

Synthesis and Reactivity of Ruthenium Hydride Complexes Containing Chelating Triphosphines. 4. Reactions of Ruthenium Hydride Complexes Containing Triphosphines with Olefins¹

Guochen Jia,* Devon W. Meek,[†] and Judith C. Gallucci

Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210

Received February 26, 1990

Methyl vinyl ketone reacts with $\text{RuH}(\text{BH}_4)(\text{triphos})$ (triphos = ttp, Cyttp) to give $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$. The compound $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$ is also formed from the reaction of $\text{RuH}_4(\text{Cyttp})$ with methyl vinyl ketone. $\text{RuH}_4(\text{Cyttp})$ reacts with 2-vinylpyridine to produce two isomers of $\text{RuH}(\text{CH}=\text{CHC}_5\text{H}_4\text{N})(\text{Cyttp})$, with vinyl acetate to give $\text{RuH}(\text{O}_2\text{CMe})(\text{Cyttp})$, and with methyl acrylate to yield $\text{RuH}_2(\text{CO})(\text{Cyttp})$. The reaction products were characterized by multinuclear NMR and IR spectroscopy. The structure of $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ has been confirmed by single-crystal X-ray diffraction. $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ crystallizes in the space group $P2_1/c$ with cell parameters $a = 10.236$ (1) Å, $b = 20.845$ (3) Å, $c = 16.922$ (2) Å, $\beta = 106.58$ (1)°, $Z = 4$, $V = 3460$ Å³, $R = 0.031$, and $R_w = 0.038$ for the 5829 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 418 variables.

Introduction

Ruthenium hydride complexes containing phosphines catalyze a variety of chemical processes involving olefins, such as hydrogenation,²⁻¹² isomerization,^{2,13-16} hydroformylation,¹⁷ hydrosilylation,^{18,19} and polymerization.²⁰ To model these processes, the reactions of various olefins with $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ ^{16,20-26} and several ruthenium monohydride phosphine complexes^{2,26-36} have been studied. The products from the reactions of olefins (especially activated olefins) with ruthenium monohydride complexes are usually the so-called insertion products if reactions occur.²⁶⁻³⁶ The reactions of olefins with $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ are more complicated, and the ruthenium complexes formed in these reactions range from ruthenium olefin, ortho-metalated phosphine, allyl, and η^4 -diene to ruthenium carboxylate complexes depending on the olefins involved.²⁰⁻²⁶ To compare the reactivity of ruthenium hydride complexes of chelating triphosphines with that of monophosphine analogues, we have investigated the reactions of olefins with ruthenium hydride complexes of triphosphines of the type $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$ ($\text{R} = \text{Ph}$, ttp; $\text{R} = \text{Cy}$, Cyttp).

Experimental Section

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

Reagent-grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Sodium tetrahydroborate was obtained from Fisher Scientific Co. Ruthenium trichloride hydrate was loaned from Johnson Matthey Inc. $\text{RuH}(\text{BH}_4)(\text{ttp})$,³⁷ $\text{RuH}(\text{BH}_4)(\text{Cyttp})$,¹ $\text{RuH}_4(\text{Cyttp})$,¹ and $\text{RuHCl}(\text{Cyttp})$ ¹ were prepared by literature methods.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1} , as pressed potassium bromide pellets, Nujol mulls, or solutions. Spectra were calibrated

against the sharp 1601- cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz),

- (1) Part 3: Jia, G.; Meek, D. W.; Gallucci, J. C. Submitted for publication in *Inorg. Chem.*
- (2) Hallman, P. S.; McGarvey, B. R.; Gilbert, B. R.; Wilkinson, G. J. *Chem. Soc. A* 1968, 3143.
- (3) Porter, R. A.; Shriver, D. F. *J. Organomet. Chem.* 1975, 90, 41.
- (4) Head, R. A.; Nixon, J. F. *J. Chem. Soc., Dalton Trans.* 1978, 913.
- (5) Hallman, P. S.; Evans, D.; Osborn, J. A.; Wilkinson, G. J. *Chem. Soc., Chem. Commun.* 1967, 305.
- (6) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. T. *J. Catal.* 1977, 48, 340.
- (7) Rose, D.; Gilbert, J. D.; Richardson, R. P.; Wilkinson, G. J. *Chem. Soc. A* 1969, 2610.
- (8) Wilson, S. T.; Osborn, J. A. *J. Am. Chem. Soc.* 1971, 93, 3068.
- (9) Romera, A.; Vegas, A.; Santos, A.; Martinez-Ripoll, M. *J. Organomet. Chem.* 1987, 319, 103.
- (10) James, B. R.; Wang, D. K. W. *Can. J. Chem.* 1980, 58, 245.
- (11) Massonneau, V.; Le Maux, P.; Simonneaux, G. *J. Organomet. Chem.* 1987, 327, 269.
- (12) James, B. R.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* 1977, 550.
- (13) Ewing, D. F.; Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* 1972, 1287.
- (14) Shunn, R. A. *Inorg. Chem.* 1970, 9, 2567.
- (15) Bingham, D.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* 1974, 1519.
- (16) Pennella, F. *Coord. Chem. Rev.* 1975, 16, 51.
- (17) Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* 1976, 399.
- (18) Watanabe, H.; Aoki, M.; Sakurai, N.; Watanabe, K.; Nagai, Y. *J. Organomet. Chem.* 1978, 160, C1.
- (19) Marciniak, B.; Gulinski, J. *J. Organomet. Chem.* 1983, 253, 349.
- (20) Komiya, S.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* 1975, 48, 101.
- (21) (a) Komiya, S.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* 1974, 523. (b) *J. Organomet. Chem.* 1975, 87, 333.
- (22) Komiya, S.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* 1972, 42, C65.
- (23) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1976, 49, 2553.
- (24) (a) Cole-Hamilton, D. J.; Wilkinson, G. J. *Chem. Soc., Chem. Commun.* 1977, 59. (b) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* 1977, 1, 141.
- (25) (a) Carrondo, M. A. F. de T.; Chaudret, B. N.; Cole-Hamilton, D. J.; Skapski, A. C.; Wilkinson, G. J. *Chem. Soc., Chem. Commun.* 1978, 463. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* 1978, 1739.
- (26) (a) Komiya, S.; Yamamoto, A. *Chem. Lett.* 1975, 475. (b) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* 1976, 98, 3874.
- (27) James, B. R.; Markham, L. D.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* 1974, 439.
- (28) Dekleva, T. W.; James, B. R. *J. Chem. Soc., Chem. Commun.* 1983, 1350.

