

in a procedure analogous to that given for $2a^+TfO^-$. The solution was stirred for 6 h. Solvent was then removed under oil pump vacuum to give a dark yellow semisolid. Then THF (5 mL) and ether (50 mL) were sequentially added with stirring. This gave $6e$ (0.204 g, 0.353 mmol, 81%) as a bright yellow powder. A sample was dissolved in THF and layered with ether. This gave bright yellow polymorphous plates of $6e^+TfO^-$, mp 104–105 °C dec. Anal. Calcd for $C_{15}H_{23}F_3NO_5ReS_2$: C, 29.80; H, 3.83; S, 10.60. Found: C, 29.88; H, 3.82; S, 10.52.

Preparation of $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(S(=O)Me_2)]^+BF_4^-$ ($4a^+BF_4^-$). Methyl complex $(\eta^5-C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.312 g, 0.558 mmol), CH_2Cl_2 (5 mL), $HBf_4 \cdot OEt_2$ (0.083 mL, 0.614 mmol), and dimethyl sulfoxide (0.119 mL, 1.67 mmol) were combined in a procedure analogous to that given for $2a^+BF_4^-$. After 30 min, the -80 °C bath was removed and the solution allowed to warm to room temperature. After 2 h, ether (20 mL) was added. The resulting yellow precipitate was washed with ether (3×10 mL)⁴³ to give $4a^+BF_4^-$ (0.339 g, 0.478 mmol, 86%). A sample was dissolved in CH_2Cl_2 and layered with ether. Bronze prisms of $4a^+BF_4^-$ formed, which were washed with ether (3×2 mL),⁴³ mp 153–156 °C dec. Anal. Calcd for $C_{25}H_{26}BF_4NO_2PR_3S$: C, 42.38; H, 3.70; S, 4.52. Found: C, 42.44; H, 3.73; S, 4.59.

Reaction of $4a^+BF_4^-$ and SMe_2 . A Schlenk flask was charged with $4a^+BF_4^-$ (0.049 g, 0.069 mmol), chlorobenzene (4 mL), and a stir bar. The flask was warmed to 65 °C, and dimethyl sulfide (0.151 mL, 2.06 mmol) was added. The mixture was stirred for 15 h. Solvent was then removed under oil pump vacuum. The resulting dark yellow powder was dissolved in CH_2Cl_2 (4 mL), and the mixture was filtered through a glass plug. Ether (15 mL) was added to the filtrate with stirring. A bright yellow powder formed, which was washed with ether (3×2 mL)⁴³ to give $2a^+BF_4^-$ (0.040 g, 0.057 mmol, 83%).

Variable-Temperature NMR Spectroscopy. Dynamic NMR studies were conducted in sealed tubes on Varian XL-300 spectrometers, as previously described.^{31a} Samples were thor-

oughly degassed (freeze–pump–thaw $\times 3$), and probe temperatures were calibrated with methanol.

Crystal Structures. The solvate $2a^+TfO^- \cdot CH_2Cl_2$ was crystallized a second time as described above. A yellow prism was mounted on a glass fiber for preliminary data collection on a Syntex P1 diffractometer. Cell constants (Table II) were determined from 15 centered reflections with $12^\circ \leq 2\theta \leq 30^\circ$. Lorentz, polarization, and empirical absorption corrections were applied to the data. The structure was solved by standard heavy-atom techniques using the SDP/VAX package.⁴⁵ Hydrogen atom positions were calculated. Non-hydrogen atoms were refined with anisotropic thermal parameters. Anomalous dispersion corrections were applied through the refinement. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.⁴⁶ The crystal structures of $4a^+BF_4^-$ and $6a^+TfO^-$ were solved in a similar manner, except that several triflate atoms in $6a^+TfO^-$ were refined isotropically.

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Supplementary Material Available: Tables of anisotropic thermal parameters for $2a^+TfO^- \cdot CH_2Cl_2$, $4a^+BF_4^-$, and $6a^+TfO^-$ (3 pages); tables of calculated and observed structure factors for $2a^+TfO^- \cdot CH_2Cl_2$, $4a^+BF_4^-$, and $6a^+TfO^-$ (72 pages). Ordering information is given on any current masthead page.

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Acidolysis of $[MeC(CH_2PPh_2)_3]Rh(CH_3)_n$ Compounds: Controlled Creation of Unsaturation

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Reaction of (triphos)RhMe₃ (triphos = MeC(CH₂PPh₂)₃) with HBF₄·OEt₂ in CH₂Cl₂ gives (triphos)RhMe₂BF₄, which readily adds MeCN and reacts with CO to give acetone and (triphos)Rh(CO)₂⁺. When the protonation product is treated with 100 psi of C₂H₄, (triphos)Rh(C₂H₄)₂⁺ is produced. This cation is intramolecularly fluxional and exchanges readily with ¹³C₂H₄. The ethylene is weakly bound and is readily replaced by water to give [(triphos)Rh(C₂H₄)(H₂O)]BF₄, whose structure was established by X-ray diffraction. Crystallographic data (-172 °C): $a = 10.502$ (2) Å, $b = 16.518$ (4) Å, $c = 24.210$ (5) Å, and $\beta = 97.81$ (1)° with $Z = 4$ in space group $P2_1/c$. The trigonal-bipyramidal rhodium has C₂H₄ equatorial and H₂O axial. The water hydrogen bonds to BF₄ (O···F = 2.665 Å). Added ethylene will, in turn, displace coordinated water. This same compound is formed on protonation of (triphos)RhMe(C₂H₄) in the presence of ethylene and water. Protonation of (triphos)RhMe(C₂H₄) in the presence of acetonitrile yields (triphos)Rh(NCCH₃)(C₂H₄)⁺, which has acetonitrile in an axial position. Analysis of variable-temperature ¹H, ¹³C, and ³¹P NMR data for these 18-electron cations suggests that they react by preliminary “arm-off” dissociation of one of the three phosphorus donor groups.

Introduction

Acidolysis of an organo-transition metal compound^{1–4} (eq 1) can be an effective method for creating an open

coordination site, since it formally removes R[–]. This



process generates a transient 16e[–] species that may be stabilized by the solvent or an available counterion (conjugate base of the acid employed). These formally unsaturated species are much more reactive toward a variety of nucleophiles (e.g., CO, MeCN, olefin, alkyne, etc.) than are their saturated precursors in eq 1. In the case of IrR₃(PMe₂Ph)₃ (R = H³ or Me^{3,4}) complexes, activation

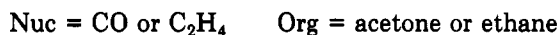
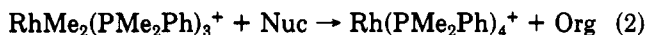
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through acidolysis has been shown to be quite effective in permitting a rich variety of chemical transformations. However, for the analogous rhodium system, $\text{RhMe}_3(\text{PMe}_2\text{Ph})_3$,³ similar reactivity studies have been less straightforward. The fact that reactions such as those shown in eq 2 occur and generate the organic products shown suggests initial coordination of the nucleophiles at



the original unsaturated metal center. However, the metal-containing product $\text{Rh}(\text{PMe}_2\text{Ph})_4^+$ suggests that these nucleophiles are unable to stabilize a RhP_3^+ moiety, which instead suffers phosphine redistribution.⁵

The undesirable phosphine redistribution pathway should be avoided by replacing the three PMe_2Ph ligands of $\text{RhMe}_2(\text{PMe}_2\text{Ph})_3^+$ with a single tridentate phosphine ligand. $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ (triphos) was chosen because of previous evidence that this ligand can stabilize unusual Rh complexes.⁶⁻⁸

This report explores the synthesis of the highly unstable species $\text{RhMe}_2(\text{triphos})^+$ and its reactivity with CO, C_2H_4 , and CH_3CN . We also report the products of protonation of a Rh(I) methyl compound.

Experimental Section

General Comments. All procedures were carried out under an atmosphere of purified nitrogen by using conventional Schlenk and drybox techniques. Measured gas quantities were handled with a conventional calibrated gas manifold. Solvents were stored under nitrogen after being distilled from appropriate drying agents (diethyl ether and pentane from sodium and benzophenone; methylene chloride from P_2O_5). Methylene- d_2 chloride (Cambridge Isotopes) was dried over P_2O_5 prior to use. Ethylene (Air Products), [$^{13}\text{C}_2$]ethylene (99% ^{13}C , Cambridge Isotopes), ethylene- d_4 (99% D, Cambridge Isotopes), and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (85% in diethyl ether, Aldrich) were used as purchased. This last reagent is very hygroscopic. Fresh material was stored cold in a Teflon-closure Schlenk vessel, opened only under an N_2 flush, and kept no more than 2 months after opening. $\text{RhMe}_3(\text{triphos})^9$ and $\text{RhMe}(\text{C}_2\text{H}_4)(\text{triphos})^8$ were prepared according to literature procedures.

