envelope, 16 H), 0.87 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 180.25 (COOH), 34.16, 31.95, 29.62, 29.51, 29.34, 29.12, 24.74, 22.73, 14.15 (CH_3).

5-Iodopentanoic Acid. Trimethylsilyl 4-pentenoate (2.0 mmol, 0.35 g, 0.44 mL) in THF (2 mL) was slowly added to freshly prepared dicyclohexylborane (2 mmol) and the mixture stirred at 0 °C for 2 h, then gradually allowed to come to room temperature, and stirred for an additional 2 h. The reaction mixture was cooled to 0 °C and shielded from light by wrapping the flask with aluminum foil, and sodium acetate (1 M in anhydrous methanol, 4 mmol) and iodine monochloride (1 M in anhydrous methanol, 2 mmol) were sequentially added. The contents were stirred for 1 min and quenched by addition of sodium thiosulfate (1 M, 5 mL). The reaction mixture was adjusted to pH 10 with 1 N NaOH, water (20 mL) and ether (20 mL) were added, the reaction mixture was saturated with salt, and the organic layer was separated. The aqueous layer was washed twice more with ether (20-mL portions), acidified to pH 3 with 1 N HCl, and extracted with ether (3 × 25 mL). The combined organic layer was then dried over anhydrous magnesium sulfate. Filtration, followed by removal of the solvent under reduced pressure gave the crude product. Purification by column chromatography (silica gel, 10%, then 15%, and then 20% ethyl acetate–petroleum ether) afforded 5-iodopentanoic acid, 0.27 g (76%), as a colorless oil: ^1H NMR ($CDCl_3$) δ 6.2 (br, COOH), 3.19 (t, 2 H, J = 6.6 Hz, CH_2I), 2.39 (t, 2 H, J = 6.6 Hz, CH_2COOH), 2.05–1.5 (m, 4 H); ^{13}C-NMR ($CDCl_3$) δ 178.60 (COOH), 32.87 (CH_2COOH), 32.68 (RCH_2CH_2I), 25.63 (RCH_2CH_2COOH), 5.67 (CH_2I).

10-Undecenylboronic Acid. An oven-dried 250-mL round-bottomed flask fitted with a septum inlet was equipped with a magnetic stirring bar and gas outlet, flame-dried, and purged with nitrogen. Trimethylsilyl 10-undecynoate (4.82 mmol, 1.23 g) was introduced to the flask, followed by the slow addition of catecholborane (4.82 mmol, 0.51 mL), and the contents were stirred at 40 °C for 19 h. Water (150 mL) was added and the mixture stirred overnight to hydrolyze the boronic ester. The aqueous layer was decanted off, the solid boronic acid dissolved in ether and washed with cold water (2 × 50 mL), and the product precipitated by addition of petroleum ether. The product was redissolved in ether and crystallized by the addition of petroleum ether to afford 0.96 g (87%) of 10-undecenylboronic acid as a white powder: ^1H NMR (DMSO-d_6) δ 11.8 (br, COOH), 6.65–6.2 (m, 1 H, $(HO)_2BCH{=}CHR$), 5.45–5.15 (m, 1 H, J_{trans} = 18.0 Hz, $(HO)_2BCH{=}CHR$), 2.3–1.8 (m, 4 H, $(HO)_2BCH{=}CHCH_2R$, CH_2COOH), 1.7–1.1 (broad envelope, 12 H); ^{13}C NMR (DMSO-d_6) δ 174.50 (COOH), 150.01 ($(HO)_2BCH{=}CHR$), 35.08, 33.70, 28.66, 28.12, 24.55; ^{13}C NMR (acetone-d_6) δ 175.74 (COOH), 152.20 ($(HO)_2BCH{=}CHR$), 36.76, 34.79, 30.67, 30.48, 30.4, 29.86, 26.15; ^{11}B NMR (THF) δ 27.3.

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Registry No. ^{29}Si, 14304-87-1; trimethylsilyl 10-undecenoate, 24338-09-8; 10-undecenoic acid, 112-38-9; trimethylsilyl 4-pentenoate, 23523-56-0; 4-pentenoic acid, 591-80-0; trimethylsilyl hexanoate, 14246-15-2; hexanoic acid, 142-62-1; trimethylsilyl (*Z*)-9-octadecenoate, 21556-26-3; oleic acid, 112-80-1; trimethylsilyl 3-cyclohexene-1-carboxylate, 104171-36-0; 3-cyclohexene-1-carboxylic acid, 4771-80-6; trimethylsilyl 10-undecynoate, 118798-27-9; 10-undecynoic acid, 2777-65-3; 11-hydroxyundecanoic acid, 3669-80-5; 11-iodoundecanoic acid, 63632-65-5; undecanoic acid, 112-37-8; propionic acid, 79-09-4; 5-iodopentanoic acid, 19448-36-3; 10-undecenylboronic acid, 118798-28-0.

Synthesis, Characterization, and Reactivity of Alkoxide and Hydroxide Complexes of Rhodium(I) and Iridium(I)[1]

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Bimetallic alkoxide- and hydroxide-bridged complexes of rhodium(I) and iridium(I), $[M(OR)COD]_2$ (M = Rh, Ir; R = H, alkyl or aryl group; COD = 1,5-cyclooctadiene), were prepared and used in the synthesis of four-coordinate alkoxide and hydroxide complexes of rhodium(I) and iridium(I) containing the chelating triphosphine ligands ttp $\{C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2\}$ or Cyttp $\{C_6H_5P[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}$, i.e. M(OR)(ttp) or M(OR)(Cyttp). The basicity of the Rh–OR bond in Rh(OH)(ttp) and $Rh(OC_6H_5)(ttp)$ was tested by use of reactions with weak organic acids; consequently, a series of rhodium carboxylates (e.g., $Rh(OC(O)CF_3)(ttp)$, $Rh(OC(O)C_6H_4Br)(ttp)$, and $Rh(OC(O)C_6H_5)(ttp)$) was formed. Sulfur dioxide insertion reactions led to metal sulfonates and metal sulfonic acids, i.e. $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$, $Rh(SO_2OC_6H_5)(Cyttp){\cdot}SO_2$, $Ir(SO_2OC_6H_5)(ttp){\cdot}SO_2$, and $Rh(SO_2OH)(ttp){\cdot}SO_2$. The three olefins ($CH_2{=}CH_2$, $Cl_2C{=}CClH$, and $(CN)_2C{=}C(CN)_2$) failed to react with Rh(OH)(ttp) or $Rh(OC_6H_5)(ttp)$ to produce insertion products or simple olefin adducts. All metal complexes were characterized by elemental analysis and infrared and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Although extensive work has been published on alkoxide derivatives of early and inner transition metals and of main-group metals,[3,4] until recently, few investigations of group VIII metal alkoxide complexes have been undertaken. In fact, this topic has been reviewed in the literature only once.[4b] Metal alkoxide intermediates have been postulated in the formation of metal hydrides from alcohols,[5-10] Pd(II)-catalyzed vinyl interchange reactions,[11,12] metal-catalyzed hydroformylation reactions,[13] and the

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metal-catalyzed hydrogenation of CO.[14]

In comparison to metal alkoxide complexes, relatively few studies of group VIII metal hydroxide complexes have been undertaken. However, platinum and rhodium hydroxide complexes catalyze the hydration of nitriles to carboxamides,[15-19] and platinum(II) hydroxide complexes catalyze hydration of olefins.[20] In addition, metal hydroxide complexes have been postulated as intermediates in the Wacker process.[13] These reactions have stimulated the current interest in alkoxide and hydroxide derivatives of the second- and third-row group VIII metal ions, and several papers on this topic have been published during the past 2 years.