* To whom correspondence should be addressed at the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

[†] Deceased December 7, 1988.

phosphorus-31 (101.25 MHz), and carbon-13 (62.9 MHz) NMR spectra in 5-mm tubes. Residual solvent proton and carbon-13 resonances were used as internal standards for the ^1H and ^{13}C NMR spectra, respectively. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

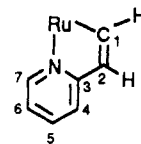
$\text{Ru}(\text{CH}_2=\text{CHCOMe})(\text{ttp})(1)$. A mixture of 0.30 g of $\text{RuH}(\text{BH}_4)(\text{ttp})(0.44 \text{ mmol})$, 0.5 mL of methyl vinyl ketone (6 mmol), and 1 mL of pyridine in 30 mL of benzene was refluxed for 2 h to give a light brown solution. The liquids of the reaction mixture were then removed completely under vacuum, and 10 mL of MeOH was added to give a yellow powder after stirring for ca. 30 min (no precipitates were formed without stirring!). The yellow powder was collected on a filter frit, washed with MeOH, and dried under vacuum overnight; yield 0.27 g, 84%. X-ray-quality crystals were obtained by slowly evaporating solvents from a saturated solution in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ with a stream of argon. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 10.3 (dd, $J(\text{PP}) = 40.6, 7.6 \text{ Hz}$), 25.2 (dd, $J(\text{PP}) = 20.1, 7.6 \text{ Hz}$), 33.0 (dd, $J(\text{PP}) = 40.6, 20.1 \text{ Hz}$). ^1H NMR (CD_2Cl_2): δ 0.44–3.32 (m, 7 CH_2), 1.5 (m, CH_3), 4.23 (m, $=\text{CH}$), 6.95–8.58 (m, 5 C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 20.7–32.1 (m, 7 CH_2), 21.9 (s, CH_3), 78.9 (s, $=\text{CH}$), 124.0–150.3 (m, 5 C_6H_5), 136.4 (s, $\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{40}\text{H}_{63}\text{OP}_3\text{Ru}$: C, 65.48; H, 5.91. Found: C, 65.60; H, 5.79.

$\text{Ru}(\text{CH}_2=\text{CHCOMe})(\text{Cytpp})(2)$. Method A, from $\text{RuH}(\text{BH}_4)(\text{Cytpp})$. A mixture of 0.15 g of $\text{RuH}(\text{BH}_4)(\text{Cytpp})(0.21 \text{ mmol})$, 0.5 mL of methyl vinyl ketone (6 mmol), and 0.5 mL of pyridine in 20 mL of benzene was refluxed for 3 h to give a light red solution. The liquids of the reaction mixture were removed completely, and 6 mL of MeOH was added to give a bright yellow solid after stirring for ca. 1 h (again, without stirring, no precipitates were formed). The yellow solid was collected on a filter frit, washed with MeOH, and dried under vacuum overnight; yield 0.12 g, 75%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 15.1 (dd, $J(\text{PP}) = 40.6, 4.8 \text{ Hz}$), 25.8 (dd, $J(\text{PP}) = 30.7, 4.8 \text{ Hz}$), 34.3 (dd, $J(\text{PP}) = 40.6, 30.7 \text{ Hz}$). ^1H NMR (CD_2Cl_2): δ 0.42–2.64 (m, 7 CH_2 and 4 C_6H_{11}), 2.04 (m, CH_3), 4.11 (m, $=\text{CH}$), 7.3 (m, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 20.6–36.0 (m, 27 CH_2), 22.1 (s, CH_3), 34.8 (dd, $J(\text{PC}) = 10.1, 5.6 \text{ Hz}$, $\text{P}-\text{CH}$), 44.6 (d, $J(\text{PC}) = 7.8 \text{ Hz}$, $\text{P}-\text{CH}$), 40.2 (d, $J(\text{PC}) = 16.2 \text{ Hz}$, $\text{P}-\text{CH}$), 42.8 (d, $J(\text{PC}) = 16.2 \text{ Hz}$, $\text{P}-\text{CH}$), 44.6 (d, $J(\text{PC}) = 7.8 \text{ Hz}$, $\text{P}-\text{CH}$), 76.8 (s, $=\text{CH}$), 127.7 (d, $^3J(\text{PC}) = 8.0 \text{ Hz}$, $m\text{-Ph}$), 127.9 (s, $p\text{-Ph}$), 129.7 (d, $^2J(\text{PC}) = 7.8 \text{ Hz}$, $o\text{-Ph}$), 138.4 (s, $\text{C}=\text{O}$), 144.8 (d, $^1J(\text{PC}) = 29.7 \text{ Hz}$, ipso-Ph). Anal. Calcd for $\text{C}_{40}\text{H}_{67}\text{OP}_3\text{Ru}$: C, 63.39; H, 8.91. Found: C, 63.12; H, 8.82.

Method B, from $\text{RuH}_4(\text{Cytpp})$. A mixture of 0.5 mL of methyl vinyl ketone (6 mmol) and $\text{RuH}_4(\text{Cytpp})$ (ca. 0.40 mmol, prepared from 0.30 g of $\text{RuCl}_2(\text{Cytpp})$ with excess NaH) in 30 mL of benzene was stirred at room temperature for 15 min to give a light reddish yellow solution. The liquids of the reaction mixture were removed completely, and then the residue was treated as in method A described above; yield 0.22 g, 73%.

$\text{RuH}(\text{CH}=\text{CHC}_5\text{H}_4\text{N})(\text{Cytpp})$, Isomer A (3A). A mixture of 0.20 mL of 2-vinylpyridine (1.8 mmol) and $\text{RuH}_4(\text{Cytpp})$ (ca. 0.26 mmol, prepared from 0.20 g of $\text{RuCl}_2(\text{Cytpp})$ with excess NaH) in 30 mL of benzene was stirred for ca. 30 min. The solvent was then removed completely, and 15 mL of acetone was added. Initially no precipitates were formed. The mixture was stirred

for 4 h to give a bright yellow solid. The solid was then collected by filtration, washed with acetone, and dried under vacuum overnight (sometimes the isolated products consist of both isomer A and isomer B); yield 0.11 g, 53%. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 10.4 (t, PPh), 28.1 (d, PCy_2), $J(\text{PP}) = 36.6 \text{ Hz}$. ^1H NMR (C_6D_6): δ -15.41 (td, $J(\text{PH}) = 23.7, 18.6 \text{ Hz}$, RuH), 0.4–3.4 (m, 6 CH_2 and 4 C_6H_{11}), 6.10–8.33 (m, C_6H_5 and $\text{C}_5\text{H}_4\text{N}$), 7.11 (d, $J = 8.1 \text{ Hz}$, $=\text{CH}$), 9.92 (t, $J = 8.4 \text{ Hz}$, RuCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6)



