RuCl}_2(\text{triphosphine})$ Complexes. Treatment of $[\text{RuCl}_2(\text{ttp})]_x$ with CO in

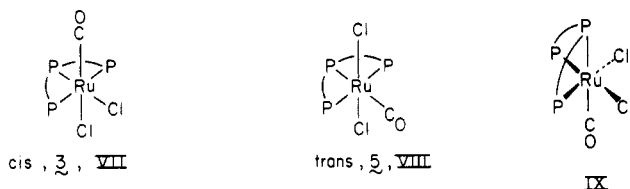
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Table I. Spectral Characterization Data for the Ru PhP(CH₂CH₂CH₂PR₂)₂ (R = C₆H₅, *c*-C₆H₁₁) Complexes

no.	complex	³¹ P NMR ^b			IR ^c	other
		δ(P ₁)	δ(P ₂)	J _{P₁-P₂}		
1	[RuCl ₂ (ttp)]x				291 (ν(Ru-Cl))	
2	RuCl ₂ (Cyttp)	-5.6	15.4	38		
3	<i>cis</i> -RuCl ₂ (CO)(ttp)	21.2	6.0	34	1970 (ν(CO))	
4	RuCl(O ₂ CCH ₃)(ttp)	34.0	39.9	36	1530, 1470 (ν(CO ₂))	
5	<i>trans</i> -RuCl ₂ (CO)(ttp)	-10.2	9.6	44	1980 (ν(CO))	
6	<i>trans</i> -RuCl ₂ (CO)(Cyttp)	-18.6	10.1	41	1950 (ν(CO))	
7	RuCl ₂ (SO ₂)(Cyttp)	9.8	5.6	29	1280, 1112 (ν(SO ₂))	
8	[Ru(NCMe) ₂ (ttp)](BF ₄) ₂	18.2	23.7	43	2325, 2295 (ν(CN))	
9	[Ru(CO) ₂ (ttp)](AsF ₆) ₂	-6.7	2.8	38	2089, 2030 (ν(CO))	
10	Ru(CO) ₂ (ttp)	-0.1	35.0	50	1900, 1845 (ν(CO))	
11	Ru(CO) ₂ (Cyttp)	4.7	38.6	48	1800, 1820 (ν(CO))	
12	<i>cis</i> -[RuBr(CO) ₂ (Cyttp)]AsF ₆	-11.3	7.9	35	2065, 2005 (ν(CO))	ΔM = 92 (CH ₃ NO ₂)
13	<i>cis</i> -[Ru(CO) ₂ (Cyttp)]I	-18.0	2.7	34	2045, 1985 (ν(CO))	ΔM = 94 (CH ₃ NO ₂)
14	<i>cis</i> -[RuH(CO) ₂ (Cyttp)]BF ₄	1.0	25.9	37	2030, 1965 (ν(CO)); 1890 (ν(RuH))	ΔM = 91 (CH ₃ NO ₂)
15	<i>cis</i> -[RuH(CO) ₂ (Cyttp)]AsF ₆	0.4	25.9	37	2030, 1975 (ν(CO)); 1905 (ν(RuH))	ΔM = 95 (CH ₃ NO ₂)
16	Ru(CO) ₂ (CO)(Cyttp)	22.7	12.0	31	1915 (ν(CO)); 1600, 1260, 1247 (ν(CO ₂))	
17	[RuH(MeCN)(PF ₃)(ttp)]BF ₄	~25 ^e	~22	~30	2305 (ν(CN)); 2005 (ν(RuH)); 820 (ν(PF ₃))	¹⁹ F NMR ^f δ = 129
18	<i>trans</i> -[RuH(P(OMe) ₃)(ttp)]BF ₄	-9.6 ^h	19.3	44	1940 (ν(RuH))	ΔM = 90
19	RuH(η ² -BH ₄)(ttp)	34.1	29.8	40	2390 m, 2380 m, 2330 m (ν(B-H)); 1880 s (ν(RuH)); 1180 s (δ(BH ₄))	MS, (M - 4) ⁺
20	<i>cis</i> -RuH ₂ (P(OMe) ₃)(ttp)	16.4 ^j	38.0	36	1925 s, 1860 s (ν(RuH))	MS, M ⁺ , (M - 2) ⁺
21	<i>cis</i> -[RuH(CH ₃ CN) ₂ (ttp)]BF ₄	34.5	27.7	45	2275 w, 2250 w (ν(CN)), 2025 s (ν(RuH))	
22	[RuH(CO)(P(OMe) ₃)(ttp)]BF ₄	-3.4 ^l	14.3	35	1995 (ν(CO)); 1900 (ν(RuH))	ΔM = 91 (CH ₃ NO ₂)