Direct studies of the syntheses, physical properties, and chemical reactivities of alkoxide and hydroxide derivatives of the group VIII metal ions should provide rich and prolific areas of investigation. However, until recently, most of the hydroxide and alkoxide derivatives of the group VIII metals were discovered fortuitously during other investigations. Mononuclear methoxide and hydroxide derivatives of platinum(II) have been studied most comprehensively;[4b] in contrast, only a few mononuclear rhodium alkoxide and hydroxide complexes are known.[21-23] Recent work on alkoxide and hydroxide derivatives of Ir(I) has been dominated by reports of $Ir(OR)(CO)(PPh_3)_2$ complexes by Atwood and co-workers.[24-30]

The focus of this investigation is the synthesis, characterization, and reactivity of alkoxide and hydroxide derivatives of mononuclear rhodium and iridium complexes of chelating triphosphines, M(OR)(triphos) (M = Rh(I) or Ir(I); triphos = $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$, ttp, or $C_6H_5P[CH_2CH_2CH_2P(C_6H_{11})_2]_2$, Cyttp). Metal complexes coordinated to triphosphine ligands offer two advantages over the more common group VIII metal alkoxide and hydroxide complexes that incorporate monophosphine analogues: first, the chelate effect reduces the tendency of the ligand to dissociate from the metal; and second, the four-coordinate geometry imposed by the triphosphine ligand leaves the molecules sterically and electronically unsaturated. In addition, the chelating triphosphine ligands provide an electron-rich metal center that should favor reactive rhodium and iridium alkoxide or hydroxide bonds. Hence, these compounds may find considerable utility as halide-free catalysts for organic transformations.

Experimental Section

A. General Procedure. All reactions were carried out by use of standard Schlenk and inert-atmosphere box techniques.[31] Reagent grade solvents were dried by use of conventional methods[32] and distilled under Ar. Absolute ethanol, distilled water, acetone, and 2,2,2-trifluoroethanol were purged with an Ar stream for 20 min prior to use. Trifluoroacetic acid (99.9%+) was degassed three times by using the freeze-thaw method. Methanol and absolute ethanol were dried over magnesium turnings and distilled under Ar. Reagent chemicals were purchased in the highest purity possible and used directly. $[Rh(OH)COD]_2$ (COD = 1,5-cyclooctadiene),[33] Cyttp,[34] and ttp[34] were prepared by use of literature procedures.

The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM250 FT NMR spectrometer operating at 101.256 MHz in 5-mm NMR tubes and are referenced to external 85% H_3PO_4. Proton NMR spectra were recorded on a Bruker WP80 FT NMR spectrometer operating at 80.07 MHz in 5-mm NMR tubes. The ^1H spectra are referenced to internal tetramethylsilane (TMS). Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. The samples were prepared as either Nujol mulls between KBr or CsI plates or as KBr pellets, and the spectra are referenced to the sharp 1601 cm^{-1} peak of a polystyrene film. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. The alkoxide and hydroxide complexes were not recrystallized before elemental analyses were performed. Recrystalizations were unsuccessful due to the thermal instabilities of the alkoxide and hydroxide complexes and solubility problems. Traces of Rh(Cl)(ttp) and Ir(Cl)(ttp) were observed in the spectra of the alkoxide and hydroxide complexes, due to the presence of residual chloride ion.

B. Synthesis of the Metal Complexes. 1. $[Rh(OC_6H_5)COD]_2$. A mixture of 10.4 g (111 mmol) of phenol and 0.63 g (11 mmol) of KOH was heated with a heat gun until the phenol melted and the KOH dissolved. This solution was added to 2.680 g (5.438 mmol) of $[RhCl(COD)]_2$[35] in 250 mL of CH_2Cl_2. A pale yellow solid precipitated immediately, and the slurry was stirred for 3 h. The solvent was removed in vacuo to give a yellow paste to which was added 150 mL of distilled water followed by 100 mL of CH_2Cl_2. The solution was stirred vigorously for several minutes, the layers were allowed to separate, and the water layer was removed with a cannula. The yellow solid remaining in the methylene chloride layer was washed four times with 100 mL aliquots of distilled water, then collected on a Schlenk frit, and dried in vacuo. Yield: 2.5 g, 75%. Anal. Calcd (Found): C, 55.28 (54.65); H, 5.75 (5.75).

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2. [Rh(OCH$_2$CF$_3$)COD]$_2$. A solution of 0.50 g (8.9 mmol) of KOH in 40 mL of CF$_3$CH$_2$OH was added to a solution of 2.00 g (4.06 mmol) of [RhCl(COD)]$_2$[35] in 200 mL of CH$_2$Cl$_2$. A yellow slurry formed immediately, and it was stirred for 1 h. The solvent was removed in vacuo, and the solid yellow residue was washed with 60 mL of CF$_3$CH$_2$OH and then 150 mL of distilled water. The solid was collected by vacuum filtration, and it was washed with water until all traces of Cl were gone from the filtrate (as tested with aqueous AgNO$_3$). The solid was dried in a dessicator and then stored under Ar. Yield: 2.4 g, 94%. Anal. Calcd (Found): C, 38.73 (39.02); H, 4.55 (4.56); F, 18.38 (18.12).

3. [Rh(OCH$_2$CH$_3$)COD]$_2$·2H$_2$O. A solution of 2.41 g (43.0 mmol) of KOH in a minimum amount of absolute ethanol was added to 4.2399 g (8.6018 mmol) of [RhCl(COD)]$_2$[35] suspended in 180 mL of acetone. The slurry immediately became yellow, and it was stirred for 2 h. The solution was concentrated to $^1/_3$ volume in vacuo, and the yellow solid was collected on a Schlenk frit, washed two times with 10-mL aliquots of acetone, and dried in vacuo. Yield: 4.66 g, 99.6%. The analytically pure sample was obtained by recrystallization from a hot 1:1 CH$_2$Cl$_2$/hexane mixture. The infrared spectrum displayed peaks due to coordinated water, perhaps arising from wet solvents. Anal. Calcd (Found): C, 43.81 (43.73); H, 6.99 (6.09).

4. Rh(OH)(ttp). A 39.0-mL (7.07-mmol) aliquot of 0.1813 M ttp in toluene was added to a suspension of 1.50 g (3.29 mmol) of [Rh(OH)COD]$_2$ in 125 mL of toluene. The slurry immediately became yellow-red, and it was stirred overnight. The solution was concentrated in vacuo to 30 mL; then 20 mL of cold hexane was added. The resultant yellow solid was collected on a Schlenk frit, washed three times with 4.0-mL aliquots of cold toluene and four times with 4.0-mL aliquots of cold hexane, and dried in vacuo. Yield: 3.06 g, 68.2%. Anal. Calcd (Found): C, 63.34 (63.28); H, 5.61 (5.73); P, 13.61 (13.48).

5. Rh(OC$_6$H$_5$)(ttp). A 15.3-mL (2.77-mmol) aliquot of a 0.1813 M solution of ttp in toluene was diluted with 60 mL of toluene and then added in small aliquots over several minutes to a suspension of 0.7081 g (1.164 mmol) of [Rh(OC$_6$H$_5$)COD]$_2$ in 30 mL of toluene. The resulting clear magenta-colored solution was stirred overnight. The solution was concentrated to 30 mL in vacuo, and 20 mL of hexane was added. The solid was collected on a Schlenk frit, washed two times with 5.0-mL aliquots of hexane, followed by 5.0 mL of cold toluene and 5.0 mL of hexane, and dried in vacuo. The solid turned orange when it was dried. Yield: 1.36 g, 76.8%. Anal. Calcd (Found): C, 66.50 (66.37); H, 5.58 (5.65); P, 12.25 (12.11).