NMR spectra were recorded on a Nicolet NT-360 (^1H , 360 MHz; ^{19}F , 340 MHz; ^{31}P , 146 MHz; ^{13}C , 91 MHz; ^2H , 55 MHz) or Varian XL-300 (^1H , 300 MHz; ^{13}C , 75 MHz) NMR spectrometer. ^1H and ^{13}C chemical shifts are relative to TMS with the solvent peak (methylene- d_2 chloride: ^1H , δ 5.32; ^{13}C , δ 53.8) as an internal reference; ^2H chemical shifts are relative to TMS with the methylene- d_2 chloride solvent peak as an external reference. ^{19}F chemical shifts are relative to CFCl_3 (δ 0.0) with trifluoroacetic acid (δ -76.5) as an external reference. ^{31}P chemical shifts are relative to an external reference of 85% H_3PO_4 (δ 0.0). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Microanalyses were performed by Oneida Research Services.

[$\text{RhMe}_2(\text{triphos})\text{BF}_4$ (1)]. A solution of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (85% solution in diethyl ether, 21 μL , $\sim 1.7 \times 10^{-4}$ mol) in 1 mL of methylene chloride was slowly added to a slurry of $\text{RhMe}_3(\text{triphos})$ (0.135 g, 1.75×10^{-4} mol) with stirring at 0 $^\circ\text{C}$. The mixture reacted with vigorous gas evolution to yield a clear, dark orange solution. After stirring for 15 min at 0 $^\circ\text{C}$, the mixture was warmed to room temperature and filtered. Addition of the acid as a

methylene chloride solution is important; direct addition of acid to a slurry of $\text{RhMe}_3(\text{triphos})$ in methylene chloride produces a less pure product and often results in failure, yielding insoluble precipitates. Although compound 1 is conveniently used in situ, the reaction solutions tend to decompose to unidentified products. A 5-mL aliquot diethyl ether was slowly added to the stirred filtrate to precipitate a yellow-orange solid. After the mixture was cooled at -20 $^\circ\text{C}$ for 2 h to ensure complete precipitation, the solid was collected by filtration, washed with 2×5 mL of pentane, and then dried overnight in vacuo. Yield: 0.130 g of 1 (88%, based on $\text{RhMe}_3(\text{triphos})$) as a yellow-orange powder. ^1H NMR (methylene- d_2 chloride, 22 $^\circ\text{C}$): δ 7.3-7.0 (overlapping multiplets, 30, PPh), 2.61 (br s, 6, P- CH_2), 1.72 (unresolved quartet, $J_{\text{P-H}} = 2.5$ Hz, 3, triphos CH_3), 1.38 (br s, 6, Rh-Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (methylene- d_2 chloride, 22 $^\circ\text{C}$): δ 13.7 (br d, $J_{\text{Rh-P}} = 103$ Hz). ^{19}F NMR (methylene- d_2 chloride, 22 $^\circ\text{C}$): δ -151.1 (br m, width at half-height = 70 Hz). ^1H NMR (methylene- d_2 chloride, -80 $^\circ\text{C}$): δ 7.3-7.0 (overlapping multiplets, 30, PPh), 2.45 (br d, $J = 5$ Hz, 6, P- CH_2), 1.57 (br s, 3, triphos CH_3), 0.98 (br s, 6, Rh-Me). The possibility of coordinated water is ruled out by the absence of an appropriate resonance in this spectrum. $^{31}\text{P}\{^1\text{H}\}$ NMR (methylene- d_2 chloride, -80 $^\circ\text{C}$): δ 44.9 (dt, $J_{\text{P-P}} = 24$ Hz, $J_{\text{Rh-P}} = 162$ Hz, 1P), -14.6 (dd, $J_{\text{Rh-P}} = 69$ Hz, 2P). ^{19}F NMR (methylene- d_2 chloride, -80 $^\circ\text{C}$): δ -149.4 (br m, width at half-height = 70 Hz). Attempted recrystallization from THF (for elemental analysis) gives only decomposition (many peaks by ^{31}P NMR analysis).

Reaction of [$\text{RhMe}_2(\text{triphos})\text{BF}_4$ (1) with Ethylene. In a typical reaction, 1 was prepared in situ in 0.6 mL of methylene- d_2 chloride as described above by using $\text{RhMe}_3(\text{triphos})$ (0.015 g, 1.9×10^{-5} mol) and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (85% solution in diethyl ether, 2.3 μL , 4.9×10^{-5} mol). The solution was placed in an NMR tube and degassed by a freeze-pump-thaw cycle. Approximately 4×10^{-5} mol of ethylene was condensed into the tube, which was subsequently flame-sealed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (-80 $^\circ\text{C}$) shows resonances consistent with 1, together with (in some cases) a small amount of [$\text{Rh}(\text{C}_2\text{H}_4)_2(\text{triphos})\text{BF}_4$ (3) and several unidentifiable resonances in the baseline noise (see below).

In an analogous reaction, 4.7×10^{-5} mol of 1 was prepared in 0.8 mL of methylene chloride and placed in an NMR tube and degassed by a freeze-pump-thaw cycle. Approximately 9.5×10^{-5} mol of ethylene- d_4 was condensed into the tube, which was subsequently flame-sealed. $^{31}\text{P}\{^1\text{H}\}$ NMR (-80 $^\circ\text{C}$) shows essentially compound 1; ^2H NMR (-80 $^\circ\text{C}$) shows a resonance at δ 5.3 consistent with free ethylene and a small peak ($\sim 9\%$) at δ 0.6; other small peaks began to appear in the ^2H spectrum after several minutes at room temperature.

In general, solutions of 1 in methylene chloride placed under an atmosphere of ethylene yield ^{31}P NMR spectra showing many unidentifiable resonances together with small amounts of 3 (see below).

[$\text{RhMe}_2(\text{CH}_3\text{CN})(\text{triphos})\text{BF}_4$ (2)]. A solution of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (85% solution in diethyl ether, 18 μL , $\sim 1.5 \times 10^{-4}$ mol) in 0.5 mL of methylene chloride was added to a slurry of $\text{RhMe}_3(\text{triphos})$ (0.114 g, 1.48×10^{-4} mol) in 2 mL of methylene chloride and acetonitrile (8.0 μL , $\sim 1.5 \times 10^{-4}$ mol) with stirring at 0 $^\circ\text{C}$. The mixture slowly (2-3 min) yielded a clear yellow-brown solution. After warming to room temperature, the solution was filtered and 15 mL diethyl ether was slowly added to the stirred filtrate to precipitate an off-white solid. After storage at -20 $^\circ\text{C}$ for several hours to ensure complete precipitation, the solid was collected by filtration, washed with 2×5 mL of diethyl ether, and then dried overnight in vacuo. Yield: 0.083 g of 2 (63%, based on $\text{RhMe}_3(\text{triphos})$) as a white powder. The two chemical shifts in the ^{31}P NMR (methylene- d_2 chloride) spectrum exhibited some broadening at room temperature; therefore, the NMR spectra were collected at -30 $^\circ\text{C}$. ^1H NMR (methylene- d_2 chloride, -30 $^\circ\text{C}$): δ 7.5-6.9 (overlapping multiplets, 30, PPh), 2.47 (s, overlapping with triphos P- CH_2 , CH_3CN), 2.4 (br m, triphos P- CH_2), 1.60 (br s, 3, triphos CH_3), 0.63 (br s, 6, Rh- CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (methylene- d_2 chloride, -30 $^\circ\text{C}$): δ 35.0 (dt, $J_{\text{P-P}} = 27$ Hz, $J_{\text{Rh-P}} = 142$ Hz, 1P), -13.4 (dd, $J_{\text{Rh-P}} = 68$ Hz, 2P). Anal. Calcd for $\text{C}_{46}\text{H}_{50}\text{BCl}_2\text{F}_4\text{NP}_3\text{Rh}$: C, 56.93; H, 5.19; N, 1.44. Found: C, 56.36; H, 5.19; N, 1.36.