^a Chemical shifts are in δ with respect to Me₄Si (δ 0.0); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; numbers in parentheses are ²J_{H-P₁} and ²J_{H-P₂} in Hz respectively; resonances due to the triphosphine ligands are not included. ^b Chemical shifts are in δ with respect to external 85% H₃PO₄ (δ 0.0); positive values are downfield, coupling constants are in Hz; P₁ is the central phosphorus and P₂ the two terminal phosphorus atoms in the triphosphine ligand. ^c Absorptions are in cm⁻¹; s = strong, w = weak. ^d ³J_{H-F} = 43 Hz; ²J_{H-P₁} = 225 Hz. ^e The chemical shift values of P₁ and P₂ are only approximate due to the complexity of the spectrum; δ(P₁) 126.0, ²J_{P₁-P₂} = 24, ²J_{P₂-P₃} = 24, ¹J_{P₂-F} = 1323, and ³J_{P₁-F} = ³J_{P₂-F} = 1323, ³J_{F-H} = 42.6, and ³J_{F-P₁} = ³J_{F-P₂} = 2.2 Hz. ^f Chemical shift with respect to CCl₄; ¹J_{F-P₁} = 137.3, ²J_{P₁-P₂} = 25, ²J_{P₁-P₃} = 22, ²J_{P₂-P₃} = 50, ²J_{P₂-P₄} = 47, and ²J_{P₃-P₄} = 18 Hz; δ(P(OMe)₃) 3.14 d, ³J_{OCH₃-P} = 10 Hz, δ(P₁) 135.6; δ(P₂) 137.3; ²J_{P₁-P₂} = 25, ²J_{P₁-P₃} = 22, ²J_{P₂-P₃} = 50, ²J_{P₂-P₄} = 47, and ²J_{P₃-P₄} = -575 Hz. ^g H_A (trans to P₃, P(OMe)₃), H_B trans to P₁; ²J_{H_A-P₃} = 134, ²J_{H_B-P₃} = 18, and ²J_{H_A-H_B} = 5 Hz; δ(P(OCH₃)) = 3.12, ³J_{OCH₃-P} = 9.5 Hz. ^h ²J_{H_A-P₃} = 18, and ²J_{H_B-P₃} = 17, ²J_{P₂-P₃} = 33 Hz). ⁱ ²J_{H_A-P₃} = 26; δ(P(OMe)₃) 2.27 d, ³J_{OCH₃-P} = 10 Hz. ^j δ(P(OMe)₃) 133.7, ²J_{P₁-P₂} = 29 Hz, ²J_{P₂-P₃} = 49 Hz.

CH_2Cl_2 at room temperature produces a white, six-coordinate compound $\text{RuCl}_2(\text{CO})(\text{ttp})$, with an infrared carbonyl absorption at 1970 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{RuCl}_2(\text{CO})(\text{ttp})$ in CH_2Cl_2 is presented in Figure 4, and the parameters are summarized in Table I. A compound of the same composition can be prepared by adding ttp to a CO-saturated, refluxing solution of "RuCl₃·3H₂O" in ethanol. In this case, however, the solid is yellow, and it has a carbonyl absorption at 1980 cm^{-1} with a shoulder at slightly higher energy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the yellow compound in CH_2Cl_2 is included in Figure 4 for direct comparison with the white compound. Note that the P₁ resonance in the yellow isomer occurs ~30 ppm to higher field than it does in the white isomer. We have observed that this chemical shift difference is associated with the relative trans influence of the ligand trans to the nucleus under observation.^{17,27} The P₁ resonance of these $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$ complexes generally shifts to higher field with an increasing trans influence of the ligand located trans to P₁. On this basis, the structure of the white compound is assigned the cis isomer VII, whereas the yellow compound is the trans isomer VIII. A folded arrangement of the ttp ligand to