6. Rh(OCH$_2$CF$_3$)(ttp). A 9.60-mL (1.74-mmol) aliquot of a 0.1813 M solution of ttp in toluene was added to a solution containing 0.5162 g (0.8322 mmol) of [Rh(OCH$_2$CF$_3$)COD]$_2$ in 40 mL of toluene. The resulting solution was stirred for 3 h, and then it was concentrated to 5 mL in vacuo and 5.0 mL of cold hexane was added. The resulting yellow solid was collected on a Schlenk frit, washed three times with 2.0-mL aliquots of cold toluene and two times with 2.0 mL aliquots of cold hexane, and dried in vacuo. Yield: 1.13 g, 89.0%. Anal. Calcd (Found): C, 59.70 (59.06); H, 5.14 (5.15); P, 12.15 (10.63); F, 7.45 (6.10).

7. [Ir(OH)COD]$_2$. A solution of 0.35 g (6.2 mmol) of KOH in 15 mL of distilled water was added to a red suspension of [Ir(Cl)COD]$_2$[36] in 100 mL of acetone. After the solution was stirred a few minutes, it began to lighten and a yellow solid began to precipitate. The mixture was stirred until the red color disappeared and then concentrated in vacuo to 40 mL; then 100 mL of distilled water was added. The resulting yellow solid was collected on a Schlenk frit, washed eight times with 20-mL aliquots of distilled water, and dried in vacuo. Yield: 1.8 g, 90%. Anal. Calcd (Found): C, 30.27 (30.42); H, 4.13 (4.12).

8. [Ir(OC$_6$H$_5$)COD]$_2$. Dichloromethane (50 mL) was added to a mixture of 0.37 g (6.0 mmol) of 87% KOH and 0.57 g (6.0 mmol) of phenol; a heavy white solid formed. The slurry was transferred to 2.00 g (2.98 mmol) of [Ir(Cl)COD]$_2$[36] in 100 mL of CH$_2$Cl$_2$, and an additional 50 mL of CH$_2$Cl$_2$ was added. A yellow solid began to precipitate immediately, and the resulting yellow-brown slurry was stirred for 2 h. The yellow solid was collected on a Schlenk frit, washed four times with 10-mL aliquots of distilled water, and dried in vacuo. Yield: 1.9 g, 80%. The infrared spectrum matches that reported.[37] Infrared data: ν(OC$_6$H$_5$) = 1581 cm^{-1}, ν(C–O) = 1060 cm^{-1}.

9. Ir(OC$_6$H$_5$)(ttp). A 6.80-mL (1.28-mmol) aliquot of 0.1883 M ttp in toluene was added to a suspension of 0.4602 g (0.5847 mmol) of [Ir(OC$_6$H$_5$)COD]$_2$ in 40 mL of toluene. After the mixture was stirred a few minutes, the solid dissolved and a clear orange solution formed. The solution was refluxed for 18 h and then cooled to room temperature. The orange solution was concentrated in vacuo to 5 mL, and then 20 mL of hexane was added, whereupon an orange solid precipitated. The solid was collected on a Schlenk frit, washed three times with 5-mL aliquots of hexane, and dried in vacuo. Yield: 1.0 g, 100%. Anal. Calcd (Found): C, 59.49 (59.36); H, 4.99 (5.17); P, 10.96 (9.69).

10. Ir(OC$_6$H$_5$)(Cyttp). A 3.50-mL (0.468-mmol) aliquot of 0.1338 M Cyttp in toluene was added to a suspension containing 0.1804 g (0.2271 mmol) of [Ir(OC$_6$H$_5$)COD]$_2$ in 20 mL of toluene. The solid dissolved immediately, and an orange solution formed. The orange solution was stirred overnight and then concentrated in vacuo to a paste. Hexane (10 mL) was added to the paste, and a small amount of red solid precipitated. The solid was collected on a Schlenk frit, and the filtrate was concentrated in vacuo. The desired complex was very soluble and remained in the filtrate. ^{31}P{^{1}H} NMR data: δ(PhP) = −19.63 ppm, δ(Cy$_2$P) = 5.16 ppm, ^2J(PhP–Cy$_2$P) = 29.1 Hz.

11. Ir(OH)(Cyttp). A 8.20-mL (1.10-mmol) aliquot of 0.1338 M Cyttp in toluene was added to a suspension containing 0.3336 g (0.5255 mmol) of [Ir(OH)COD]$_2$ in 30 mL of toluene. The solid dissolved immediately, and an orange solution formed. The solution was reluxed for 17.5 h, cooled to room temperature, and then concentrated in vacuo to 3 mL. Hexane (15 mL) was added, and a small amount of precipitate formed. The solution was then cooled in an ice/water bath for 30 min, and a solid was collected on a Schlenk frit. The desired complex was very soluble and remained in the filtrate. ^{31}P{^{1}H} NMR data: δ(PhP) = 0.90 ppm, δ(Cy$_2$P) = −17.96 ppm, ^2J(PhP–Cy$_2$P) = 31.1 Hz.

12. Rh(OC(O)CF$_3$)(ttp). (a) From Rh(OH)(ttp). Trifluoroacetic acid (0.10 mL, 1.3 mmol) was added to a suspension containing 0.242 g (0.355 mmol) of Rh(OH)(ttp) in 30 mL of benzene. The solid dissolved immediately to give a yellow solution. The solution was stirred for 3 h and concentrated in vacuo to 2 mL, and then 10 mL of hexane was added. The resulting cream-colored precipitate was collected on a Schlenk frit, washed two times with 1.0-mL aliquots of hexane, and dried in vacuo. Yield: 0.12 g, 43%.

(b) From Rh(OC$_6$H$_5$)(ttp). The compound was prepared in a manner similar to the above Rh(OH)(ttp) reaction. Yield: 0.24 g, 83%. Anal. Calcd (Found): C, 58.63 (58.20); H, 4.79 (4.31); P, 11.94 (12.39); F, 7.32 (7.68).

13. Rh(OC(O)C$_6$H$_4$Br)(ttp). (a) From Rh(OH)(ttp). A solution containing 0.077 g (0.38 mmol) of p-bromobenzoic acid in 10 mL of diethyl ether was added to a suspension containing 0.26 g (0.38 mmol) of Rh(OH)(ttp) in 30 mL of toluene. The solid disappeared, and a clear orange solution formed. The solution was stirred for 2.5 h and then concentrated in vacuo to 5 mL. A yellow solid precipitated when 20 mL of hexane was added to the concentrated solution. The solid was collected on a Schlenk frit, washed with 5 mL of hexane, and dried in vacuo. Yield: 0.25 g, 76%.

(b) From Rh(OC$_6$H$_5$)(ttp). The compound was prepared in a similar manner to the above Rh(OH)(ttp) reaction. Yield: 0.19 g, 76%. Anal. Calcd (Found): C, 59.67 (59.51); H, 4.77 (4.86); P, 10.74 (10.89); Br, 9.63 (9.27).