[$\text{Rh}(\text{C}_2\text{H}_4)_2(\text{triphos})\text{BF}_4$ (3)]. In a typical preparation, [$\text{RhMe}_2(\text{triphos})\text{BF}_4$ (1) was prepared in situ by adding a solution

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of $HBf_4 \cdot Et_2O$ (85% solution in diethyl ether, 9.5 μL , $\sim 7.8 \times 10^{-5}$ mol) in 0.4 mL of methylene- d_2 chloride to a stirred slurry of $RhMe_3(\text{triphos})$ (0.056 g, 7.2×10^{-5} mol) as described above. The solution was filtered and placed in a glass insert in a high-pressure vessel of local construction. The bomb was pressurized with 100 psi (6.8 atm) of ethylene and magnetically stirred for 1 h at room temperature. After the pressure was released from the bomb, the reaction mixture containing **3** was filtered and placed in an NMR tube under nitrogen. The reaction is essentially quantitative by NMR analysis; attempts to isolate solid **3** have been unsuccessful. 1H (methylene- d_2 chloride, 22 °C): δ 7.3–7.0 (overlapping multiplets, 30, PPh), 3.65 (br, overlapping with Et_2O , C_2H_4), 2.54 (d, $J_{P-H} = 7$ Hz, 6, P- CH_2), 1.71 (unresolved quartet, $J_{P-H} = 3$ Hz, 3, triphos CH_3). $^{31}P\{^1H\}$ NMR (methylene- d_2 chloride, 22 °C): δ 13.3 (br). 1H NMR (methylene- d_2 chloride, -80 °C): δ 7.5–7.0 (overlapping multiplets, 30, PPh), 2.73, 2.47 (broad doublets, $J = 18$ Hz, 8 (4 H each), C_2H_4), 2.53 (br s, partially overlapping C_2H_4 , 6, P- CH_2), 1.70 (br s, 3, triphos CH_3). $^{31}P\{^1H\}$ NMR (methylene- d_2 chloride, -80 °C): δ 9.5 (d, $J_{Rh-P} = 105$ Hz).

For ^{13}C NMR spectroscopy, a 1.2×10^{-4} mol sample of **3** was prepared in 1 mL of methylene chloride as described above and placed in an NMR tube. The solution was degassed by a freeze-pump-thaw cycle, and then approximately 4×10^{-5} mol of $[^{13}C_2]$ ethylene was condensed into the tube, which was subsequently flame-sealed. The $^{13}C\{^1H\}$ spectrum (methylene- d_2 chloride, -80 °C), recorded immediately after shaking the thawed sample to equilibrate the mixture, shows a broad resonance at δ 57.0 in addition to free ethylene (δ 122). The room-temperature ^{13}C NMR spectrum shows only a broad resonance ($\Delta\nu_{1/2} = 250$ Hz) for free ethylene.

[Rh(CO) $_2$ (triphos)]BF $_4$ from $[RhMe_3(\text{triphos})]BF_4$ and CO. $[RhMe_3(\text{triphos})]BF_4$ (0.065 mmol, produced in situ) dissolved in CH_2Cl_2 (15 mL) was placed under an atmosphere of CO (1.5 mmol). The solution turned orange and then bright yellow almost immediately and was allowed to stir for an addition 1 h. 1H and ^{31}P NMR and IR spectra were identical with those of $Rh(CO)_2(\text{triphos})^+$.^{7,10,11} Repeating this experiment in CD_2Cl_2 showed acetone (2.09 ppm) as the only organic product. Integration of the 1H NMR spectrum showed the yield of $Rh(CO)_2(\text{triphos})^+$ to be quantitative and that of acetone to be 90%.

[Rh(H $_2$ O)(C $_2$ H $_4$)(triphos)]BF $_4 \cdot CH_2Cl_2$ (4). (a) **Synthesis in the Presence of Adventitious H $_2$ O.** In a typical preparation, a solution of $HBf_4 \cdot Et_2O$ (85% solution in diethyl ether, 7.5 μL , $\sim 6.2 \times 10^{-5}$ mol; containing adventitious water) in 0.5 mL of methylene chloride was added to a stirred slurry of $RhMe(C_2H_4)(\text{triphos})$ (0.045 g, 5.8×10^{-5} mol) in 1.0 mL of methylene chloride with stirring under an atmosphere of ethylene at -78 °C. Upon warming of the reaction mixture to room temperature, the mixture yielded a clear bright orange solution. The solution was sealed in the reaction flask under ethylene and set aside. After standing for several hours, red-orange crystals began to form. After 3 days, the mother liquor was withdrawn and the crystals were washed with 3×0.5 mL of methylene chloride and 2×5 mL of diethyl ether and then dried in vacuo. Yield: 0.022 g of **4** (40%, based on $RhMe(C_2H_4)(\text{triphos})$) as bright red-orange crystals. Anal. Calcd for $C_{44}H_{47}BCl_2F_4OP_3Rh$: C, 55.90; H, 5.01; F, 8.04. Found: C, 55.11; H, 5.04; F, 7.57.

Characteristic IR peaks (O-H stretches): 3588 (weak, sharp) and 3368 cm^{-1} (weak, broad).

(b) **^{31}P NMR Spectroscopy of the Reaction Mixture.** ^{31}P NMR (-80 °C) spectra of the initial orange reaction solution show essentially a mixture of **3** (approximately 20–50% for different NMR assays) and a variable mixture of unidentified species with AMX_2 resonance patterns: species A δ 46.2 (dt, $J_{P-P} = 31$ Hz, $J_{Rh-P} = 138$ Hz, 1 P), -3.6 (dd, $J_{Rh-P} = 111$ Hz, 2 P); species B δ 46.6 (dt, $J_{P-P} = 31$ Hz, $J_{Rh-P} = 139$ Hz, 1 P), -4.9 (dd, $J_{Rh-P} = 112$ Hz, 2 P). Compound **3** is observed in these mixtures even in the absence of an ethylene atmosphere; however, in the absence of either water or an ethylene atmosphere, crystals of **4** do not form nor is **4** observed by ^{31}P NMR analysis.

(c) **Synthesis of **4** Using Anhydrous Acid and H $_2$ O or D $_2$ O.** Compound **4** was prepared by using fresh anhydrous $HBf_4 \cdot Et_2O$

(85% solution in diethyl ether (12 μL , $\sim 9.9 \times 10^{-5}$ mol) and $RhMe(C_2H_4)(\text{triphos})$ (0.076 g, 9.9×10^{-5} mol) as described above except that following the formation of the clear orange solution, approximately 5 μL of D_2O was added to the reaction flask. Yield: 0.026 g of **4** (28%, based on $RhMe(C_2H_4)(\text{triphos})$) as bright red-orange crystals. Compound **4** was also prepared similarly by using H_2O . When D_2O is used, the following new bands appear which are not present when H_2O is used: 2658, 2641 (weak, sharp), and 2495 cm^{-1} (weak, broad).

(d) **Synthesis of **4** from **3** and H $_2$ O.** A 1.5-mL methylene chloride solution containing 6.7×10^{-5} mol of **3** was prepared as described above (using anhydrous $HBf_4 \cdot Et_2O$). The solution was placed in a Schlenk flask under ethylene, and then approximately 5 μL of H_2O was added. Upon standing, bright red-orange crystals formed, which were isolated and characterized as described above. Yield: 0.012 g of **4** (19%, based on **3**).

(e) **NMR Spectroscopy of **4**.** Under nitrogen, the low-temperature $^{31}P\{^1H\}$ NMR (methylene- d_2 chloride, -80 °C) spectrum, upon dissolving the sparingly soluble crystals of **4**, shows a mixture of $[Rh(C_2H_4)_2(\text{triphos})]BF_4$ (**3**) (δ 9.5, d, $J_{Rh-P} = 105$ Hz) and an AMX_2 resonance pattern [δ 46.3 (dt, $J_{P-P} = 32$ Hz, $J_{Rh-P} = 140$ Hz, 1 P); δ -3.2 (dd, $J_{Rh-P} = 111$ Hz, 2 P)] consistent with **4**. The ratio of **3**:**4** varies, for different NMR assays, from approximately 1:2 to 1:3. Other minor ^{31}P NMR resonances, present in varying amounts are δ 23.1 (dd, $J = 31$, 126 Hz) and δ 1.3 (dd, $J = 44$, 109 Hz). The room-temperature $^{31}P\{^1H\}$ NMR spectrum (methylene- d_2 chloride, 22 °C) shows a broad resonance at 13 ppm. The 1H NMR spectrum (methylene- d_2 chloride) shows a broad resonance consistent with $Rh-OH_2$ of δ 13.9 at room temperature and of δ 10.9 at -80 °C. The remainder of the 1H NMR spectrum is obscured by overlapping peaks. ^{19}F NMR (methylene- d_2 chloride): (22 °C) δ -150.2 (sharp s); (-80 °C) δ -149.8 (sharp s).