δ 22.8–34.4 (m, 26 CH_2), 36.9 (td, $J(\text{PC}) = 13.8, 4.8 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 41.2 (t, $J(\text{PC}) = 5.8 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 114.6 (s, C6), 119.4 (s, C4), 127.5 (d, $^3J(\text{PC}) = 7.8 \text{ Hz}$, $m\text{-Ph}$), 128.1 (s, $p\text{-Ph}$), 130.5 (s, C2), 131.5 (d, $^2J(\text{PC}) = 8.7 \text{ Hz}$, $o\text{-Ph}$), 132.1 (s, C5), 145.8 (d, $^1J(\text{PC}) = 8.3 \text{ Hz}$, ipso-Ph), 154.5 (d, $^3J(\text{PC}) = 1.7 \text{ Hz}$, C7), 169.9 (d, $^3J(\text{PC}) = 5.9 \text{ Hz}$, C3), 213.6 (dt, $^2J(\text{PC}) = 45.9, 15.4 \text{ Hz}$, C1). IR (KBr): $\nu(\text{Ru}-\text{H})$ 1930 (m) cm^{-1} ; $\nu(\text{CH}=\text{CH})$ 1590 (m) cm^{-1} . Anal. Calcd for $\text{C}_{43}\text{H}_{68}\text{NP}_3\text{Ru}$: C, 65.13; H, 8.64; N, 1.77. Found: C, 65.04; H, 8.50; N, 1.67.

$\text{RuH}(\text{CH}=\text{CHC}_5\text{H}_4\text{N})(\text{Cytpp})$, Mixture of Isomer A and Isomer B. Almost the same procedure was followed as above except that the reaction mixture was stirred 3 h or overnight. The product isolated usually consists of both isomer A and isomer B.

$\text{RuH}(\text{CH}=\text{CHC}_5\text{H}_4\text{N})(\text{Cytpp})$, Isomer B (3B). A mixture of 0.60 mL of 2-vinylpyridine (5.6 mmol) and $\text{RuH}_4(\text{Cytpp})$ (ca. 0.26 mmol, prepared from 0.20 g of $\text{RuCl}_2(\text{Cytpp})$ with excess NaH) in 30 mL of benzene was stirred overnight. The liquids of the reaction mixture were removed completely under vacuum, and 6 mL of hexane was added to give an orange solid. The orange solid was then collected on a filter frit, washed with hexane and acetone, and dried under vacuum overnight. Sometimes the isolated products consist of both isomer A and isomer B, yield 0.12 g, 58%. Orange crystals could be obtained by slowly evaporating solvents from a saturated solution in $\text{C}_6\text{H}_6/\text{acetone}$ with a stream of argon. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 19.3 (d, PCy_2), 38.5 (t, PPh), $J(\text{PP}) = 47.3 \text{ Hz}$. ^1H NMR (C_6D_6): δ -5.90 (td, $J(\text{PH}) = 26.2, 12.6 \text{ Hz}$, RuH), 0.6–3.6 (m, 6 CH_2 and 4 C_6H_{11}), 6.3–9.3 (m, C_6H_5 and $\text{C}_5\text{H}_4\text{N}$), 7.92 (d, $J = 9.7 \text{ Hz}$, $=\text{CH}$), 11.07 (dd, $J = 9.7, 5.1 \text{ Hz}$, RuCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 ; please refer to the vinylpyridine numbering scheme above for the ^{13}C NMR assignments): δ 20.3–31.0 (m, 26 CH_2), 34.5 (t, $J(\text{PC}) = 6.1 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 41.0 (t, $J(\text{PC}) = 12.7 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 114.4 (s, C6), 119.9 (s, C4), 127.5 (d, $^3J(\text{PC}) = 8.2 \text{ Hz}$, $m\text{-Ph}$), 129.0 (s, $p\text{-Ph}$), 131.6 (d, $J(\text{PC}) = 2.9 \text{ Hz}$, C2), 132.5 (s, C5), 134.2 (d, $^2J(\text{PC}) = 11.4 \text{ Hz}$, $o\text{-Ph}$), 138.3 (d, $^1J(\text{PC}) = 8.5 \text{ Hz}$, ipso-Ph), 157.6 (s, C7), 169.7 (s, C3), 229.4 (q, $^2J(\text{PC}) = \text{C1}$). IR (KBr): $\nu(\text{Ru}-\text{H})$ 1795 (m) cm^{-1} ; $\nu(\text{CH}=\text{CH})$ 1590 (m) cm^{-1} . Anal. Calcd for $\text{C}_{40}\text{H}_{63}\text{OP}_3\text{Ru}$: C, 65.13; H, 8.64; N, 1.77. Found: C, 65.23; H, 8.77; N, 1.74.

$\text{RuH}(\text{O}_2\text{CMe})(\text{Cytpp})(4)$. A mixture of 0.3 mL of vinyl acetate (3 mmol) and $\text{RuH}_4(\text{Cytpp})$ (ca. 0.26 mmol, prepared from 0.20 g of $\text{RuCl}_2(\text{Cytpp})$ with excess NaH) in 30 mL of benzene was stirred for 3 h to give a yellow solution. The liquids of the reaction mixture were removed completely, and then 5 mL of MeOH was added to give a yellow powder. The powder was collected on a filter frit, washed with a small amount of MeOH, and dried under vacuum overnight; yield 0.13 g, 67%. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 26.7 (d, PCy_2), 51.7 (t, PPh), $J(\text{PP}) = 38.3 \text{ Hz}$. ^1H NMR (CD_2Cl_2): δ -22.41 (dt, $J(\text{PH}) = 38.2, 20.8 \text{ Hz}$, RuH), 0.8–2.0 (m, 6 CH_2 and 4 C_6H_{11}), 1.97 (s, CH_3), 7.3 (m, p - and m -Ph), 7.95 (t, $J = 8.3 \text{ Hz}$, o -Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 21.7–34.1 (m, 26 CH_2), 24.6 (s, CH_3), 35.6 (t, $J(\text{PC}) = 16.6 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 37.0 (t, $J(\text{PC}) = 11.8 \text{ Hz}$, 2 $\text{P}-\text{CH}$), 127.6 (d, $^3J(\text{PC}) = 8.4 \text{ Hz}$, $m\text{-Ph}$), 128.8 (s, $p\text{-Ph}$), 132.9 (d, $^2J(\text{PC}) = 10.0 \text{ Hz}$, $o\text{-Ph}$), 140.1 (d, $^1J(\text{PC}) = 28.4 \text{ Hz}$, ipso-Ph), 179.6 (s, OCO). IR (KBr): $\nu(\text{Ru}-\text{H})$ 1975 (m) cm^{-1} ; $\nu(\text{OCO})$ 1560 (m) cm^{-1} . Anal. Calcd for $\text{C}_{38}\text{H}_{55}\text{O}_2\text{P}_3\text{Ru}$: C, 61.02; H, 8.76. Found: C, 60.96; H, 8.81.