give a structure like IX can be excluded on the basis of the P₂ chemical shift values, which are more shielded than would be expected if those phosphorus nuclei were trans to chlorides (e.g., see 4 in Table I). The slightly different carbonyl stretching frequencies are also consistent with this structural assignment; a CO ligand trans to a phosphine is expected to have its $\nu(\text{CO})$ at higher energy than when it is trans to chloride, owing to the reduced effectiveness of $d\pi^* \text{M} \rightarrow \text{CO}$ bonding when CO is competing with a phosphorus atom. Mawby found the same effect in the infrared spectra of *cis*- and *trans*- $\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3$ ($\nu(\text{CO})$: *cis*, 1952 cm^{-1} ; *trans*, 1980 cm^{-1}).²⁸ Chatt et al. prepared *cis*- and *trans*- $\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3$; the *cis* isomer is white and the *trans* isomer is yellow, as observed for our compounds VII and VIII.²⁹ It is interesting that for *trans*- $\text{RuCl}_2(\text{CO})(\text{ttp})$ the P–P coupling is 10 Hz greater than it is for the *cis* isomer; the reason for the different P–P couplings is not obvious to us.

Exposure of green $\text{RuCl}_2(\text{Cytpp})$ to carbon monoxide yields a pale yellow carbonyl complex. Its infrared spectrum shows a carbonyl absorption at 1950 cm^{-1} , and its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (toluene solution) has $\delta(\text{P}_1)$ -18.6 and $\delta(\text{P}_2)$ 10.1 , indicating that the product is *trans*- $\text{RuCl}_2(\text{CO})(\text{Cytpp})$. Thus, carbon monoxide appears to add to $[\text{RuCl}_2(\text{ttp})]_x$ to give a *cis*- $\text{RuCl}_2(\text{CO})(\text{ttp})$ product, whereas it adds to $\text{RuCl}_2(\text{Cytpp})$ to produce the *trans* isomer.

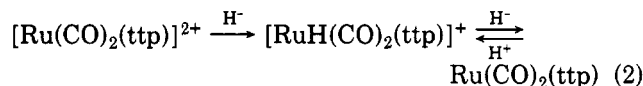
The reactivities of $[\text{RuCl}_2(\text{ttp})]_x$ and $\text{RuCl}_2(\text{Cytpp})$ toward SO_2 at room temperature are markedly different. The insoluble, polymeric ttp compound is unaffected by SO_2 , whereas $\text{RuCl}_2(\text{Cytpp})$ quickly forms a pink SO_2 adduct which has strong $\nu(\text{S}-\text{O})$ absorptions at 1280 cm^{-1} (asym) and 1112 cm^{-1} (sym). These S–O stretching fre-

quencies indicate that the geometry of the M–SO₂ unit is coplanar rather than pyramidal. A related compound, $\text{OsH}(\text{Cl})(\text{CO})(\text{PCy}_3)_2\text{SO}_2 \cdot 2\text{CHCl}_3$, was reported recently; it has SO_2 absorptions at 1284 and 1109 cm^{-1} , and an X-ray crystallography study showed that the Os–SO₂ geometry is coplanar.³⁰ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a toluene solution of the SO_2 adduct shows a decreased phosphorus–phosphorus coupling constant ($^2J_{\text{P-P}} = 29\text{ Hz}$), which is generally associated with higher metal oxidation states,³¹ perhaps reflecting the π acidity of the SO_2 ligand.

D. $\text{Ru}^0\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$ Complexes. The ruthenium(0) complexes $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Ru}(\text{CO})_3(\text{diphos})$, and $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ catalyze the hydroformylation of olefins¹¹ and the conversion of aldehydes and ketones to alcohols.³² Thus, we were interested in comparing the structural and catalytic properties of ruthenium(0) complexes of the tridentate ligands ttp and Cytpp with those of stoichiometrically analogous complexes of monophosphines.

The sparsely soluble polymeric compound $[\text{RuCl}_2(\text{ttp})]_x$ was reduced with Na/Hg amalgam in THF, while a stream of carbon monoxide was bubbled through the solution. The product $\text{Ru}(\text{CO})_2(\text{ttp})$ was isolated from the reaction mixture in 55% yield. The compound has carbonyl absorptions in the infrared spectrum at 1900 and 1845 cm^{-1} ; however, elemental analysis showed that a small amount of chloride was present, so another route was sought for preparation of pure $\text{Ru}(\text{CO})_2(\text{ttp})$. Prolonged refluxing of $\text{Ru}_3(\text{CO})_{12}$ with ttp in benzene also produced $\text{Ru}(\text{CO})_2(\text{ttp})$. This material was purified by column chromatography to give pure $\text{Ru}(\text{CO})_2(\text{ttp})$ as the primary product, along with some starting material, $\text{Ru}_3(\text{CO})_{12}$. The infrared spectrum of this sample shows two carbonyl absorptions at 1900 and 1845 cm^{-1} and vector analysis of these infrared absorptions gives an OC–Ru–CO angle of 104° . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a THF solution of $\text{Ru}(\text{CO})_2(\text{ttp})$ is an A₂B pattern with $^2J_{\text{P-P}} = 50\text{ Hz}$. The relative position of $\delta(\text{P}_1)$ (upfield from $\delta(\text{P}_2)$) indicates that P₁ is probably trans to a carbonyl.¹⁷