14. Rh(OC(O)C$_6$H$_5$)(ttp). (a) From Rh(OH)(ttp). A solution of 0.050 g (0.41 mmol) of benzoic acid in 10 mL of benzene was added to a suspension containing 0.20 g (0.29 mmol) of Rh(OH)(ttp) in 20 mL of benzene. The solid dissolved, and a clear orange solution formed. The solution was stirred for 1 h and then concentrated in vacuo to 5 mL. A pale orange-yellow solid precipitated when 20 mL of hexane was added to the concentrated solution. The solid was collected on a Schlenk frit, washed two times with 2.0-mL aliquots of hexane, and dried in vacuo. Yield: 0.18 g, 78%.

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(b) From $Rh(OC_6H_5)(ttp)$. The compound was prepared by a procedure similar to the above Rh(OH)(ttp) reaction. Yield: 0.19 g, 95%. Anal. Calcd (Found): C, 65.66 (65.71); H, 5.38 (5.42); P, 11.81 (11.69).

15. $Rh(SO_2OH)(ttp)\cdot SO_2$. Anhydrous SO_2 gas was bubbled through a solution of Rh(OH)(ttp) (0.25 g, 0.37 mmol) in 60 mL of THF for 1 h. The color of the solution lightened immediately to yellow. The resulting yellow solution was concentrated in vacuo to 10 mL. Addition of 4 mL of cyclohexane caused precipitation of a yellow solid, which was collected on a Schlenk frit and dried in vacuo. Yield: 0.23 g, 77%. Anal. Calcd (Found): C, 53.34 (53.12); H, 4.72 (4.86); P, 11.46 (11.33); S, 7.91 (7.77).

16. $Rh(SO_2OC_6H_5)(ttp)\cdot SO_2$. Anhydrous SO_2 gas was bubbled through a solution of $Rh(OC_6H_5)(ttp)$ (0.34 g, 0.45 mmol) in 20 mL of THF for 1 h. A yellow solid precipitated. The slurry was concentrated to $^2/_3$ volume in vacuo, and 4 mL of cyclohexane was added. The solid was collected on a Schlenk frit, washed with 2.0 mL of cyclohexane, and dried in vacuo. Yield: 0.27 g, 73%. Anal. Calcd (Found): C, 56.78 (56.65); H, 4.77 (4.94); P, 10.48 (10.57); S, 7.23 (7.23).

17. $Rh(SO_2OC_6H_5)(Cyttp)\cdot SO_2$. The compound was prepared similarly to the procedure used for **16**. Yield: 0.15 g, 79%. Anal. Calcd (Found): C, 51.68 (51.53); H, 4.34 (4.60); P, 9.52 (9.37); S, 6.57 (6.28).

18. $Ir(SO_2OC_6H_5)(ttp)\cdot SO_2$. Anhydrous SO_2 gas was bubbled through a solution of 0.16 g (0.19 mmol) of $Ir(OC_6H_5)(ttp)$ in 20 mL of THF for 10 min. The solution immediately lightened in color; then it became a cloudy yellow-green slurry; finally it became a clear yellow solution. The yellow solution was concentrated in vacuo to 5 mL, and 10 mL of hexane was added. The resulting yellow solid was collected on a Schlenk frit, washed with 2.0 mL of hexane, and dried in vacuo. Yield: 0.15 g, 79%. Anal. Calcd (Found): C, 51.68 (51.53); H, 4.34 (4.60); P, 9.52 (9.37); S, 6.57 (6.28).

Results and Discussion

A. Synthesis and Characterization of Metal Complexes. The standard method of preparing metal alkoxide and hydroxide complexes involves metathesis reactions between a metal chloride complex and sodium or potassium salts (i.e. KOR or NaOR). In our system, numerous attempts to synthesize Rh(OH)(ttp) from Rh(Cl)(ttp) and KOH were unsuccessful, even in the presence of chloride abstractors such as $TlNO_3$. Hence, a new approach was designed for the synthesis of Rh(OR)(ttp) complexes. It involves isolation of a rhodium hydroxide or alkoxide compound before treating it with a chelating triphosphine ligand. By analogy to the synthesis of Rh(Cl)(ttp),[38] a convenient reagent would be the alkoxide- or hydroxide-bridged bimetallic complex, $[Rh(OR)COD]_2$. In fact, the hydroxide and methoxide complexes $[Rh(OH)COD)]_2$ and $[Rh(OCH_3)COD]_2$ have been prepared recently via eq 1.[33]

$$[Rh(Cl)COD]_2 + 2KOH + 2ROH \rightarrow [Rh(OR)COD]_2 + 2KCl + 2H_2O \quad (1)$$

We found that it is important to wash the yellow solids extensively with water to dissolve all traces of KCl. We have extended this method to the synthesis of $[Rh(OC_6H_5)COD]_2$, $[Rh(OCH_2CF_3)COD]_2$, and $[Rh(OCH_2CH_3)COD]_2\cdot 2H_2O$. The ethoxide complex $[Rh(OCH_2CH_3)COD]_2$ had been prepared previously by the reaction of ethanol with the oxygen-bridged dimer $[Rh(O)COD]_2$.[39]

Table I. Proton NMR Data for $[Rh(OR)COD]_2$ Complexes[a]

OR		
OCH_2CH_3	OC_6H_5	OCH_2CF_3[b]
3.8 (8 H, br)	6.86 (10 H, br)	1.73 (br)
2.4 (10 H, br)	3.08 (8 H, br)	2.52 (br)
1.6 (10 H, br)	2.16 (8 H, br)	3.57 (br)
0.99 (4 H, t, $^3J_{HH}$ = 7.1 Hz)	1.26 (8 H, br)	

[a] The spectra were recorded in CD_2Cl_2. Chemical shifts are reported in ppm. [b] The OCH_2CF_3 protons could not be located in the proton NMR spectrum. The integration ratios suggest that it is buried under the peaks due to the protons of the COD ligand.

The rhodium(I) alkoxide and hydroxide bridged bimetallic complexes were characterized by proton NMR (Table I) and infrared spectroscopy. The three sets of inequivalent hydrogen atoms of the 1,5-cyclooctadiene ligand appear as three broad peaks in the proton NMR spectra due to coupling with the ^{103}Rh nucleus. The infrared spectra display peaks characteristic of the alkoxide or hydroxide ligands. For example, the O–H stretch of the bridging hydroxide group in $[Rh(OH)COD]_2$ shows a sharp absorption at 3580 cm^{-1}. The CO stretch of alkoxide ligands bound to group VIII metals typically exhibit infrared absorptions between 1000 and 1100 cm^{-1}.[37] We found the C–O stretching vibration at 1065 cm^{-1} for $[Rh(OC_6H_5)COD]_2$, 1070 cm^{-1} for $[Rh(OCH_3)COD]_2$, 1082 cm^{-1} for $[Rh(OCH_2CF_3)COD]_2$, and 1093 and 1057 cm^{-1} for $[Rh(OCH_2CH_3)COD]_2\cdot 2H_2O$. Despite recrystallization from CH_2Cl_2/hexane mixtures, the ethoxide complex retains two molecules of water, based on elemental analysis and the infrared spectrum. The OH stretching vibration occurs at 3330 cm^{-1}.[33] The CF_3 group of $[Rh(OCH_2CF_3)COD]_2$ exhibits a distinctive absorption in the infrared spectrum at 1150 cm^{-1}, and the C=C bonds of the phenoxide ligand in $[Rh(OC_6H_5)COD]_2$ exhibit a distinctive absorption at 1582 cm^{-1}.