Crystallographic Analysis of $\text{Ru}(\text{CH}_2=\text{CHCOCH}_3)(\text{ttp})$. The data collection crystal was a rectangular rod cut from a larger yellow crystal and was coated with a thin layer of epoxy as protection against possible air sensitivity. Preliminary examination of the diffraction pattern on a Rigaku AFC5 diffractometer in-

(29) Grassi, M.; Mann, B. E.; Manning, P.; Spencer, C. M. *J. Organomet. Chem.* **1986**, *307*, C55.

(30) Hiraki, K.; Sasada, Y.; Kitamura, T. *Chem. Lett.* **1980**, 449.

(31) Hiraki, K.; Ochi, N.; Kitamura, T.; Sasada, Y.; Shinoda, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2356.

(32) Gopinathan, S.; Joseph, K.; Gopinathan, C. *J. Organomet. Chem.* **1984**, *269*, 273.

(33) Hiraki, K.; Ochi, N.; Sasada, Y.; Hayashida, H.; Fuchita, Y.; Yamanaka, S. *J. Chem. Soc., Dalton Trans.* **1985**, 873.

(34) (a) Ashworth, T. V.; Singleton, E.; Laing, M.; Pope, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1032. (b) Ashworth, T. V.; Chalmers, A. A.; Meintjies, E.; Oosthuizen, H.; Singleton, E. *J. Organomet. Chem.* **1984**, *276*, C19.

(35) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106.

(36) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1283.

(37) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898.

Table I. Crystallographic Details for Ru(η^4 -CH₂=CHCOMe)(ttp)

formula	C ₄₀ H ₄₈ OP ₃ Ru
fw	733.77
space group	P2 ₁ /c
a, Å	10.236 (1)
b, Å	20.845 (3)
c, Å	16.922 (2)
β , deg	106.58 (1)
V, Å ³	3460
Z	4
d(calcd), g/cm ³	1.41
cryst size, mm	0.19 × 0.31 × 0.35
radiation	Mo K α with graphite monochromator
linear abs coeff, cm ⁻¹	6.15
temp	ambient
scan type	ω
2 θ limits, deg	4 ≤ 2 θ ≤ 55
scan speed, deg/min	8 (in ω with a max of 8 scans, ref)
scan range, deg	(1.00 + 0.35 tan θ) in ω
data collected	+h,+k,+l
no. of unique data	8232
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	5829
final no. of variables	418
R(F) ^a	0.031
R _w (F) ^b	0.038
goodness of fit	1.25

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

indicated a monoclinic crystal system with systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$). The space group is uniquely determined as P2₁/c. At room temperature the cell constants are $a = 10.236$ (1) Å, $b = 20.845$ (3) Å, $c = 16.922$ (2) Å, and $\beta = 106.58$ (1)° and are based on a least-squares fit of the diffractometer setting angles for 25 reflections with 2θ values in the range 20–30° with Mo K α radiation.

Intensities were measured by the ω -scan method. Six standard reflections were measured after every 150 reflections and indicated that the crystal was stable during the course of data collection. Data reduction and all further calculations were done with the TEXSAN package of crystallographic programs.³⁸ The structure was solved by locating the ruthenium atom from a Patterson map. The ruthenium atom was then used as a phasing model in DIRDIF,³⁹ and the remainder of the structure was located on the resulting electron density map. Full-matrix least-squares isotropic refinement of the model with use of the subset of reflections with $F_o^2 > 3\sigma(F_o^2)$ converged at an R value of 0.064. After a cycle of anisotropic refinement the hydrogen atoms were located on a difference electron density map. In particular, the three methyl hydrogen atoms bonded to C(40), one hydrogen atom bonded to C(38), and two hydrogen atoms bonded to C(39) were evident on this map. The hydrogen atoms bonded to C(38) and C(39) were included in the model at their positions as located in the map; the methyl hydrogen atoms were idealized to tetrahedral geometry, and all the other hydrogen atoms were included in the model and fixed at their calculated positions with the assumptions that C–H = 0.98 Å and $B_H = 1.2[B_{eq}(\text{attached carbon atom})]$. In the final refinement cycles the hydrogen atoms bonded to C(38) and C(39) were refined with isotropic temperature factors. All least-squares refinements were based on F so that the function minimized in least-squares was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final refinement cycle for the 5829 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 418 variables (anisotropic non-hydrogen atoms, three hydrogen atoms isotropic, all the other hydrogen atoms fixed) resulted in agreement indices of $R = 0.031$ and $R_w = 0.038$. The final dif-