When the crystals are dissolved in methylene- d_2 chloride saturated with water (0.8 mL of methylene- d_2 chloride was layered under 1.0 mL of degassed distilled water, the system was shaken and allowed to settle, and then a 0.5-mL aliquot of this solvent was withdrawn; approximately 0.003 g of **4** were used), the $^{31}P\{^1H\}$ NMR spectrum (methylene- d_2 chloride, -80 °C) shows an approximately 1:8 mixture of **3** and **4**, respectively. In this case, the overlap with **3** in the 1H NMR spectrum was mitigated and the 1H NMR spectrum of **4** could be obtained. 1H NMR (methylene- d_2 chloride, -80 °C): δ 8.3 (br, $Rh-OH_2$), 7.5–6.5 (multiplets, 30, PPh), 2.90, 2.13, 1.92 (broad doublets, $J_{P-H} =$ approximately 9, 9, and 7 Hz, respectively, 2 H each, P- CH_2), 2.75, 2.24 (broad doublets, $J =$ approximately 16 Hz, 2 H each, C_2H_4), 1.58 (quartet, $J = 3$ Hz, triphos CH_3).

Under an atmosphere of ethylene, crystals of **4** (approximately 0.003 g) rapidly dissolved in methylene- d_2 chloride (0.5 mL) to quantitatively yield **3** by ^{31}P NMR analysis.

[Rh(CH $_3$ CN)(C $_2$ H $_4$)(triphos)]BF $_4$ (5). Compound **5** was prepared in a manner similar to **2** using $HBf_4 \cdot Et_2O$ (85% solution in diethyl ether, 14 μL , $\sim 1.1 \times 10^{-4}$ mol), $RhMe(C_2H_4)(\text{triphos})$ (0.083 g, 1.1×10^{-4} mol), and acetonitrile (6.0 μL , $\sim 1.2 \times 10^{-4}$ mol) to yield **5** as a bright yellow powder. Yield: 0.074 g (77%, based on $RhMe(C_2H_4)(\text{triphos})$). 1H NMR (methylene- d_2 chloride, 22 °C): δ 7.5–6.4 (multiplets, 30, PPh), 2.82, 2.07, 1.90 (doublets, $J_{P-H} = 10$, 11, and 11 Hz, respectively, 2 H each, P- CH_2), 2.56, 2.22 (broad doublets, $J =$ approximately 15 Hz, 2 H each, C_2H_4), 1.50 (s, overlapping with triphos CH_3 , CH_3CN), 1.48 (quartet, $J_{P-H} = 3$ Hz, triphos CH_3). $^{31}P\{^1H\}$ NMR (methylene- d_2 chloride, 22 °C): δ 35.5 (dt, $J_{P-P} = 35.5$ Hz, $J_{Rh-P} = 124$ Hz, 1 P), -1.2 (dd, $J_{Rh-P} = 109.5$ Hz, 2 P). Anal. Calcd for $C_{46}H_{49}BCl_2F_4NP_3Rh$: C, 57.04; H, 4.99; N, 1.45. Found: C, 56.46; H, 4.81; N, 1.84.

For ^{13}C NMR, a 0.02-g ($\sim 2 \times 10^{-5}$ mol) sample of **5** was dissolved in 0.5 mL of methylene chloride and the solution was placed in an NMR tube. The solution was degassed by a freeze-pump-thaw cycle, and then approximately 4×10^{-5} mol of $[^{13}C_2]$ ethylene was condensed into the tube, which was subsequently flame-sealed. The $^{13}C\{^1H\}$ NMR spectrum (methylene- d_2 chloride, 22 °C), recorded immediately after shaking the thawed sample to equilibrate the mixture, shows an apparent quartet at δ 39.5 ($J = 9$ Hz) in addition to free ethylene (δ 122).

X-ray Structure Determination of **4.** A suitable crystal was located, transferred to the goniostat by using inert-atmosphere handling techniques, and cooled to -172 °C for characterization and data collection. A systematic search of a limited hemisphere

(10) Johnston, G. G.; Baird, M. C. *Organometallics* 1989, 8, 1894.

(11) Behrens, H.; Ellermann, J.; Hohenberger, E. F. Z. *Naturforsch.* 1980, 35B, 661.

Table I. Crystallographic Data for (triphos)Rh(H₂O)(C₂H₄)BF₄ • CH₂Cl₂

chem formula	C ₄₄ H ₄₇ P ₃ Cl ₂ BF ₄ ORh	space group	P2 ₁ /c
a, Å	10.502 (2)	T, °C	-172
b, Å	16.518	λ, Å	0.710 69
c, Å	24.210 (5)	ρ _{calcd} , g cm ⁻³	1.509
β, deg	97.81 (1)	μ(Mo Kα), cm ⁻¹	6.98
V, Å ³	4160.70	R	0.0594
Z	4	R _w	0.0583
fw	945.39		

Table II. Selected Bond Distances (Å) and Angles (deg) for (triphos)Rh(H₂O)(C₂H₄)BF₄ • CH₂Cl₂

Rh(1)-P(2)	2.2086 (21)	F(50)-B(49)	1.403 (14)
Rh(1)-P(3)	2.3605 (21)	F(51)-B(49)	1.409 (10)
Rh(1)-P(4)	2.3845 (20)	F(52)-B(49)	1.304 (13)
Rh(1)-O(7)	2.215 (5)	F(53)-B(49)	1.385 (12)
Rh(1)-C(5)	2.144 (7)	C(5)-C(6)	1.406 (11)
Rh(1)-C(6)	2.148 (8)		
P(2)-Rh(1)-P(3)	91.12 (7)	O(7)-Rh(1)-C(5)	82.52 (27)
P(2)-Rh(1)-P(4)	87.94 (7)	O(7)-Rh(1)-C(6)	85.0 (3)
P(2)-Rh(1)-O(7)	176.46 (15)	C(5)-Rh(1)-C(6)	38.2 (3)
P(2)-Rh(1)-C(5)	94.26 (24)	Rh(1)-C(5)-C(6)	71.0 (4)
P(2)-Rh(1)-C(6)	91.53 (25)	Rh(1)-C(6)-C(5)	70.7 (4)
P(3)-Rh(1)-P(4)	89.48 (7)	Cl(54)-C(55)-Cl(55)	112.6 (6)
P(3)-Rh(1)-O(7)	91.46 (15)	F(50)-B(49)-F(51)	109.3 (8)
P(3)-Rh(1)-C(5)	112.19 (23)	F(50)-B(49)-F(52)	111.0 (15)
P(3)-Rh(1)-C(6)	150.43 (23)	F(50)-B(49)-F(53)	100.2 (9)
P(4)-Rh(1)-P(7)	94.51 (15)	F(51)-B(49)-F(52)	110.8 (8)
P(4)-Rh(1)-C(5)	158.13 (23)	F(51)-B(49)-F(53)	109.6 (7)
P(4)-Rh(1)-C(6)	120.04 (23)	F(52)-B(49)-F(53)	115.4 (14)

of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group P2₁/c. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected (6° < 2θ < 45°)¹² by using a continuous θ-2θ scan with fixed backgrounds (Table I). Data were reduced to a unique set of intensities and associated σ's in the usual manner. No correction was necessary for absorption or crystal decay. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The presence of the bonded H₂O molecule was somewhat unexpected and presented an interesting crystallographic challenge. Initial difference Fourier maps indicated that it could be a fluorine atom, and it refined satisfactorily when assigned neutral-F scattering factors, although the thermal parameter was somewhat larger than expected. Electronic considerations (and the M-F distance) indicated that it could not be a simple fluoride, and in fact, a peak was found which could reasonably be called a hydrogen atom, thus making the ligand -FH. The elemental analysis and the absence of any ¹⁹F NMR signal other than that of BF₄ led to the conclusion that the ligand was, in fact, water. When the oxygen scattering factor was utilized, the thermal parameter did behave better, but no hydrogen atoms could be located. The proximity of F(51) (O...F = 2.665 (18) Å) indicates a relatively strong hydrogen bond, and no other acceptor atoms are near. A 75:25 rotational disorder of three fluorines was present about the B-F(51) vector. Dimensions of only the major conformer are given here. All other hydrogen atoms were clearly visible and were refined isotropically. A final difference Fourier was featureless, with the largest peak being 0.68 e/Å³. The results of the structure determination are shown in Tables II and III and Figure 1. Further details are available as supplementary material.