The $\text{Ru}(\text{CO})_2(\text{ttp})$ complex can also be prepared by reduction of $[\text{Ru}(\text{CO})_2(\text{ttp})][\text{BF}_4]_2$ with at least a twofold excess of LiHBEt_3 in THF. The reaction is stepwise and goes through the monohydride intermediate $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4$ as shown in eq 2. No evidence for hydride



attack at the carbonyl carbon could be found in the ¹H NMR spectrum. Furthermore, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ reacts with $\text{Ru}(\text{CO})_2(\text{ttp})$ to produce $[\text{RuH}(\text{CO})_2(\text{ttp})]\text{BF}_4$ directly. The compound $\text{Ru}(\text{CO})_2(\text{ttp})$ can also be prepared from $[\text{Ru}(\text{CO})_2(\text{ttp})]^{2+}$ by using an excess of CH_3Li , although the analogous methyl intermediate $[\text{RuCH}_3(\text{CO})_2(\text{ttp})][\text{BF}_4]$ was not detected.

The compounds $\text{Ru}(\text{CO})_2(\text{ttp})$ and $[\text{Ru}(\text{CO})_2(\text{ttp})][\text{BF}_4]_2$ are interesting examples of isoleptic complexes, in which the occupancy of the metal's d orbitals differ by two electrons. On the basis of the analysis of Rossi and Hoffman,³³ the cationic complex (d^6 electronic configuration) should be square pyramidal with the triphosphine in the basal plane, whereas the d^8 complex should be

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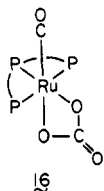
trigonal bipyramidal, with the triphosphine spanning axial-equatorial-axial positions. From the infrared $\nu(\text{CO})$ data the calculated angle between the CO ligands in the d⁶ compound is 97°, whereas this angle is calculated to be 104° for the d⁸ complex.

The more bulky triphosphine ligand Cyttp also forms Ru(CO)₂(Cyttp) directly from Ru₃(CO)₁₂. The carbonyl infrared absorptions are shifted to lower energies than in the ttp compound (1880 and 1820 cm⁻¹), which is consistent with the expected effect of a more basic ligand. From the relative intensities of these absorptions the OC-Ru-CO angle is calculated to be 95°. The ³¹P{¹H} NMR spectrum of Ru(CO)₂(Cyttp) in toluene is an A₂B pattern with ²J_{P-P} = 48 Hz. The relative positions of $\delta(\text{P}_1)$ and $\delta(\text{P}_2)$ ($\delta(\text{P}_1)$ upfield) again shows that P₁ is trans to a carbonyl ligand.

Gladysz^{34a} found that LiHBEt₃ reacts with certain carbonyl complexes such as (CO)₅Re-Re(CO)₅ and CpRe(CO)₂NO⁺BF₄⁻ to give Li[(CO)₅Re-Re(CHO)(CO)₄·THF] and CpRe(CO)(NO)(CHO), respectively. At room temperature, we can find no evidence for a formyl intermediate in the reaction of LiHBEt₃ with [Ru(CO)₂(ttp)][BF₄]₂. The reduction of [Ru(CO)₂(ttp)][BF₄]₂ to Ru(CO)₂(ttp) (Ru(II) → Ru(0)) with LiHBEt₃ has precedence in the literature; for example, H₂Ru₄(CO)₁₄ reacts with 2 equiv of K[*sec*-C₄H₉]₃BH] to give K₂[H₂Ru₄(CO)₁₂] and hydrogen—a net four-electron reduction.³⁵ In view of Gladysz' recent low-temperature syntheses of kinetically unstable formyls, our [Ru(CO)₂(ttp)]²⁺ cation will be reinvestigated at low temperature, perhaps via Gladysz' "transformylation" reactions.^{34b}