Table II. Final Positional Parameters for Ru(η^4 -CH₂=CHCOMe)(ttp)^a

atom	x	y	z	B(eq), Å ²
Ru	0.19222 (2)	0.19088 (1)	0.76977 (1)	2.092 (8)
P(1)	-0.01238 (7)	0.13720 (4)	0.73219 (4)	2.52 (3)
P(2)	0.13678 (7)	0.23875 (4)	0.87384 (4)	2.56 (3)
P(3)	0.33885 (7)	0.12121 (4)	0.86004 (4)	2.51 (3)
O	0.2804 (2)	0.1743 (1)	0.6663 (1)	3.17 (8)
C(1)	-0.1577 (3)	0.1867 (2)	0.7386 (2)	3.3 (1)
C(2)	-0.1480 (3)	0.2163 (2)	0.8227 (2)	3.8 (1)
C(3)	-0.0394 (3)	0.2682 (2)	0.8509 (2)	3.5 (1)
C(4)	0.1455 (3)	0.1936 (2)	0.9682 (2)	3.4 (1)
C(5)	0.2718 (3)	0.1521 (2)	1.0048 (2)	3.6 (1)
C(6)	0.2880 (3)	0.0959 (2)	0.9514 (2)	3.3 (1)
C(7)	-0.0428 (3)	0.0614 (1)	0.7797 (2)	3.0 (1)
C(8)	0.0415 (3)	0.0100 (2)	0.7763 (2)	3.5 (1)
C(9)	0.0284 (4)	-0.0484 (2)	0.8122 (2)	4.3 (1)
C(10)	-0.0687 (4)	-0.0564 (2)	0.8526 (2)	4.9 (2)
C(11)	-0.1531 (5)	-0.0074 (2)	0.8563 (3)	5.7 (2)
C(12)	-0.1423 (4)	0.0517 (2)	0.8193 (2)	4.6 (2)
C(13)	-0.0689 (3)	0.1127 (1)	0.6228 (2)	2.9 (1)
C(14)	-0.2045 (3)	0.1061 (2)	0.5795 (2)	4.2 (1)
C(15)	-0.2433 (4)	0.0888 (2)	0.4970 (2)	5.0 (2)
C(16)	-0.1475 (5)	0.0771 (2)	0.4576 (2)	4.9 (2)
C(17)	-0.0119 (4)	0.0825 (2)	0.4998 (2)	5.2 (2)
C(18)	0.0268 (4)	0.1005 (2)	0.5821 (2)	4.4 (2)
C(19)	0.2246 (3)	0.3144 (1)	0.9113 (2)	2.8 (1)
C(20)	0.3140 (3)	0.3222 (2)	0.9891 (2)	3.7 (1)
C(21)	0.3779 (4)	0.3804 (2)	1.0128 (2)	4.7 (2)
C(22)	0.3527 (4)	0.4314 (2)	0.9600 (3)	5.1 (2)
C(23)	0.2634 (4)	0.4253 (2)	0.8830 (2)	4.6 (2)
C(24)	0.1998 (3)	0.3671 (2)	0.8590 (2)	3.6 (1)
C(25)	0.5122 (3)	0.1493 (2)	0.9150 (2)	2.9 (1)
C(26)	0.5349 (3)	0.2141 (2)	0.9300 (2)	4.0 (1)
C(27)	0.6591 (4)	0.2365 (2)	0.9787 (3)	5.4 (2)
C(28)	0.7626 (4)	0.1945 (3)	1.0115 (2)	6.0 (2)
C(29)	0.7435 (4)	0.1301 (2)	0.9958 (2)	5.4 (2)
C(30)	0.6195 (3)	0.1076 (2)	0.9483 (2)	4.1 (1)
C(31)	0.3822 (3)	0.0448 (1)	0.8195 (2)	3.2 (1)
C(32)	0.3869 (4)	-0.0142 (2)	0.8579 (2)	4.5 (1)
C(33)	0.4244 (5)	-0.0690 (2)	0.8239 (3)	6.0 (2)
C(34)	0.4598 (5)	-0.0660 (2)	0.7525 (3)	6.5 (2)
C(35)	0.4554 (5)	-0.0081 (2)	0.7127 (3)	5.9 (2)
C(36)	0.4154 (4)	0.0467 (2)	0.7455 (2)	4.3 (1)
C(37)	0.3367 (3)	0.2268 (2)	0.7029 (2)	3.0 (1)
C(38)	0.2488 (3)	0.2760 (2)	0.7111 (2)	3.1 (1)
C(39)	0.1053 (3)	0.2637 (2)	0.6793 (2)	3.1 (1)
C(40)	0.4876 (3)	0.2340 (2)	0.7246 (2)	4.2 (1)
H(41)	0.283 (3)	0.314 (1)	0.742 (2)	3.0 (7)
H(42)	0.042 (3)	0.296 (1)	0.688 (2)	2.5 (6)
H(43)	0.073 (3)	0.241 (1)	0.628 (2)	3.2 (7)

$$^a B(\text{eq}) = \frac{8}{3}\pi^2 \sum_i \mu_i a_i^* a_j^* a_j$$

ference electron density map contained maximum and minimum peak heights of 0.38 and -0.34 e/Å³. Scattering factors are from the usual sources⁴⁰ and contain correction terms for anomalous dispersion effects. Further crystallographic details are given in Table I. Final atomic coordinates and selected bond lengths and bond angles are presented in Tables II and III, respectively.

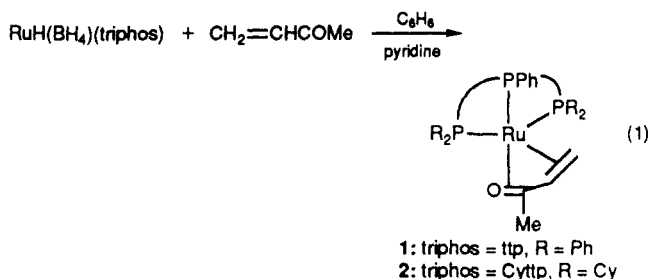
Results and Discussion

Reactions with CH₂=CHCOMe. In the presence of pyridine, in refluxing benzene, the hydride complexes RuH(BH₄)(ttp) and RuH(BH₄)(Cytpp) reacted with excess methyl vinyl ketone to give Ru(η^4 -CH₂=CHCOMe)(ttp) (1) and Ru(η^4 -CH₂=CHCOMe)(Cytpp) (2), respectively (eq 1). The purpose of pyridine in these reactions is to remove the BH₃ group to generate dihydride intermediates.³⁷ Thus, no reaction occurred between RuH(BH₄)(ttp) and methyl vinyl ketone in the absence of pyridine. The

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

(38) TEXSAN, TEXRAY Structure Analysis Package, Version 2.1; Molecular Structure Corp.: College Station, TX, 1987.

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



compound $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$ was also obtained readily from the instant reaction of $\text{RuH}_4(\text{Cyttp})$ with excess methyl vinyl ketone. During the reaction, ethyl methyl ketone was also produced, as indicated by an in situ ^1H NMR spectrum. Thus, compounds $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ (triphos = ttp, Cyttp) are probably formed via reductive elimination of ethyl methyl ketone from hydrido alkyl intermediates formed by insertion of the olefin into Ru-H bonds⁴¹ and coordination of the methyl vinyl ketone molecule. Formation of hydrogenated products of olefins from reactions of olefins with $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ ^{14,26} has been reported previously.

In contrast to the formation of $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$ from the reaction of methyl vinyl ketone with $\text{RuH}_4(\text{Cyttp})$, interaction of methyl vinyl ketone with $\text{RuH}_2(\text{PPh}_3)_4$ caused the polymerization of methyl vinyl ketone and no ruthenium complexes were characterized in this reaction.²⁰ However, the reaction of $\text{RuH}_4(\text{Cyttp})$ with methyl vinyl ketone is similar to the reaction of $\text{RuH}_4(\text{PPh}_3)_3$ with 1,3-butadiene in that the similar complex $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCH}=\text{CH}_2)(\text{PPh}_3)_3$ was isolated from the latter reaction.²⁴

The ^{31}P NMR spectra of $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ at room temperature showed three doublet of doublets phosphorus resonances, indicating that the triphosphines have a facial arrangement around ruthenium and that the complexes are rigid at room temperature. This is in contrast to $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCH}=\text{CH}_2)(\text{PPh}_3)_3$, which is fluxional at room temperature. The difference might be ascribed to the presence of chelating triphosphines, which slow down fluxional processes, or the characteristics of vinyl ketone coordinated complexes.

No infrared bands above 1500 cm^{-1} assignable to $\nu(\text{C}=\text{O})$ were observed for the $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ complexes. This is consistent with the observations in other similar complexes^{42,43} and is caused by a significant decrease of C=O double-bond character due to the π -bonding. $\nu(\text{C}=\text{O})$ in $\text{W}(\eta^4\text{-CH}_2=\text{CHCOMe})_3$ ⁴³ was observed at 1495 cm^{-1} . However, the $\nu(\text{C}=\text{O})$ bands for the triphosphine complexes could not be assigned confidently because the triphosphine ligands also have absorptions between 1400 and 1500 cm^{-1} .