Results

Protonation of Rh^{III} Alkyls. (a) Synthesis and Characterization of [RhMe₂(triphos)]BF₄ (1). The reaction of 1 equiv of HBF₄·Et₂O with RhMe₃(triphos) in methylene chloride results in vigorous gas evolution (CH₄

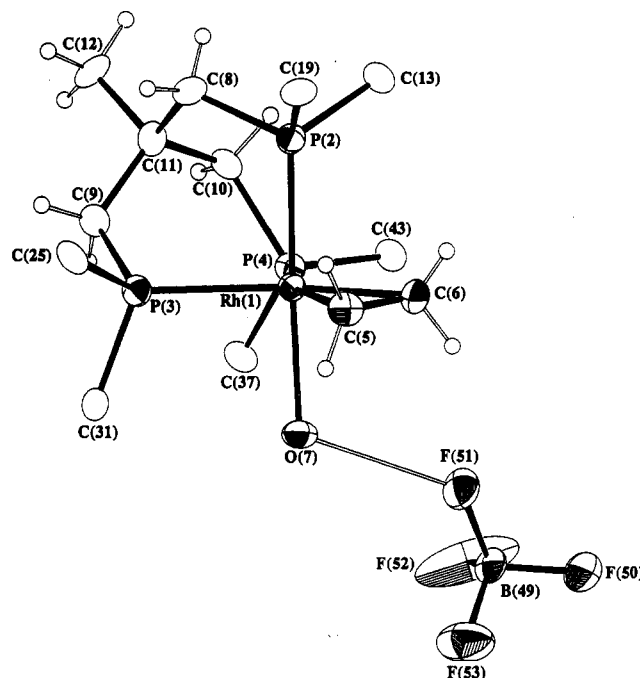
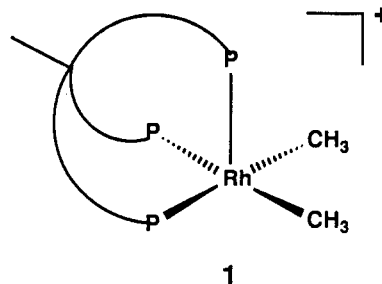


Figure 1. ORTEP drawing of (triphos)Rh(C₂H₄)(OH₂)BF₄, showing selected atom labeling. For clarity, only the phenyl ipso carbons are shown.

by ¹H NMR analysis) concomitant with formation of an orange solution of [RhMe₂(triphos)]BF₄ (1). The low-temperature (-80 °C) ³¹P NMR spectrum of 1 exhibits an AMX₂ (M = Ph) spin system consistent with two equivalent and one unique phosphorus nuclei. At higher temperatures, a fluxional process is observed which exchanges the two phosphorus environments. At room temperature the spectrum consists of a rhodium-coupled doublet. The observation of rhodium-phosphorus coupling in the fast-exchange ³¹P NMR spectra indicates that the fluxional process exchanging the phosphorus nuclei does not involve phosphine dissociation. The ¹J(¹⁰³Rh-³¹P) coupling constant of 103 Hz is consistent with the weighted average of 100 Hz calculated by using the stopped-exchange ¹J_{Rh-P} coupling constants.

The low-temperature (-80 °C) ¹H NMR spectrum of 1 exhibits a single rhodium-methyl resonance, indicating the two methyl ligands are equivalent. Assuming that 1 is a 16e⁻, five-coordinate species, these NMR observations suggest a square-pyramidal ground-state structure for 1.



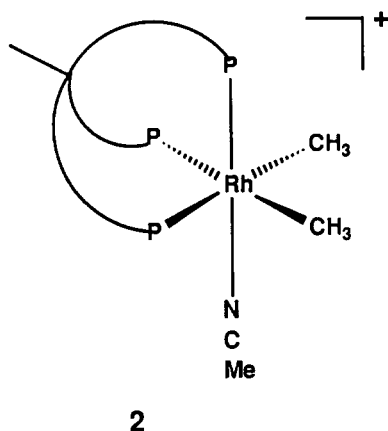
Alternatively, an 18e⁻ six-coordinate ground state could be achieved by coordination of the BF₄⁻ anion as found for the compounds [MMe₂(PMe₂Ph)₃]BF₄ (M = Rh, Ir). The ¹⁹F NMR spectrum of 1 in CH₂Cl₂ exhibits a single resonance at δ -151.1 and -149.4 at 22 and -80 °C, respectively. These chemical shifts are consistent with the free (uncoordinated) BF₄⁻ anion.

Reactivity of [RhMe₂(triphos)]BF₄ with C₂H₄, MeCN, and CO. Since 1 in CH₂Cl₂ is coordinatively un-

(12) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* 1980, 19, 1840.

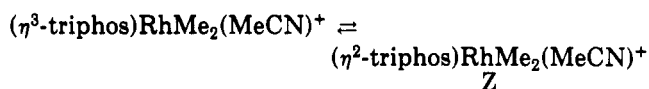
saturated (or has, at best, a weakly bound sixth ligand), we sought to investigate its ability to coordinate ethylene. ^{31}P NMR monitoring of the reaction between 1 and ethylene (1 atm) showed no evidence for formation of the compound $[RhMe_2(C_2H_4)(triphos)]BF_4$. Instead, the reaction gives an unattractive variety of products, one of which will be discussed further (vide infra). In contrast, whereas $[IrMe_2(PMe_2Ph)_3]BF_4$ readily reacts with ethylene to form $[IrMe_2(C_2H_4)(PMe_2Ph)_3]BF_4$, no such reaction (monitored at low temperature) occurs for $[RhMe_2(PMe_2Ph)_3]BF_4$.

If the protonation of $RhMe_3(triphos)$ (i.e., generating 1 in situ) is performed in the presence of 1 equiv of acetonitrile, a new compound, $[RhMe_2(CH_3CN)(triphos)]BF_4$ (2), is isolated. Unlike 1, compound 2 is stereochemically rigid on the NMR time scale. The ^{31}P NMR spectrum exhibits an AMX_2 spin system consistent with two equivalent and one unique phosphorus nuclei at 22 °C. A single rhodium-methyl 1H resonance is observed. These observations are consistent with a structure for 2 as shown.



The Rh-P coupling constant to the phosphorus trans to CH_3CN in 2 is unusually large (142 Hz).

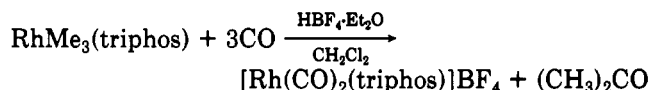
If the 1H NMR spectrum of 2 is recorded in CD_3CN , only free CH_3CN is observed. Thus 2 exchanges with free acetonitrile within minutes at 25 °C. The mechanism of this exchange was studied in more detail. The 1H NMR spectrum of 2 in CD_2Cl_2 shows a sharp peak for coordinated acetonitrile. If 0.5 equiv of free MeCN is added to this solution, only a broad resonance ($\nu_{1/2} \sim 37$ Hz) for free MeCN is observed (δ 1.98); the distinct coordinated MeCN resonance, no longer a sharp peak, is now obscured by triphos resonances. Additional MeCN causes the free MeCN peak to sharpen. Since the lifetime of coordinated acetonitrile depends upon the concentration of free acetonitrile (hence the change in shape of the peak of coordinated MeCN), it follows that the exchange medium is associated and first order in free MeCN. A dissociative mechanism predicts that the coordinated MeCN line widths would be the same in all spectra recorded. How free MeCN can attack $(triphos)RhMe_2(MeCN)^+$ is evident from the variable-temperature $^{31}P\{^1H\}$ NMR spectrum (in CH_2Cl_2) in the absence of added MeCN. At -30 °C, one observes a well-resolved AMX_2 pattern, but at 25 °C one sees only two doublets (intensity 1:2), where the smallest line spacing (J_{P-P}) is no longer resolved due to lifetime broadening of all lines. We attribute this to the following equilibrium:



Transient Z, a $16e^-$ species, is then sufficient to add MeCN

and effect the associative exchange process evident from the 1H NMR spectrum.