E. Oxidative Addition Reactions of the Ruthenium(0) Triphosphine Complexes. Ruthenium(0) carbonyl phosphine complexes would be expected to undergo oxidative addition reactions;³⁶ however, Ru(CO)₃(PPh₃)₂ is remarkably stable toward hydrogen at room temperature and atmospheric pressure³⁷ possibly due to the electron-withdrawing property of the three carbonyl ligands. Higher temperatures (130 °C) and pressures (120 atm) are required for Ru(CO)₃(PPh₃)₂ to react with hydrogen to give RuH₂(CO)₂(PPh₃)₂. The complex Ru(CO)₂(PPh₃)₃ exhibits greater reactivity—a direct result of the larger number of phosphine ligands.⁸ In fact, addition of various ligands L (L = H₂, C₂H₄, PhC≡CPh, and O₂) to Ru(CO)₂(PPh₃)₃ at room temperature and atmospheric pressure produced the corresponding adducts RuL(CO)₂(PPh₃)₂. The reactivity of the stoichiometrically analogous complexes Ru(CO)₂(ttp) and Ru(CO)₂(Cyttp) with various oxidative addition reagents is of interest, since neither of these complexes should lose a phosphine ligand, due to the chelate effect.

The Ru(CO)₂(triphosphine) complexes described in section D are very reactive toward oxygen; yet the triphosphine ligand is not oxidized. Oxygen was bubbled through a solution of Ru(CO)₂(Cyttp) in benzene to give the carbonate-carbonyl complex Ru(CO₃)(CO)(Cyttp), 16.



The infrared spectrum of this compound exhibited strong

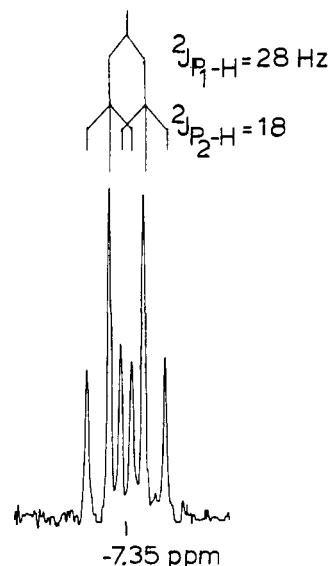
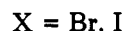


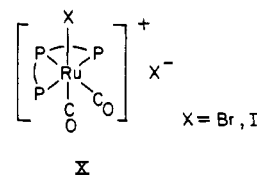
Figure 5. The ruthenium hydride region of the proton NMR spectrum of [RuH(CO)₂(Cyttp)]BF₄ at 90 MHz in acetone-d₆.

absorptions characteristic of a bidentate carbonate at 1600, 1260, and 1247 cm⁻¹, in addition to the CO stretching frequency at 1915 cm⁻¹.²⁴ The same compound can also be prepared simply by allowing solid Ru(CO)₂(Cyttp) to stand in air for several weeks. The analogous reaction of Ru(CO)₂(ttp) with oxygen in solution or in the solid state gave an uncharacterizable brown solid. It is known that the complexes IrCl(CO)(tripod)³⁸ (tripod = 1,1,1-tris((diphenylphosphino)methyl)ethane) and OsCl(CO)(NO)(PPh₃)₂³⁹ react with molecular oxygen to give Ir(CO₃)(Cl)(tripod) and Os(CO₃)(Cl)(NO)(PPh₃)₂, respectively. Nappier and Meek found a similar result in the reaction between carbon monoxide and RhCl(O₂)(ttp), which gave the carbonate complex [Rh(CO₃)(Cl)(ttp)].⁴⁰

A variety of electrophilic reagents react with Ru(CO)₂(Cyttp) to give oxidative addition products. Molecular halogens (e.g., Br₂ and I₂) produce dicarbonyl complexes that are uni-univalent electrolytes (eq 3). If two or more Ru(CO)₂(Cyttp) + X₂ → *cis*-[RuX(CO)₂(Cyttp)]X (3)



equivalents of either Br₂ or I₂ are used, the same cations are obtained. The products obtained via eq 3 have the coordinated halide located *cis* to the three meridional phosphorus atoms, since the infrared spectra of these complexes show two equally strong carbonyl absorptions characteristic of *cis* carbonyls. Also, the ³¹P NMR spectra of these complexes support the proposed structure X. In



both cases, the phosphorus chemical shift of P₁ is located upfield from that of P₂, which suggests that a carbonyl ligand is trans to P₁. The reaction of Ru(CO)₂(ttp) with

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either Br₂ or I₂ produced a mixture of products, which proved to be very difficult to separate from each other, since these compounds are much less soluble than the Cyttp analogues.