The selected ^1H and ^{13}C NMR spectral assignments are listed in Table IV. As shown in Table IV, the chemical shifts for the CH proton of the $\eta^4\text{-CH}_2=\text{CHCOMe}$ ligand are very similar among the three methyl vinyl ketone complexes and are also comparable with that in the bu-

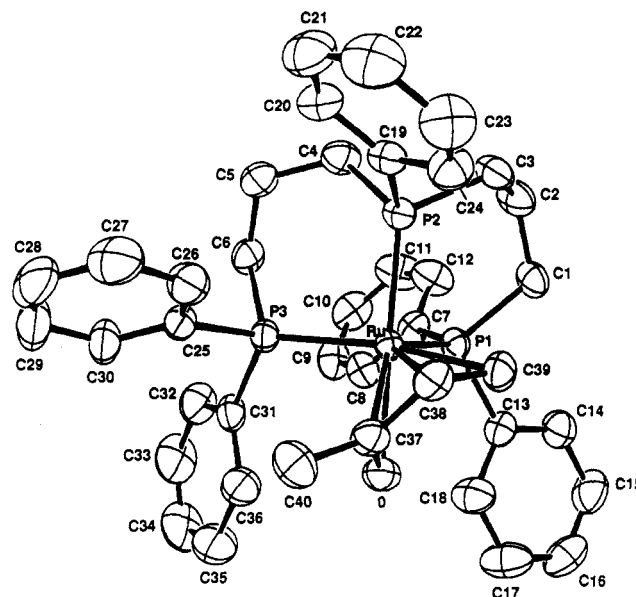


Figure 1. ORTEP drawing of $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

tadiene complex $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCH}=\text{CH}_2)(\text{CO})_3$.⁴⁴ The methyl proton chemical shift in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$ (2.04 ppm) is comparable with that in $\text{W}(\eta^4\text{-CH}_2=\text{CHCOMe})_3$ (2.13 ppm).⁴³ However, the chemical shift for the methyl protons in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ is considerably smaller (1.50 ppm). The relatively high field chemical shift for the methyl protons in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ is probably caused by the "ring current" shielding effect⁴⁵ of one of the phenyl rings attached to one of the terminal phosphorus atoms.⁴⁶ The resonances for the CH_2 groups in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ are not assigned because they are buried in the signals of triphosphine ligands in the aliphatic region (1.4–3.3 ppm, triphos = ttp; 0.4–2.6 ppm, triphos = Cyttp).

The ^{13}C NMR data for $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ are also comparable with those of similar compounds. For example, the resonance for the CH adjacent to C=O appeared at 86.6 ppm in $[\text{CpW}(\text{CO})_2(\eta^4\text{-PhCH}=\text{CHCOMe})]\text{BF}_4$,⁴² compared to that at 78.9 ppm in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ and 76.8 ppm in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$. The CH chemical shifts are also close to the value of 86.3 ppm in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCH}=\text{CH}_2)(\text{CO})_3$.⁴⁴ The chemical shifts for the C=O groups in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ (136.4 ppm, triphos = ttp; 138.4 ppm, triphos = Cyttp) are low compared with those in $\eta^4\text{-PhCH}=\text{CHCOMe}$ and $\eta^4\text{-MeCH}=\text{CHCOMe}$ tungsten complexes (ranging from 157.9 to 167.0 ppm).⁴² However, the relative upfield chemical shifts for π -bound C=O in $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{triphos})$ is not extremely unusual, since the chemical shift for π -bonded $\text{H}_2\text{C}=\text{O}$ in $\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{O})$ is only 60.56 ppm.⁴⁷ As in the ^1H NMR spectra, the resonances of the CH_2 groups could not be assigned confidently due to the presence of the

(41) When $\text{RuH}_4(\text{Cyttp})$ was treated with 1 equiv of methyl vinyl ketone, an intermediate was formed. This intermediate could be converted into $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{Cyttp})$ upon addition of excess methyl vinyl ketone. This intermediate is probably the ruthenium hydride alkyl complex $\text{RuH}(\text{CH}_2\text{CH}_2\text{COMe})(\text{Cyttp})$. In fact, the ^1H NMR spectrum of the intermediate showed a broad hydride resonance at -24.5 ppm. Unfortunately, the resonances for the methylene CH_2 groups could not be identified due to the presence of resonances from the triphosphine ligand. The high solubility and air sensitivity properties prevented purification and further characterization of this intermediate.

(42) Alt, H. G.; Herrmann, G. S.; Thewalt, U. *J. Organomet. Chem.* **1987**, *327*, 237.

(43) King, R. B.; Fronzaglia, A. *Chem. Commun.* **1966**, 274.

(44) Ruh, S.; Von Philipsborn, W. *J. Organomet. Chem.* **1977**, *127*, C59.

(45) Becker, E. D. *High Resolution NMR, Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980; p 73.

(46) The methyl protons are probably located in the shielding region of one of the phenyl rings on P(3). The related intramolecular distances are as follows: C(31)---H(38), 3.81 Å; C(36)---H(38), 3.39 Å; C(35)---H(38), 4.44 Å; C(36)---H(39), 4.25 Å.

(47) Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

Table III. Selected Bond Lengths and Angles for Ru(η^4 -CH₂=CHCOMe)(ttp)^a

		Bond Lengths (Å)			
Ru-P(1)	2.2983 (8)	Ru-P(2)	2.2339 (7)	Ru-P(3)	2.3209 (7)
Ru-C(37)	2.232 (3)	Ru-C(38)	2.190 (3)	Ru-C(39)	2.159 (3)
Ru-O	2.213 (2)	C(37)-C(38)	1.398 (4)	C(37)-C(40)	1.490 (4)
C(38)-C(39)	1.436 (4)	O-C(37)	1.306 (4)		
		Bond Angles (deg)			
P(1)-Ru-P(2)	91.09 (3)	O-Ru-P(1)	104.52 (6)		
P(1)-Ru-P(3)	104.16 (3)	O-Ru-P(3)	95.16 (6)		
P(2)-Ru-P(3)	91.30 (3)	C(37)-Ru-P(2)	127.18 (8)		
C(39)-Ru-C(38)	38.5 (1)	C(37)-Ru-P(1)	134.92 (8)		
C(39)-Ru-O	74.2 (1)	C(37)-Ru-P(3)	98.39 (8)		
C(39)-Ru-C(37)	66.6 (1)	O-C(37)-C(38)	116.9 (3)		
C(39)-Ru-P(2)	95.7 (1)	O-C(37)-C(40)	119.2 (3)		
C(39)-Ru-P(1)	89.28 (9)	O-C(37)-Ru	72.1 (2)		
C(39)-Ru-P(3)	164.76 (9)	C(38)-C(37)-C(40)	123.5 (3)		
C(38)-Ru-O	63.1 (1)	C(38)-C(37)-Ru	69.9 (2)		
C(38)-Ru-C(37)	36.8 (1)	C(40)-C(37)-Ru	134.4 (2)		
C(38)-Ru-P(2)	98.91 (9)	C(37)-C(38)-C(39)	116.8 (3)		
C(38)-Ru-P(1)	127.36 (9)	C(37)-C(38)-Ru	73.2 (2)		
C(38)-Ru-P(3)	126.89 (9)	C(39)-C(38)-Ru	69.6 (2)		
O-Ru-C(37)	34.1 (1)	C(38)-C(39)-Ru	71.9 (2)		
O-Ru-P(2)	161.04 (6)				