Alkoxide-bridged bimetallic complexes of iridium, $[Ir(OR)COD]_2$ (OR = OCH_3, OCH_2CH_3, OC_6H_5, $O(CH_2)_2CH_3$, $O(CH_2)_3CH_3$, and $O(CH_2)_7CH_3$), were reported in 1971.[37] Synthesis of the methoxide-bridged complex $[Ir(OCH_3)COD]_2$ has also been reported by a method similar to that used for the synthesis of $[Rh(OR)COD]_2$ complexes (eq 1).[33] We have extended this method to the synthesis of the hydroxide complex $[Ir(OH)COD]_2$, which has not been reported previously. In addition, a reaction similar to that depicted in eq 1 was used to synthesize $[Ir(OC_6H_5)COD]_2$, which had been prepared previously by an exchange reaction between $[Ir(OCH_3)COD]_2$ and C_6H_5OH.[37]

The $[Ir(OR)COD]_2$ complexes (OR = OH, OCH_3, OC_6H_5) have been characterized by infrared spectroscopy. The OH stretching frequency of the $[Ir(OH)COD]_2$ complex exhibits a strong, sharp absorption at 3542 cm^{-1}. The alkoxide complexes show strong absorptions due to the CO stretching vibration at 1068 and 1060 cm^{-1} for $[Ir(OC_6H_5)COD]_2$ and $[Ir(OCH_3)COD]_2$, respectively. In addition, the phenoxide group of $[Ir(OC_6H_5)COD]_2$ exhibits a strong absorption at 1581 cm^{-1}, due to the C=C ring stretching frequency.

The hydroxide- and alkoxide-bridged rhodium(I) bimetallic compounds $[Rh(OR)COD]_2$ were used successfully for the synthesis of monomeric four-coordinate hydroxide and alkoxide rhodium complexes of chelating triphosphine ligands (eq 2, triphos = chelating triphosphine ligand).

$$[Rh(OR)COD]_2 + 2\ \text{triphos} \rightarrow 2Rh(OR)(\text{triphos}) + 2COD \quad (2)$$

The reactions involve addition of an aliquot of a known concentration solution of the chelating triphosphine ligand to a suspension of a $[Rh(OR)COD]_2$ complex in toluene. The resulting Rh(OH)(ttp) (I), $Rh(OC_6H_5)(ttp)$, and $Rh(OCH_2CF_3)(ttp)$ complexes are air-sensitive yellow solids that are unstable thermally, decomposing at temperatures above 130 °C. Numerous attempts were made to prepare the methoxide complex $Rh(OCH_3)(ttp)$; however, all of the

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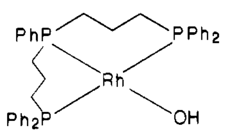

I

reactions failed to give identifiable products. For example, proton-decoupled phosphorus NMR spectra of reaction mixtures that combined $[Rh(OCH_3)COD]_2$ and ttp were very complicated, exhibiting over 80 unidentified peaks.

The $^{31}P\{^1H\}$ NMR spectra of the Rh(OR)(ttp) complexes are consistent with an A_2MX spin system (Figure 1). The spectra exhibit a doublet of doublets due to splitting of the two equivalent $(C_6H_5)_2P$ groups (P2) of the ttp ligand by the ^{103}Rh nucleus and then by the central phosphorus atom ($(C_6H_5)P$ = P1) of the ttp ligand. The central phosphorus atom (P1) exhibits a doublet of triplets due to splitting by the ^{103}Rh nucleus and then by the two equivalent terminal phosphorus atoms of the ttp ligand (P2).

Phosphorus-31 NMR data of the Rh(OR)(ttp) complexes (OR = OH, OC_6H_5, OCH_2CF_3) are given in Table II. Data for Rh(Cl)(ttp)[40] are given for comparison. The magnitudes of the one-bond coupling constant between rhodium and the phosphorus atom trans to the alkoxide ligand, ^1J(Rh–P1), for Rh(OH)(ttp) (^1J(Rh–P1) = 136.1 Hz), $Rh(OCH_2CF_3)(ttp)$ (^1J(Rh–P1) = 145.1), and $Rh(OC_6H_5)(ttp)$ (^1J(Rh–P1) = 147.0) are smaller than that for Rh(Cl)(ttp) (^1J(Rh–P1) = 162.3). The above trend is opposite to the accepted positions for Cl^- and OH^- in the trans influence series: H_2O, OH^-, NH_3, pyridine < Cl^-, Br^- < SCN^-, I^-, NO_2^-. One might expect the Rh–OR bonds to be weak (or reactive) due to the electron-rich "soft" metal center. Therefore, it is surprising that, based on this NMR spectroscopic trans influence series, the hydroxide and alkoxide ligands apparently form a stronger trans-bonding interaction with rhodium than does the chloride ligand. This finding may have a precedent in the $Pt(OH)(CH_3)(dppe)$ complex.[41] Although the trans influence between metal alkoxide and hydroxide complexes and metal chloride complexes has not been compared directly, the hydroxide ligand in $Pt(OH)(CH_3)(dppe)$ exhibits a trans influence similar to that of typical sulfur donors (i.e. SCN^- and SPh^-) and greater than that of other anionic oxygen donors (i.e. $CH_3CO_2^-$ and ONO_2^-).[41]

The Rh(OR)(ttp) complexes (OR = OH, OC_6H_5, OCH_2CF_3) exhibit characteristic stretching vibrations in the infrared spectra. For example, the OH stretching vibration of the hydroxide complex Rh(OH)(ttp) is a weak sharp absorption at 3600 cm^{-1}, diagnostic of a hydroxide group coordinated to a group VIII metal ion.[42,43] The phenoxide group of $Rh(OC_6H_5)(ttp)$ shows absorptions due to the C=C ring stretching vibration at 1590 and 1581 cm^{-1}, and the 2,2,2-trifluoroethoxide complex $Rh(OCH_2CF_3)(ttp)$ exhibits a strong, broad peak centered at 1108 cm^{-1}, characteristic of the CF_3 group. The CO stretching vibration of the alkoxide complexes (OR = OC_6H_5, OCH_2CF_3) cannot be identified due to numerous peaks from the ttp ligand in the 1000–1100 cm^{-1} region.

Several attempts were made to synthesize the hydroxide and alkoxide complexes Rh(OR)(Cyttp) (OR = OH, OC_6H_5, OCH_2CH_3) of the more basic ligand Cyttp, using the procedure employed for the synthesis of Rh(OR)(ttp) complexes (eq 2). However, solid products could not be isolated from the reaction mixtures. Removal of the reaction solvent under vacuum leads to formation of oils. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures exhibit a pattern consistent with the A_2MX spin system of Rh(OR)(Cyttp) complexes. The data for Rh(OH)(Cyttp) and $Rh(OC_6H_5)(Cyttp)$ are given in Table II; also, data for Rh(Cl)(Cyttp)[44] are given for comparison. Identification of $Rh(OC_6H_5)(Cyttp)$ and Rh(OH)(Cyttp) is tentative, since only $^{31}P\{^1H\}$ NMR spectroscopy was used to characterize these complexes.