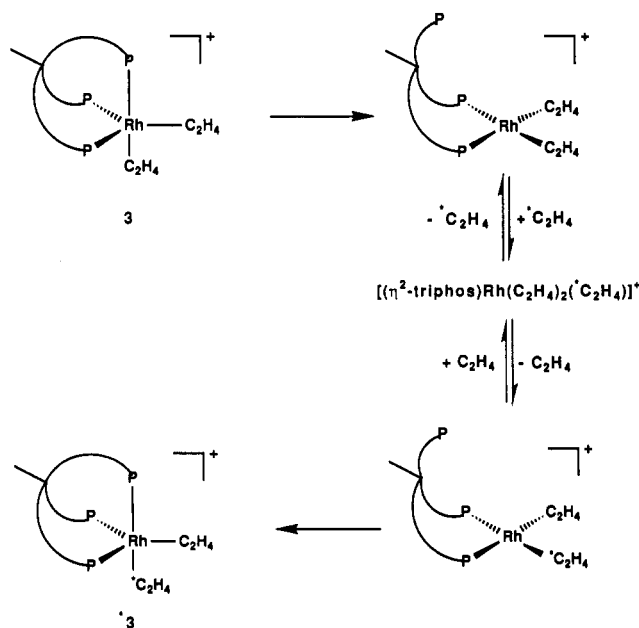
If, instead of acetonitrile, 1 is generated in situ in the presence of excess carbon monoxide, $[Rh(CO)_2(triphos)]BF_4$ and acetone are produced:



Ethane is noteworthy by its absence as a product of this reaction. The $[Rh(CO)_2(triphos)]BF_4$ product was readily characterized by comparison to the literature.^{7,10,11}

(b) **Synthesis and Characterization of $[Rh(C_2H_4)_2(triphos)]BF_4$ (3).** In an attempt to promote a clean reaction between 1 and ethylene, a solution of 1 generated in situ in methylene chloride was subsequently placed under 100 psi of ethylene in a high-pressure bomb. NMR analysis of the reaction solution shows that $[Rh(C_2H_4)_2(triphos)]BF_4$ (3) has been formed nearly quantitatively. Compound 3 appears to be sensitive to loss of ethylene and all attempts to isolate 3 as solid or crystalline material have been unsuccessful. The ^{31}P NMR spectrum for 3 shows a single rhodium-coupled doublet at -80 °C, consistent with a rapid averaging of environments on the NMR time scale by a low-energy fluxional process. At room temperature, the ^{31}P NMR spectrum is a broad unstructured resonance without observable couplings, indicating that a second fluxional process, of higher energy, involving phosphine dissociation is taking place (hence, a loss of rhodium-phosphorus coupling).

The low-temperature (-80 °C) 1H NMR spectrum exhibits two non-first-order doublets of equal intensity (4 H). Interestingly, a single ethylene resonance without resolvable coupling is observed in the ^{13}C NMR spectrum at -80 °C. A ^{13}C NMR experiment with $[^{13}C_2]$ ethylene shows that coordinated ethylene in 3 rapidly (less than 10 min) exchanges with free ethylene. Moreover, the observation of a broad ^{13}C resonance for added free ethylene at room temperature indicates this exchange is taking place on the NMR time scale. In view of the ^{31}P NMR behavior of 3 (indicative of a phosphine dissociation), the following ethylene exchange mechanism is proposed:



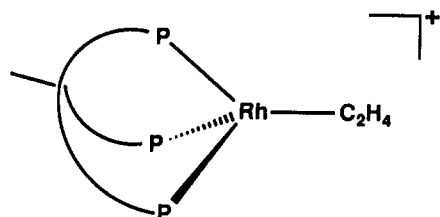
The first step of the mechanism generates what should be a relatively stable, Rh^I square-planar intermediate. As

Table III. Fractional Coordinates and Isotropic Thermal Parameters^a for (triphos)Rh(H₂O)(C₂H₄)BF₄•CH₂Cl₂

	10 ⁴ x	10 ⁴ y	10 ⁴ z	10B _{iso} , Å ²		10 ⁴ x	10 ⁴ y	10 ⁴ z	10B _{iso} , Å ²
Rh(1)	3110 (1)	1725.0 (4)	8425.5 (2)	15	F(53)	7533 (9)	3835 (6)	9306 (3)	50
P(2)	1998 (2)	586 (1)	8374 (1)	16	CL(54)	6001 (3)	3089 (1)	11618 (1)	44
P(3)	1445 (2)	2391 (1)	7845 (1)	17	C(55)	5567 (15)	3807 (8)	11081 (5)	61
P(4)	2103 (2)	2076 (1)	9218 (1)	16	CL(55)	4636 (2)	4589 (2)	11290 (1)	54
C(5)	4558 (8)	1263 (5)	7965 (3)	20	F(50)'	7257 (30)	2985 (13)	10120 (8)	32 (8)
C(6)	4897 (8)	1073 (5)	8532 (4)	22	F(52)'	7989 (41)	3372 (34)	9476 (21)	37 (12)
F(7)	4333 (5)	2823 (3)	8471 (2)	23	F(53)'	6062 (32)	3915 (18)	9680 (15)	38 (17)
C(8)	263 (8)	794 (5)	8241 (4)	22	H(1)	422 (7)	88 (5)	768 (3)	31 (13)
C(9)	-52 (8)	2324 (5)	8159 (3)	20	H(2)	492 (6)	173 (4)	778 (3)	60 (13)
C(10)	450 (7)	1657 (5)	9128 (3)	19	H(3)	562 (7)	134 (4)	874 (3)	19 (11)
C(11)	9803 (7)	1561 (4)	8509 (3)	18	H(4)	491 (6)	59 (4)	863 (3)	15 (13)
C(12)	-1651 (7)	1456 (6)	8546 (3)	21	H(5)	3 (8)	80 (5)	785 (3)	47 (14)
C(13)	2179 (7)	-58 (4)	8993 (3)	18	H(6)	988 (6)	37 (4)	837 (2)	10 (11)
C(14)	1380 (8)	9258 (5)	9024 (4)	27	H(7)	994 (6)	281 (4)	839 (3)	21 (12)
C(15)	1550 (8)	-1229 (5)	9488 (4)	27	H(8)	-68 (7)	238 (4)	789 (3)	26 (12)
C(16)	2457 (8)	-1045 (5)	9930 (3)	23	H(9)	54 (6)	112 (4)	930 (3)	19 (12)
C(17)	3246 (8)	-390 (5)	9912 (3)	21	H(10)	988 (6)	202 (4)	933 (3)	14 (11)
C(18)	3118 (7)	94 (5)	9439 (3)	17	H(11)	802 (7)	194 (4)	869 (3)	29 (13)
C(19)	2311 (7)	9856 (5)	7836 (3)	21	H(12)	-211 (7)	137 (5)	820 (3)	35 (13)
C(20)	1743 (8)	-59 (5)	7288 (3)	23	H(13)	-184 (6)	100 (4)	880 (3)	16 (11)
C(21)	2072 (8)	9438 (5)	6872 (3)	23	H(14)	85 (8)	-86 (5)	872 (3)	46 (14)
C(22)	2945 (8)	-1184 (5)	7006 (4)	29	H(15)	90 (6)	-174 (4)	947 (2)	6 (11)
C(23)	3502 (8)	8722 (6)	7554 (4)	31	H(16)	250 (6)	865 (4)	25 (3)	19 (12)
C(24)	3174 (7)	-766 (5)	7962 (3)	22	H(17)	389 (6)	972 (4)	19 (2)	11 (11)
C(25)	1004 (8)	2098 (4)	7110 (3)	19	H(18)	368 (7)	55 (4)	941 (3)	28 (12)
C(26)	1951 (8)	1791 (5)	6823 (3)	27	H(19)	107 (6)	31 (4)	719 (3)	19 (12)
C(27)	1666 (10)	1583 (6)	6249 (3)	34	H(20)	161 (9)	958 (6)	647 (4)	68 (15)
C(28)	433 (9)	1670 (5)	5988 (3)	31	H(21)	318 (7)	-157 (5)	672 (3)	35 (13)
C(29)	9485 (9)	1974 (5)	6270 (3)	29	H(22)	404 (7)	-168 (5)	767 (3)	40 (14)
C(30)	-236 (8)	2196 (5)	6829 (3)	24	H(23)	361 (6)	-85 (4)	834 (3)	21 (12)
C(31)	1803 (7)	3475 (4)	7771 (3)	17	H(24)	281 (6)	173 (4)	701 (2)	10 (11)
C(32)	2705 (9)	3683 (5)	7421 (4)	28	H(25)	232 (8)	132 (5)	605 (4)	55 (15)
C(33)	3113 (9)	4468 (6)	7394 (4)	32	H(26)	28 (6)	151 (4)	558 (2)	14 (11)
C(34)	2625 (9)	5073 (5)	7696 (3)	26	H(27)	-139 (6)	204 (4)	609 (3)	20 (12)
C(35)	1733 (10)	4887 (5)	8031 (4)	31	H(28)	-83 (7)	244 (4)	699 (3)	28 (13)
C(36)	1315 (8)	4091 (5)	8075 (3)	26	H(29)	307 (9)	327 (6)	725 (4)	74 (16)
C(37)	1914 (7)	3163 (4)	9363 (3)	20	H(30)	370 (7)	458 (5)	717 (3)	37 (14)
C(38)	3023 (8)	3622 (5)	9489 (3)	23	H(31)	291 (8)	560 (6)	773 (4)	58 (15)
C(39)	2972 (8)	4435 (5)	9626 (3)	24	H(32)	150 (8)	521 (5)	825 (4)	57 (15)
C(40)	1799 (9)	4806 (5)	9618 (3)	29	H(33)	66 (7)	400 (4)	825 (3)	32 (13)
C(41)	684 (8)	4369 (5)	9499 (3)	23	H(34)	390 (5)	341 (4)	950 (2)	4 (11)
C(42)	735 (8)	3549 (5)	9375 (3)	21	H(35)	371 (7)	474 (5)	972 (3)	37 (14)
C(43)	2749 (7)	1782 (5)	9934 (3)	18	H(36)	172 (6)	536 (4)	971 (3)	19 (12)
C(44)	4068 (7)	1808 (5)	10101 (3)	18	H(37)	980 (6)	459 (4)	949 (3)	20 (12)
C(45)	4595 (8)	1636 (5)	10638 (3)	23	H(38)	-2 (6)	327 (4)	924 (3)	15 (11)
C(46)	3800 (8)	1420 (5)	11021 (3)	26	H(39)	459 (5)	196 (3)	987 (2)	5 (11)
C(47)	2484 (8)	1370 (6)	10875 (3)	31	H(40)	546 (6)	165 (4)	1073 (3)	22 (12)
C(48)	1961 (8)	1563 (5)	10331 (3)	24	H(41)	406 (7)	128 (5)	1141 (3)	32 (13)
B(49)	6958 (9)	3296 (6)	9635 (3)	22	H(42)	197 (7)	122 (4)	1118 (3)	30 (13)
F(50)	8051 (14)	2944 (6)	9939 (6)	72	H(43)	117 (8)	150 (5)	1019 (3)	51 (14)
F(51)	6281 (4)	2703 (3)	9295 (2)	30	H(44)	648 (13)	406 (8)	1093 (6)	114 (27)
F(52)	6224 (9)	3623 (10)	9968 (9)	89	H(45)	525 (16)	354 (10)	1073 (7)	153 (29)