^a Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Selected ¹H and ¹³C NMR Data for Diene Complexes^a

compd	¹ H NMR			¹³ C NMR			
	CH ₂	CH	Me	CH ₂	CH	C=O	Me
Ru(η^4 -CH ₂ =CHCOMe)(ttp) (1)	<i>d</i>	4.23 (m)	1.50 (m)	<i>d</i>	78.9	136.4 (br)	21.9
Ru(η^4 -CH ₂ =CHCOMe)(Cyttp) (2)	<i>d</i>	4.11 (m)	2.04 (m)	<i>d</i>	76.8	138.4 (br)	21.1
Ru(η^4 -CH ₂ =CHCH=CH ₂)(CO) ₃ ^b	0.12	4.88		32.7	86.3		
W(η^4 -CH ₂ =CHCOMe) ₃ ^c	1.6	4.38	2.13				

^a Spectra for the triphosphine complexes were obtained in CD₂Cl₂. Chemical shifts are in δ with respect to Me₄Si (δ 0.0): br = broad; m = multiplet. ^b Taken from ref 44. ^c Taken from ref 43. ^d Not assigned; buried in the resonances of the triphosphines.

signals from the triphosphine ligands in the expected region for such resonances.

Description of the Structure of Ru(η^4 -CH₂=CHCOMe)(ttp). The molecular structure of Ru(η^4 -CH₂=CHCOMe)(ttp) is shown in Figure 1. CH₂=CHCOMe is η^4 -bonded to ruthenium. The coordination sphere geometry of this compound can be regarded as a distorted trigonal bipyramid (TBP) with the two terminal phosphorus atoms of ttp and the olefinic double bond occupying the equatorial positions and the central phosphorus atom of ttp and the oxygen atom taking the apical positions. C(39) is cis to P(1) (C(39)-Ru-P(1) = 89.28 (9)°) and trans to P(3) (C(39)-Ru-P(3) = 164.76 (9)°). The angles C(38)-Ru-P(1) and C(38)-Ru-P(3) are comparable at 127.36 (9) and 126.89 (9)°, respectively, and define an approximate trigonal plane with the P(1)-Ru-P(3) angle. The oxygen atom is trans to P(2) and cis to P(1) and P(3). The apical Ru-P(2) bond (2.2339 (7) Å) is shorter than the two equatorial Ru-P bonds. For the two equatorial Ru-P bonds, the bond Ru-P(3) (2.3209 (7) Å), which is trans to the CH₂ group of methyl vinyl ketone, is longer than the Ru-P(1) bond (2.2983 (8) Å) due to the trans influence of the olefin or the CH₂ group.

The bond C(39)-C(38) (1.436 (4) Å) is longer than the bond C(37)-C(38) (1.398 (4) Å). This trend was observed in other similar compounds such as W(η^4 -CH₂=CHCOMe)₃,⁴⁸ Fe(η^4 -PhCH=CHCHO)(CO)₂(PPh₃),⁴⁹ Fe(CO)₃(η^4 -PhCH=CHCHO),⁵⁰ and [C₅Me₅W(CO)₂(η^4 -PhCH=CHCOMe)]BF₄·CH₂Cl₂.⁴² The angles involving the carbon atoms in the η^4 -CH₂=CHCOMe unit are close

to those in [C₅Me₅W(CO)₂(η^4 -PhCH=CHCOMe)]BF₄·CH₂Cl₂.⁴² The bond distance of C(37)-O (1.306 (4) Å) is considerably longer compared with those for σ -bonded C=O double bonds, for example, 1.254 (12) Å in RuH(CH=C(Me)CO₂Bu)(PPh₃)₃,^{26b} and 1.238 (9) Å in RuCl(CO)(SnCl₃)(Me₂CO)(PPh₃)₂·Me₂CO.⁵¹ However, it is shorter than those for π -bonded C=O double bonds in formaldehyde complexes (ranging from 1.32 (2) to 1.584 (11) Å).⁴⁷ Thus, the C=O double-bond character in the η^4 -CH₂=CHCOMe triphosphine complex is significantly reduced, but not as much as in π -bonded formaldehyde complexes. The Ru-O distance at 2.213 (2) Å is comparable with the Ru-O distances in the acetate complex RuH(O₂CMe)(PPh₃)₃ (2.198 (13) and 2.2210 (10) Å),⁵² the formate complex RuH(O₂CH)(PPh₃)₃ (2.27 and 2.22 Å),⁵³ and the σ -bonded acetone complexes RuCl(CO)(SnCl₃)(Me₂CO)(PPh₃)₂·Me₂CO (2.194 Å)⁵¹ and [Ru(η^6 -C₆H₃Me₃)(MeC(O)CH₂C(OH)Me₂)(Me₂CO)](BF₄)₂ (2.11 Å).⁵⁴ The Ru-C distances are in the range for ruthenium olefin^{25,55} and allyl⁵⁶ complexes. The Ru-C bond lengths

(51) Gould, R. O.; Sime, W. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* 1978, 76.

(52) Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* 1974, 390.

(53) Kolomnikov, I. S.; Gusev, A. I.; Alesksandrov, G. G.; Lobeveva, T. S.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* 1973, 59, 349.

(54) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Steffen, W. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* 1979, 32.

(55) (a) Ball, R. G.; Kiel, G. Y.; Takats, J.; Kruger, C.; Raabe, E.; Grevels, F. W.; Moser, R. *Organometallics* 1987, 6, 2260. (b) Ashworth, T. V.; Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* 1978, 1040. (c) Manoli, J. M.; Gaughan, A. P., Jr.; Ibers, J. A. *J. Organomet. Chem.* 1974, 72, 247. (d) Potvin, C.; Manoli, J. M.; Pannetier, G.; Chevalier, R.; Platzer, N. *J. Organomet. Chem.* 1976, 113, 273. (e) Potvin, C.; Manoli, J. M.; Pannetier, G.; Chevalier, R. *J. Organomet. Chem.* 1978, 146, 57. (f) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* 1977, 129. (g) McNair, A. M.; Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* 1987, 326, 99.