Table II. $^{31}P\{^1H\}$ NMR Data for Rh(X)(ttp) and Rh(X)(Cyttp) Complexes[a]

complex	δ(P1)	δ(P2)	^1J(Rh–P1)	^1J(Rh–P2)	^2J(P1–P2)
Rh(Cl)(ttp)[b]	15.48	8.20	162.3	128.8	52.5
Rh(OH)(ttp)	16.57	7.87	136.1	141.6	54.0
$Rh(OC_6H_5)(ttp)$	18.04	3.31	147.0	137.0	54.0
$Rh(OCH_2CF_3)$-(ttp)	18.76	3.92	145.1	140.2	55.0
Rh(Cl)(Cyttp)[c]	20.6	9.2	174	126	49
Rh(OH)(Cyttp)	24.7	11.2	164	132	53
$Rh(OC_6H_5)$-(Cyttp)	24.1	8.6	159	134	50

[a] Chemical shifts are reported in ppm; coupling constants are reported in Hz. The Rh(X)(ttp) spectra were recorded in THF and the Rh(X)(Cyttp) spectra were recorded in toluene. C_6D_6 was added as an internal lock. [b] Reference 40. [c] Reference 44.

Table III. $^{31}P\{^1H\}$ NMR Data for Ir(X)(ttp) and Ir(X)(Cyttp) Complexes[a]

complex	δ(P1)	δ(P2)	^2J(P1–P2)
Ir(Cl)(ttp)[b]	−19.9	2.7	32.8
$Ir(OC_6H_5)(ttp)$[c]	−42.17	−28.83	26.3
Ir(Cl)(Cyttp)[d]	−16.8	1.98	30.5
Ir(OH)(Cyttp)[e]	−17.96	0.90	31.1
$Ir(OC_6H_5)(Cyttp)$[e]	−19.63	5.15	29.1

[a] Chemical shifts are reported in ppm. Coupling constants are reported in Hz. [b] Reference 60. [c] THF/C_6D_6. [d] Reference 61. [e] Toluene/C_6D_6

The four-coordinate iridium(I) complexes Ir(OR)(triphos) (triphos = ttp and Cyttp) were prepared analogously to the rhodium(I) complexes. However, in order to displace the 1,5-cyclooctadiene ligand from $[Ir(OR)COD]_2$ complexes, the reactions were carried out in refluxing toluene over an 18-h period. This reaction lead to the successful isolation of $Ir(OC_6H_5)(ttp)$ from $[Ir(OC_6H_5)COD]_2$ and 2 equiv of ttp. The $[Ir(OC_6H_5)COD]_2$ complex was treated with Cyttp at room temperature to give the desired complex $Ir(OC_6H_5)(Cyttp)$; however, it could not be isolated as a solid, and it was subsequently characterized in solution by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction of $[Ir(OH)COD]_2$ with Cyttp in refluxing toluene leads to formation of Ir(OH)(Cyttp); once again, the desired complex could not be isolated as a solid. Treatment of $[Ir(OH)COD]_2$ with 2 equiv of ttp at refluxing conditions gave an uncharacterized product in which the 1,5-cyclooctadiene ligand remained bound to the metal.

The $^{31}P\{^1H\}$ NMR doublet and triplet patterns of $Ir(OC_6H_5)(ttp)$, Ir(OH)(Cyttp), and $Ir(OC_6H_5)(Cyttp)$ are characteristic of a first-order A_2M spin system. The data are compiled in Table III, and the data for Ir(Cl)(ttp) and Ir(Cl)(Cyttp) are included for comparison.

B. Reaction Chemistry. 1. Condensation Reactions. The basicity of metal alkoxide and hydroxide complexes can be tested by use of a general acid–base

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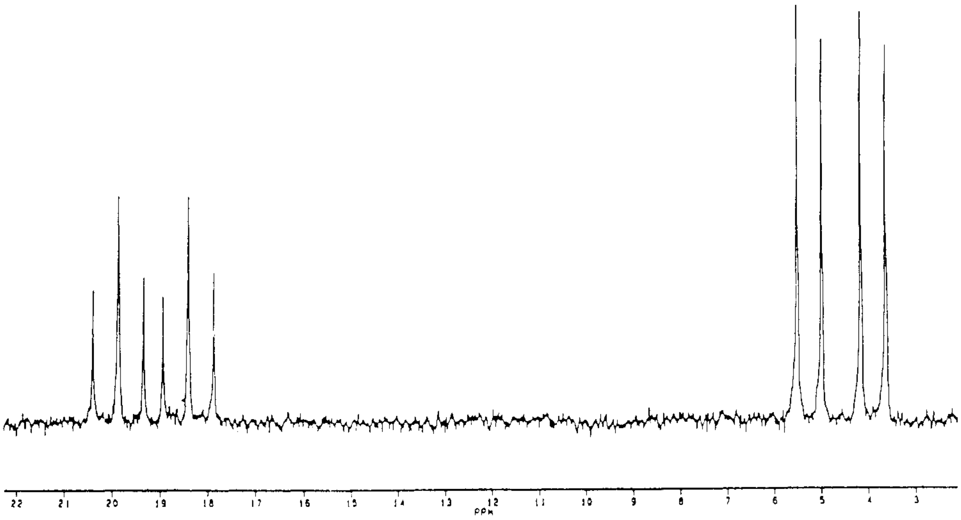

Figure 1. 250-MHz $^{31}P\{^1H\}$ NMR spectrum of $Rh(OC_6H_5)(ttp)$ in THF with C_6D_6 added as an internal lock.

Table IV. $^{31}P\{^1H\}$ **NMR Data for Rh(OC(O)R)(ttp) Complexes**[a]

OC(O)R	δ(P1)	δ(P2)	^1J(Rh-P1)	^1J(Rh-P2)	^2J(P1-P2)
$OC(O)CF_3$	26.01	10.84	123.2	95.4	38.4
$OC(O)C_6H_4Br$	18.10	9.38	155.3	135.7	54.0
$OC(O)C_6H_5$	18.22	9.03	155.1	135.9	54.1

[a] The chemical shifts are reported in ppm; coupling constants are reported in Hz. The spectra were recorded in THF with C_6D_6 added as an internal lock.

reaction as depicted in eq 3 (M = group VIII metal; HA = acid; OR = hydroxide or alkoxide group). Although

$$M\text{-}OR + HA \rightarrow M\text{-}A + HOR \qquad (3)$$

reactions between platinum(II) hydroxide complexes have been investigated extensively,[44-49] such reactions with rhodium(I) alkoxide and hydroxide complexes have not been examined. The Rh(OH)(ttp) and $Rh(OC_6H_5)(ttp)$ complexes prepared in this investigation were treated with a series of organic acids (eq 4). Reactions between Rh-

$$Rh(OR)(ttp) + R'CO_2H \rightarrow Rh(OC(O)R')(ttp) + ROH \qquad (4)$$

(OR)(ttp) (OR = OH, OC_6H_5) and trifluoroacetic acid (pK_a = 0.2), *p*-bromobenzoic acid (pK_a = 3.97), and benzoic acid (pK_a = 4.20) in benzene proceeded smoothly to give the metal carboxylates and water or phenol, respectively. The $^{31}P\{^1H\}$ NMR spectra of these carboxylate complexes, characteristic of an A_2MX spin system, are given in Table IV. Since the $^{31}P\{^1H\}$ NMR data for $Rh(OC(O)C_6H_4Br)(ttp)$ and $Rh(OC(O)C_6H_5)(ttp)$ are nearly identical, the para bromine atom exhibits only a small effect on the $^{31}P\{^1H\}$ NMR spectra.