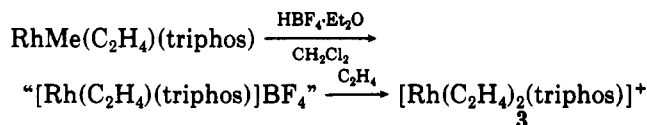
^a Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

well as accounting for the ³¹P NMR data, this mechanism avoids formation of a tetrahedral Rh^I intermediate via ethylene dissociation:



Protonation of Rh^I Alkyls. (a) **Synthesis and Characterization of [Rh(H₂O)(C₂H₄)(triphos)]BF₄ (4).** We considered that protonation of RhMe(C₂H₄)(triphos) should yield, formally, [Rh(C₂H₄)(triphos)]BF₄ as an intermediate and that this species would rapidly coordinate

free ethylene (or another 2e⁻, neutral donor ligand) as an alternative route to synthesizing 3:



The reaction under ethylene of RhMe(C₂H₄)(triphos) and HBF₄•Et₂O at -78 °C in methylene chloride yields a clear orange solution with ¹H NMR evidence for CH₄. The low-temperature (-80 °C) ³¹P NMR spectrum of this solution revealed a mixture of 3 (typically 20–50%) and varying amounts of two unidentified compounds with AMX₂ spin systems. Moreover, these same mixtures were observed even in the absence of an ethylene atmosphere, indicating the reaction is more complicated than anticipated.

Fortuitously, one reaction mixture was allowed to stand under ethylene and produced red-orange crystals. An X-ray diffraction study revealed the compound to be $[\text{Rh}(\text{H}_2\text{O})(\text{C}_2\text{H}_4)(\text{triphos})]\text{BF}_4$ (4). Selected bond distances and angles are listed in Table II. As shown in Figure 1, the coordination geometry around Rh is distorted trigonal bipyramidal, with P(2), P(3), P(4), the midpoint of the ethylene ligand, and O(7) occupying the five coordination sites. The aquo ligand is hydrogen-bonded to the BF_4^- anion, as indicated by the short O(7)–F(51) separation of 2.665 (18) Å.

Although there appear to be no structures available for direct comparison, the Rh–O bond length of 2.215 (5) Å probably represents a long bond due to the situation of a weakly coordinating ligand (aquo) trans to a ligand (phosphine) having a significant trans influence. Conversely, the rhodium–phosphorus bond distance for the phosphine moiety trans to the aquo ligand is approximately 0.16 Å ($\sim 80\sigma$) shorter than the bond lengths for the phosphine moieties trans to ethylene. Interestingly, while the rhodium–carbon bond lengths for the ethylene ligand are essentially the same, the rhodium–phosphine bond lengths trans to ethylene differ by approximately 0.024 Å ($\sim 12\sigma$). In addition, the atoms Rh(1), P(3), P(4), C(5), and C(6) are essentially coplanar; however, the angles P(3)–Rh(1)–C(5) (112.19 (23°)) and P(4)–Rh(1)–C(6) (120.04 (23°)) differ substantially. In the absence of any overriding electronic considerations, these effects must be due to a steric constraint associated with coordination of the triphos ligand. A similar distortion is observed in the X-ray structure of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$.⁵

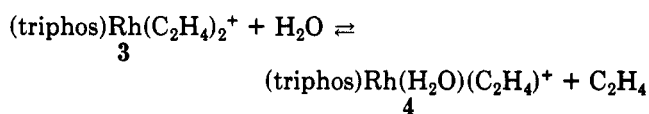
Compound 4 forms from the reaction mixture due to adventitious water in the $\text{HBF}_4\cdot\text{Et}_2\text{O}$. Accordingly, 4 can be prepared by using anhydrous (fresh) $\text{HBF}_4\cdot\text{Et}_2\text{O}$ and added water. Compound 4 can also be prepared from 3 and added water. In each case, 4 will *not* form in the absence of either an ethylene atmosphere or water.

When crystals of 4 are dissolved in methylene chloride, low-temperature (-80°C) ^{31}P NMR spectroscopy reveals a mixture of 3 and 4 in a 1:2 to 1:3 ratio. The ^1H NMR spectrum exhibits a resonance consistent with the aquo ligand protons at δ 13.9 and 10.9 at 22 and -80°C , respectively. This temperature-dependent chemical shift is due to hydrogen-bonding equilibria. Fortunately, when crystals of 4 are dissolved in methylene chloride *saturated with water*, the concentration of 3 is low. The low-temperature (-80°C) ^{31}P NMR spectrum of 4 exhibits an AMX_2 spin system consistent with solid-state structure of 4 for two equivalent and one unique phosphorus nuclei. The room-temperature ^{31}P NMR spectrum shows a broad resonance, indicating a fluxional process that involves phosphine dissociation, as discussed for 3. The low-temperature (-80°C) ^1H NMR spectrum exhibits three inequivalent triphos CH_2 resonances, and an AA'BB' pattern of two doublets for the ethylene hydrogens. Also, in "wet" methylene chloride (-80°C) the aquo ligand resonance moves upfield ~ 2.6 ppm (toward the resonance for free water) to 8.3 ppm. When crystals of 4 are dissolved in methylene chloride under *ethylene*, compound 3 is quantitatively formed.

The infrared spectrum of 4 in the solid state (Nujol mull) is consistent with the solid-state structure (Figure 1). A sharp band at 3588 cm^{-1} and a broad band at 3368 cm^{-1} are observed in the region expected for O–H stretching vibrations in agreement with, respectively, one free and one hydrogen-bonded OH moiety. When the complex is prepared with anhydrous acid and D_2O , two sharp bands are present at 2658 and 2641 cm^{-1} along with a broad band

at 2495 cm^{-1} . These isotopic shifts are in good agreement with the expected isotopic shift calculated for a simple diatomic oscillator.