Treatment of Ru(CO)₂(Cyttp) with HBF₄ produces [RuH(CO)₂(Cyttp)]BF₄, 14. This complex has the hydride ligand located cis to the three phosphorus atoms; the stereochemistry is deduced from the ¹H NMR spectrum (Figure 5), which has ²J_{P-H} = 28 and 18 Hz. These coupling constants are in the range observed for metal hydrides coupled to cis phosphine ligands (13–39 Hz);⁴¹ the analogous complex of the ttp ligand exhibited ²J_{P-H} values of 27 and 19 Hz.^{21,43} The infrared spectrum of 14 showed two equally strong carbonyl stretching frequencies at 2030 and 1965 cm⁻¹ and a ν(Ru–H) absorption at 1905 cm⁻¹. Addition of 1 equiv of either aqueous HCl or HBr to Ru(CO)₂(Cyttp) produces the analogous complexes [RuH(CO)₂(Cyttp)]X (X = Cl, Br). The cationic nature of the chloride and bromide complexes was confirmed by treating them with NaAsF₆ in ethanol to produce [RuH(CO)₂(Cyttp)]AsF₆. Table I contains additional data on those complexes.

We could not find from the literature that Ru(CO)₂(PPh₃)₃ has been reacted with halogens or strong protonic acids; in contrast, Ru(CO)₃(PPh₃)₂ has been reacted with I₂, Br₂, HCl, and HBr to give the dihalide complexes RuX₂(CO)₂(PPh₃)₂.⁴² Since Cyttp is both more basic (or nucleophilic) and bulky than the two triphenylphosphine

ligands in Ru(CO)₃(PPh₃)₂, a comparison of the reactivity of Ru(CO)₂(Cyttp) with Ru(CO)₃(PPh₃)₂ may not be appropriate. However, if the ruthenium atom in Ru(CO)₃(PPh₃)₂ is replaced with the more basic metal osmium, the resultant complex Os(CO)₃(PPh₃)₂ should better mimic the reactivity of Ru(CO)₂Cyttp. Indeed, Os(CO)₃(PPh₃)₂ reacts with HX (X = Cl, Br, I) to give OsX₂(CO)₂(PPh₃)₂ and with X₂ (X = Br, I) to produce [OsX(CO)₃(PPh₃)₂]X;³⁶ the latter is very similar to products obtained from the reaction of Ru(CO)₂(Cyttp) with various oxidative addition reagents.

The complex Ru(CO)₂(ttp) is reactive and functions chemically in a manner similar to Ru(CO)₂(PPh₃)₃, whereas Ru(CO)₂(Cyttp) is intermediate in reactivity between Ru(CO)₃(PPh₃)₂ and Ru(CO)₂(PPh₃)₃, due to its increased basicity and steric bulk. Furthermore, the chelating nature of Cyttp causes loss of a carbonyl ligand from ruthenium during the oxidative addition reactions rather than detachment of one of the phosphine groups of Cyttp.

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Registry No. 1, 81616-72-0; 2, 84623-42-7; 3, 84623-43-8; 4, 84623-44-9; 5, 84709-74-0; 6, 84623-45-0; 7, 84623-46-1; 8, 84623-48-3; 9, 84623-50-7; 10, 84623-51-8; 11, 83146-93-4; 12, 84623-53-0; 13, 84623-54-1; 14, 84623-56-3; 15, 84623-57-4; 16, 84623-58-5; 17, 84623-60-9; 18, 81654-88-8; 19, 81624-51-3; 20, 81616-41-3; 21, 81616-38-8; 22, 84623-62-1; [RuBr₂(ttp)]_x, 84623-64-3; [Ru(ttp)(NCMe)₂][(AsF₆)₂], 84623-65-4; [Ru(ttp)(CO)₂][BF₄]₂, 84623-66-5; [RuH(CH₃CN)(P(OMe)₃)(ttp)]BF₄, 84623-68-7; RuCl₂(PPh₃)₃, 15529-49-4; Ru₃(CO)₁₂, 15243-33-7; *cis*-[RuH(CO)₂(ttp)]BF₄, 81616-36-6.

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