Metal acetate complexes are known to coordinate through one or both oxygen atoms;[50] however, the two coordination geometries can be differentiated by use of infrared spectroscopy. A peak at 1778 cm^{-1} in the infrared spectrum of $Rh(OC(O)CF_3)(ttp)$ is assigned to a C=O stretching vibration;[51] hence, the acetate group is coordinated to rhodium through one oxygen atom (RhOC(=O)R). Likewise, peaks observed at 1609 and 1710 cm^{-1} in the spectra of $Rh(OC(O)C_6H_4Br)(ttp)$ and $Rh(OC(O)C_6H_5)(ttp)$ are also indicative of monodentate coordination.[51]

Four-coordinate platinum(II) hydroxide complexes are reactive toward organic acids, including very weak organic acids such as acetone (pK_a = 20) and acetonitrile (pK_a = 25). In contrast, the Rh(OR)(ttp) complexes (OR = OH, OC_6H_5) react only with organic acids with pK_a values less than or equal to 4.20. For example, reactions of acetic acid (pK_a = 4.76) and *p*-nitrophenol (pK_a = 7.15) led consistently to decomposition of the metal complexes, with the only characterized products being oxidized triphosphine ligands. A novel six-coordinate iridium hydrido–hydroxo complex, $[IrH(OH)(PMe_3)_4]^+PF_6^-$, undergoes reaction with methanol to form the corresponding methoxide complex $[IrH(OMe)(PMe_3)_4]^+PF_6^-$ and reacts with D_2O to give $[IrH(OD)(PMe_3)_4]^+PF_6^-$.[52] A similar reaction between Rh(OH)(ttp) and phenol (pK_a = 10) was not successful, based on spectroscopic data. Only Rh(OH)(ttp) was recovered from the reaction mixture. Likewise, the phenoxide complex $Rh(OC_6H_5)(ttp)$ failed to react with water to give the hydroxide complex, despite the fact that hydrolysis reactions are generally facile.

Platinum(II) complexes are more reactive toward organic acids as the Pt–OH bond becomes more ionic.[45] This suggests that the lack of reactivity of Rh(OH)(ttp) and $Rh(OC_6H_5)(ttp)$ may be related to a reduced ionic character of the Rh–OR bond (OR = OH, OC_6H_5), although rhodium(I) should not polarize the Rh–O bond as much as Pt(II). Hence, the Rh–OR bonds may be more covalent than originally predicted. This proposal is supported by the lack of reactivity toward organic acids and the unusually high position of the $OC_6H_5^-$ and OH^- ligands in the ^{31}P NMR spectroscopic trans-influence series. However, Bergman and co-workers report the reaction of similar complexes, $Rh(OR)(PMe_3)_3$ (OR = *p*-(trifluoromethyl)phenoxy, trifluoroethoxy, *p*-methylphenoxy, and hexafluoroisopropoxy) with alcohol to give hydrogen-bonded

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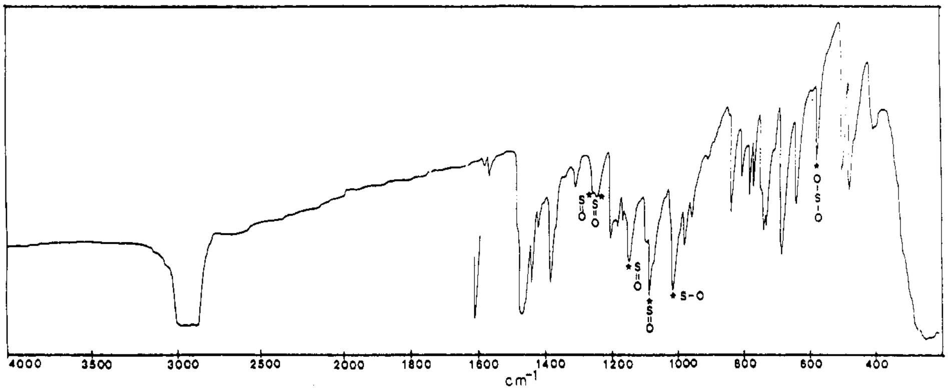

Figure 2. A portion of the infrared spectrum of $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$ (Nujol mull).

Table V. Infrared Data for Rhodium and Iridium Sulfonate Complexes[a]

complex	$(S{=}O)_{as}$	$(S{=}O)_s$	S—O	O—S—O	$(S{=}O)_{as}$[b]	$(S{=}O)_s$[b]
$Rh(SO_2OPh)(ttp){\cdot}SO_2$	1260	1150	1015	590	1250	1085
$Rh(SO_2OH)(ttp){\cdot}SO_2$	1260	1148	1015	589	1250	1085
$Rh(SO_2OPh)(Cyttp){\cdot}SO_2$	1271	1148	1009	582	1259	1095
$Ir(SO_2OPh)(ttp){\cdot}SO_2$	1280	1155	1018	596	1260	1095

[a] Stretching frequencies are reported in cm^{-1}. The spectra were recorded in the solid state as Nujol mulls or KBr pellets. [b] SO_2 adduct.

Table VI. $^{31}P\{^1H\}$ NMR Data for Rhodium and Iridium Sulfonate Complexes in CD_2Cl_2 Solution[a]

complex	δ(P1)	δ(P2)	^1J(Rh–P1)	^1J(Rh–P2)	^2J(P1–P2)	T,[a] K
$Rh(SO_2OH)(ttp){\cdot}SO_2$						
major	14.87	1.98	147	114	39	303
minor	-4.18	1.46	115	124	45	303
major	15.97	2.01	146	113	39	183
$Rh(SO_2OPh)(ttp){\cdot}SO_2$						
major	-4.02	1.43	115	125	45	303
minor	21.86	-0.06	161	114	40	303
major	-4.59	2.19	112	122	44	183
minor	23.43	-0.06	158	112	39	183
$Ir(SO_2OPh)(ttp){\cdot}SO_2$						
major	-34.38	-16.84			31.7	303
major	-42.97	-24.93			24.2	303
$Rh(SO_2OPh)(Cyttp){\cdot}SO_2$						
	18.45	2.92	156	107	37	303

[a] Chemical shifts are reported in ppm; coupling constants are reported in Hz. K = degrees Kelvin; P1 = PhP; P2 = Ph_2P, Cy_2P.

species $(PMe_3)_3RhOR(HOR')$, which react slowly to give $(PMe_3)_3RhOR'(HOR)$.[53] Hence, it is possible tht Rh(OR)(ttp) species may be reactive toward other R'OH compounds (of relatively high pH), but the reaction kinetics are unfavorable.

2. SO_2 Insertion Reactions. Anhydrous sulfur dioxide gas reacts with Rh(OH)(ttp) and $Rh(OC_6H_5)(ttp)$ to yield a rhodium sulfonic acid, $Rh(SO_2OH)(ttp){\cdot}SO_2$, and a rhodium sulfonate, $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$, respectively. This is the first report of SO_2 insertions into a Rh–OR bond to yield rhodium sulfonates and sulfonic acids. On the basis of elemental analyses, the complexes contain two molecules of SO_2. In addition, six new peaks are observed in the infrared spectrum of $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$ (Figure 2). Four of the peaks are assigned on the basis of assignments for platinum and palladium sulfonates.[48,54-57] The peaks at 1260, 1150, 1015, and 590 cm^{-1} in the infrared spectrum of $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$ are assigned to the asymmetric S=O stretch, symmetric S=O stretch, S—O stretch, and O—S—O bend, respectively, of an SO_2 molecule inserted into the Rh—OC_6H_5 bond. The two remaining peaks at 1250 and 1085 cm^{-1} are assigned to a second molecule of SO_2, which is coordinated to rhodium to form a square-pyramidal coomplex. This assignment is consistent with those made for a series of $Rh(X)(ttp){\cdot}SO_2$ complexes.[40]

The infrared assignments for both the inserted SO_2 molecule and the apical adduct SO_2 molecule are characteristic of SO_2 molecules coordinated to the metal through the sulfur atom. The asymmetric S=O stretching frequency for a sulfur-bound SO_2 molecule is in the range 1250–1100 cm^{-1}, and the symmetric S=O stretching frequency is in the range 1100–1000 cm^{-1}; the stretching frequencies for SO_2 molecules coordinated through oxygen absorb at lower energy.[57] The infrared spectrum of $Rh(SO_2OH)(ttp){\cdot}SO_2$ exhibits six peaks in addition to those observed in the infrared spectrum of Rh(OH)(ttp); similar assignments to those described above are made. Diagnostic infrared data are given in Table V. The proposed structure of the $Rh(SO_2OR)(ttp){\cdot}SO_2$ complexes (OR = OH, OC_6H_5) is shown in II.