The routes used to synthesize 4, together with the observation of compound 3 in the NMR spectra, suggest that 4 may be in equilibrium with 3 (and indeed, with other species as well) and that 4 is isolated due to its poor solubility.



(b) **Synthesis and Characterization of $\text{Rh}(\text{MeCN})(\text{C}_2\text{H}_4)(\text{triphos})^+$.** When $\text{HBF}_4\cdot\text{Et}_2\text{O}$ is reacted with $\text{RhMe}(\text{C}_2\text{H}_4)(\text{triphos})$ in methylene chloride in the presence of 1 equiv of acetonitrile, a new compound $[\text{Rh}(\text{CH}_3\text{CN})(\text{C}_2\text{H}_4)(\text{triphos})]\text{BF}_4$ (5) is obtained. Therefore, in the presence of acetonitrile, a more nucleophilic ligand than ethylene, protonation of $\text{RhMe}(\text{C}_2\text{H}_4)(\text{triphos})$ yields a *single* product. The molecule is static on the NMR time scale at room temperature. The ^{31}P NMR consists of an AMX_2 spin system. The triphos CH_2 protons exhibit three ^1H resonances, and the ethylene hydrogens give rise to an AA'BB' pattern.

^{13}C NMR spectroscopy shows that the ethylene ligand rapidly exchanges with free ethylene on the laboratory time scale, but unlike 3, the exchange is slow on the NMR time scale. The mechanism of exchange is probably similar to that proposed for 3. The observed $^1J_{\text{Rh-C}}$ coupling to ethylene of 9 Hz is in agreement with other reported Rh-olefin complexes.¹³

Discussion

In contrast to the chemistry that evolves from *mer,cis*- $\text{RhMe}_2(\text{PMe}_2\text{Ph})_3\text{BF}_4$, the $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ analogue shows several differences. First, the tripodal phosphine ligand demands *facial* stereochemistry of the three phosphorus nuclei. Next, this change is successful in preventing the phosphine redistribution that led to formation of $\text{Rh}(\text{PMe}_2\text{Ph})_4^+$ in earlier work.⁵ As a consequence, the tris(phosphine) Rh(I) compounds $(\text{triphos})\text{Rh}(\text{C}_2\text{H}_4)(\text{L})^+$ ($\text{L} = \text{C}_2\text{H}_4, \text{CH}_3\text{CN}, \text{H}_2\text{O}$) now become accessible. The cation $(\text{triphos})\text{Rh}(\text{C}_2\text{H}_4)_2^+$ contrasts both in structure and stability with $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})_3^+$, which has a *mer* arrangement of phosphines and dissociates ethylene to only a minute (spectroscopically undetectable) extent.¹⁴

While the differences in stability and reactivity have been noted for the rhodium and iridium complexes $[\text{MMe}_2(\text{PMe}_2\text{Ph})_3]^+$, this report shows that, in addition to preventing phosphine redistribution, the triphos ligand can also effect other differences.

The reactivity of $[\text{RhMe}_2(\text{triphos})]\text{BF}_4$ (1) with CO or ethylene is markedly different from that observed for $[\text{MMe}_2(\text{PMe}_2\text{Ph})_3]^+$ ($\text{M} = \text{Rh}, \text{Ir}$). While both the rhodium and iridium form stable CO adducts,⁴ $[\text{MMe}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$, in the presence of CO, $[\text{RhMe}_2(\text{triphos})]^+$ transforms rapidly (with reductive elimination of acetone) to $[\text{Rh}(\text{CO})_2(\text{triphos})]^+$. (No intermediates are observed, although it is reasonable to propose that $[\text{RhMe}_2(\text{CO})(\text{triphos})]^+$ must be an intermediate.) $[\text{RhMe}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ next reacts with excess CO in methylene chloride to yield $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$ and acetone.

$[\text{IrMe}_2(\text{PMe}_2\text{Ph})_3]^+$ reacts with ethylene to form $[\text{IrMe}_2(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_3]^+$ and can react with additional

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ethylene to produce $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})_3]^+$.¹⁴ $[\text{RhMe}_2(\text{PMe}_2\text{Ph})_3]^+$ rapidly reacts with ethylene with reductive elimination of ethane. In contrast $[\text{RhMe}_2(\text{triphos})]^+$ does not react with ethylene under mild conditions (~ 1 atm); the adduct $[\text{RhMe}_2(\text{C}_2\text{H}_4)(\text{triphos})]^+$ is not formed. Forcing conditions (100 psi C_2H_4) are required to produce $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{triphos})]\text{BF}_4$ (3).

While triphos acts to stabilize these complexes, the triphos ligand is not necessarily confined to a tridentate bonding mode during reaction mechanisms. Although no net loss of tripodal phosphine occurs, the available evidence indicates that a mechanism involving dissociation of one arm of $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ best accounts for the ligand exchanges displayed by saturated species containing the $(\text{triphos})\text{Rh}^{\text{I}}$ moiety. These include exchange of $(\text{triphos})\text{Rh}(\text{C}_2\text{H}_4)_2^+$ and $(\text{triphos})\text{Rh}(\text{MeCN})(\text{C}_2\text{H}_4)^+$ with $^{13}\text{C}_2\text{H}_4$, replacement of one ethylene in $(\text{triphos})\text{Rh}(\text{C}_2\text{H}_4)_2^+$ by water, and replacement of water in $(\text{triphos})\text{Rh}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})^+$ by ethylene. The implication of an "arm-off" associative mechanism is that it *avoids* a four-coordinate $\text{Rh}(\text{I})$ species with a facial (thus pseudotetrahedral) $(\eta^3\text{-triphos})\text{RhL}^+$ form, which is required in a dissociative mechanism. Since four-coordinate Rh^{I} is known to prefer a planar geometry, the arm-off mechanism is most suitable. This mechanism is implicated for $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{triphos})^+$ by loss of $^1J_{\text{Rh-P}}$ at 25 °C. Protonation of $\text{RhMe}(\text{C}_2\text{H}_4)(\text{triphos})$ proceeds through an intermediate which is so short-lived, even in the presence of additional ethylene, that the reaction leads only to small amounts of $(\eta^3\text{-triphos})\text{Rh}(\text{C}_2\text{H}_4)_2^+$, together with a large array of "decomposition products".

The question which remains is why $(\eta^3\text{-triphos})\text{RhL}_2^+$ species are kinetically labile. We propose that this results from a general tendency for $16e^-$ species to be thermally accessible (i.e., have a free energy only moderately above that of the $18e^-$ relative) at or below 25 °C, *together with* an inherent tendency of $\eta^3\text{-triphos}$ to dissociate one arm to give planar $\text{Rh}(\text{I})$. This "inherent tendency" we attribute to strain in transforming from the normal "open" ground-state geometry of free $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ into the "prepared" geometry for coordination. In particular, the $\eta^2\text{-geometry}$ is not too very different from that of the free

ligand,¹⁵ and thus dissociation of one arm sufficient to remove a large fraction of the strain energy of the $\eta^3\text{-form}$. In addition, the P–M–P angle of coordinated triphos is invariably $83 \pm 3^\circ$. This angle is so unsuitable for the two equatorial sites in a trigonal bipyramid that additional strain is created.

Phosphine arm dissociation has been proposed for reactions of triphos metal complexes, and previous studies have emphasized the mechanistic importance of this process.^{8,9,16–18} Triphos metal complexes having dihapto ground states have, in fact, been observed.^{18–20} In particular, if $\text{RhMe}(\text{CO})(\text{triphos})$ is placed under an atmosphere of CO, the $\eta^2\text{-triphos}$ species $\text{Rh}[\text{C}(\text{O})\text{Me}](\text{CO})_2\text{-}(\eta^2\text{-triphos})$ is directly detectable as an intermediate in the mechanism of CO exchange.

In the case of Rh^{III} , P–M–P angular strain is less apt to explain a phosphine arm dissociation process. The idealized octahedral P–M–P angles create a clearly more suitable $\eta^3\text{-triphos}$ geometry than a trigonal-bipyramidal environment. The fact that a phosphine arm-off process is implicated for Rh^{III} octahedral complexes such as $[\text{RhMe}_2(\text{CH}_3\text{CN})(\text{triphos})]\text{BF}_4$ (2), or $\text{RhX}_3(\text{triphos})$ (X = H, Me) indicates the generality of an arm-off process for triphos.

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Supplementary Material Available: Tables of full crystallographic details and anisotropic thermal parameters (3 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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