The $^{31}P\{^1H\}$ NMR spectra of $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$ and $Rh(SO_2OH)(ttp){\cdot}SO_2$ exhibit two sets of peaks characteristic of an A_2MX spin system. A variable-temperature $^{31}P\{^1H\}$ NMR experiment was performed to determine if the two different complexes interconverted. The peaks observed in the $^{31}P\{^1H\}$ NMR spectrum of Rh-

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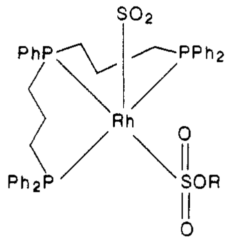

II

$(SO_2OC_6H_5)(ttp)\cdot SO_2$ moved apart as the temperature was lowered to 183 K. One of the two sets of peaks in the $^{31}P\{^1H\}$ NMR spectrum of $Rh(SO_2OH)(ttp)\cdot SO_2$ broadened as the temperature was lowered to 183 K; the second set of peaks remained sharp. The $^{31}P\{^1H\}$ NMR data are compiled in Table VI. The phosphorus NMR spectra recorded at temperatures above 303 K exhibited many unidentified peaks, indicating that the complexes decompose at higher temperatures. The two sets of peaks in the $^{31}P\{^1H\}$ NMR spectra of these complexes apparently do not result from dissociation of the SO_2 adduct. Argon gas was bubbled through solutions of $Rh(SO_2OR)(ttp)\cdot SO_2$ (OR = OH, OC_6H_5) in an attempt to displace the SO_2 molecule, but $^{31}P\{^1H\}$ NMR spectra of the reaction solutions still displayed two sets of peaks. The related complex $Rh(Cl)(ttp)\cdot SO_2$ does not undergo dissociation of SO_2.[40] We observed that the minor set of peaks (303 K) for $Rh(SO_2OH)(ttp)\cdot SO_2$ and the major set of peaks for $Rh(SO_2OC_6H_5)(ttp)\cdot SO_2$ are identical within experimental error (Table VI). Hence, it is tentatively suggested that the sulfonate or sulfonic acid group partially dissociates in THF to form ions in solution, i.e., $[Rh(SO_2)(ttp)]^+[SO_2OC_6H_5]^-$ or $[Rh(SO_2)(ttp)]^+[SO_2OH]^-$ (eq 5).

$$Rh(SO_2OR)(ttp)\cdot SO_2 \rightarrow [Rh(SO_2)(ttp)]^+[SO_2OR]^- \quad (5)$$

Anhydrous sulfur dioxide gas also reacts with $Ir(OC_6H_5)(ttp)$ to give an iridium sulfonate, $Ir(SO_2OC_6H_5)(ttp)\cdot SO_2$, which has a structure similar to the rhodium sulfonates, based on the infrared data. The $^{31}P\{^1H\}$ NMR spectrum also exhibits two sets of peaks, of nearly equivalent intensity, suggesting that this complex also forms ions in solution, i.e. $[Ir(SO_2)(ttp)]^+[SO_2OC_6H_5]^-$ (Table VI).

3. Olefin Reactions. The fact that platinum(II) hydroxide complexes have been claimed to act as catalysts for olefin hydration[20] makes the present rhodium hydroxide and alkoxide complexes possible catalysts for olefin hydration. One of the most exciting reactions of platinum alkoxide complexes was the insertion of tetrafluoroethylene into the $Pt-OCH_3$ bond of $Pt(OCH_3)(CH_3)(dppe)$ to give $Pt(CF_2CF_2OCH_3)(CH_3)(dppe)$.[58,59] An iridium complex, $Ir(OCH_3)(CO)(PPh_3)_2$, reacts with tetracyanoethylene (TCNE) to give the adduct $Ir(OCH_3)(CO)(PPh_3)_2TCNE$.[30]

The $Rh(OH)(ttp)$ and $Rh(OC_6H_5)(ttp)$ complexes were treated with a series of olefins. Both complexes failed to react with ethylene gas (1 atm, 25 °C); only starting material was recovered from the reaction mixtures. Similar results were obtained in reactions between $Rh(OR)(ttp)$ (OR = OH, OC_6H_5) and trichloroethylene, even under refluxing conditions. Treatment of $Rh(OH)(ttp)$ with tetracyanoethylene in benzene gives a purple solid which shows no evidence of phosphorus in the $^{31}P\{^1H\}$ NMR spectrum; the reaction filtrate showed no ^{31}P NMR signal. A reaction between $Rh(OC_6H_5)(ttp)$ and tetracyanoethylene in benzene yields a purple solution which gives only a few, weak unidentified peaks in the $^{31}P\{^1H\}$ NMR spectrum. The TCNE reactions probably involve redox chemistry to produce a paramagnetic product; the absence of phosphorus signals in the $^{31}P\{^1H\}$ spectra indicate that the desired complexes (either an inserted product or an adduct) did not form.

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Registry No. I, 69069-21-2; II (R = H), 118682-20-5; II (R = Ph), 118682-18-1; $[Rh(OC_6H_5)COD]_2$, 60166-13-4; $[RhCl(COD)]_2$, 12092-47-6; $[Rh(OCH_2CH_3)COD]_2\cdot 2H_2O$, 73456-54-9; $[Rh(OH)COD]_2$, 73468-85-6; $Rh(OC_6H_5)(ttp)$, 118657-58-2; $[Rh(OCH_2CF_3)COD]_2$, 109926-61-6; $Rh(OCH_2CF_3)(ttp)$, 118657-59-3; $[IrCl(COD)]D_2$, 12112-67-3; $[Ir(OC_6H_5)COD]_2$, 35429-67-5; $[Ir(OH)COD]_2$, 118657-60-6; $Ir(OC_6H_5)(Cyttp)$, 118657-61-7; $Ir(OH)(Cyttp)$, 118681-35-9; $Rh(OC(O)CF_3)(ttp)$, 118657-62-8; $Rh(OC(O)C_6H_4Br)(ttp)$, 118657-63-9; $Rh(OC(O)C_6H_5)(ttp)$, 118657-64-0; SO_2, 7446-09-5; $Rh(SO_2OC_6H_5)(Cyttp)\cdot SO_2$, 118713-54-5; $Rh(OPh)(Cyttp)$, 118657-65-1; $Ir(SO_2OC_6H_5)ttp)\cdot SO_2$, 118682-19-2; $Rh(OH)Cyttp)$, 118657-66-2; OH^-, 14280-30-9; PhO^-, 3229-70-7; $Ir(OC_6H_5)(ttp)$, 118657-67-3.

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