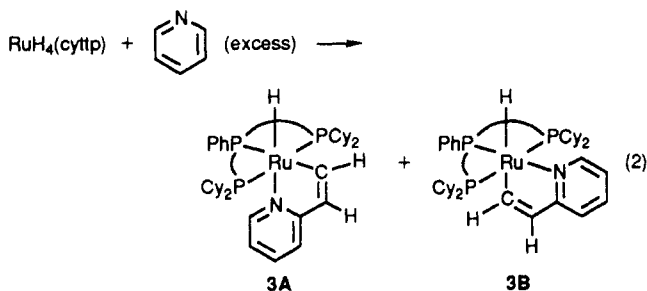
(48) Moriarty, R. E.; Ernst, R. D.; Bau, R. *J. Chem. Soc., Chem. Commun.* 1972, 1242.

(49) Sacerdoti, M.; Bertolasi, V.; Gilli, G. *Acta Crystallogr. Sect. B* 1972, 28, 3273.

(50) de Cian, P. A.; Weiss, R. *Acta Crystallogr., Sect. B* 1972, 28, 3273.

increased in the order of Ru-C(39) (2.159 (3) Å), Ru-C(38) (2.190 (3) Å), and Ru-C(37) (2.232 (3) Å). The bonding pattern for M-C is similar to that observed in complexes^{42,48-50} containing similar η^4 ligands such as CH₂=CHCOMe, PhCH=CHCHO, and PhCH=CHCOMe.

Reaction with 2-Vinylpyridine. The reaction of RuH₄(Cyttp) with 2-vinylpyridine produced two compounds having a composition of Ru(CH₂=CHC₅H₄N)(Cyttp) along with 2-ethylpyridine (eq 2). In fact, on the



basis of spectroscopic data, the ruthenium compounds formed are two isomers of RuH(CH=CHC₅H₄N)(Cyttp), **3A** and **3B**, which must be formed via oxidative addition of one of the sp² C-H bonds of 2-vinylpyridine on a Ru(0) center. This is very similar to the reactions of methacrylates with RuH₂(PPh₃)₄²⁶ and MoH₄(dppe)₂,⁵⁷ where sp² C-H bonds of methacrylates were oxidatively added to Ru(0) and Mo(0) centers to form the corresponding hydride vinyl complexes.

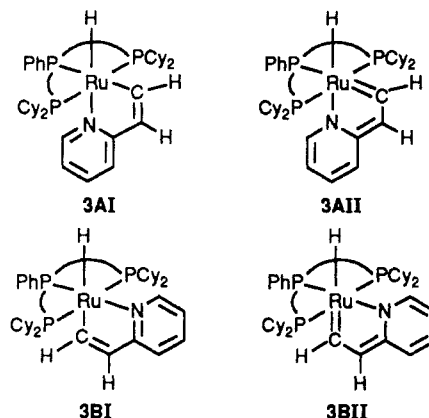
Although a mixture of the two isomers was usually obtained from the 2-vinylpyridine reaction, each isomer could be selectively synthesized by controlling reaction conditions, especially relative amounts of reagents and reaction time. For example, if RuH₄(Cyttp) was allowed to react with excess 2-vinylpyridine for only ca. 30 min, usually only **3A** was isolated. If a large excess of 2-vinylpyridine was employed and the reaction time was overnight, usually only **3B** was formed. Thus, it appears that **3A** is the kinetic product and **3B** the thermodynamic product. However, isolated pure forms of **3A** and **3B** did not interconvert upon refluxing in benzene or in acetone. It is possible that excess 2-vinylpyridine, the impurities in 2-vinylpyridine, or the 2-ethylpyridine formed catalyzed the isomerization, but isolated **3A** or **3B** failed to interconvert in the presence of 2-vinylpyridine or pyridine. Therefore, the exact mechanisms for the formation of **3A** and **3B** are still unclear.

The spectroscopic data are consistent with the structural assignments that both isomers are meridional complexes and that the hydride is cis to the vinyl carbon atom in isomer **3A** and trans to the vinyl carbon atom in **3B**. Both isomers showed a hydride resonance with small ²J(PH) coupling constants (<26 Hz), indicating that the triphosphine is meridional around ruthenium and that the hydride is cis to the three phosphorus atoms of the triphosphine in both isomers. The resonances for the vinyl α -protons appeared at relatively downfield positions in both **3A** (9.92 ppm) and **3B** (11.07 ppm) compared with those in other ruthenium vinyl complexes, for example, 8.16 ppm in RuH(CH=C(Me)CO₂Bu)(PPh₃)₃^{26b} and 8.43 ppm in RuCl(CH=CHPh)(CO)(PPh₃)₂.⁵⁸ The downfield

chemical shifts for the vinyl α -protons indicate that the carbon atoms bonded to ruthenium have some carbenoid character. For example, the chemical shifts for the carbene protons in Ru(=CH₂)Cl(NO)(PPh₃)₂ and Ru(=CHNMe₂)Cl₂(CO)(PEt₃)₂ are 13.30 and 10.53 ppm, respectively.⁵⁹

The carbenoid character of the carbon atoms bound to ruthenium in **3** is also reflected in their ¹³C NMR spectra. The resonance for the carbon atom bound to ruthenium appeared at 213.6 ppm (dt, ²J(PC) = 45.9 Hz (trans), ²J(PC) = 15.4 Hz (cis)) in **3A** and 229.4 ppm (q, ²J(PC) = 8.5 Hz) in **3B**. The chemical shifts for the RuC resonances are relatively high compared with those for metal vinyl complexes; for example, 150.23 ppm in RuCl(CH=CHPh)(CO)(P(*i*-Pr)₃)₂⁶⁰ and 185.97 ppm in Rh(CH=CHC₅H₄N)Cl₂(P(*n*-Bu)₃)₂.⁶¹ In fact, they are close to the values for several ruthenium carbene complexes: for example, ⁵⁹ 248.5 ppm in Ru(=CHNMe₂)Cl₂(CO)(PEt₃)₂ and 222.28 ppm in [Ru(=CCINMe₂)Cl(CO)(CN-*p*-tolyl)(PPh₃)₂]⁺. The ²J(PC) coupling constants for the RuC resonances strongly support the structural assignments for both **3A** (the carbon atom is trans to the central phosphorus atom and cis to the two terminal phosphorus atoms) and **3B** (the carbon atom is cis to the three phosphorus atoms). For comparison, cis ²J(PC) coupling constants were observed at ca. 10 Hz in several ruthenium carbene complexes⁶² and 11.0 Hz in RuCl(CH=CHPh)(CO)(P(*i*-Pr)₃)₂.⁶⁰

Thus, on the basis of the ¹H and ¹³C NMR data, the true structures of both **3A** and **3B** might possess the conjugated nature of two canonical forms as described by **3AI** and **3AII** for **3A** and **3BI** and **3BII** for **3B**. Similar canonical



forms have been proposed for MoH(CH=C(Me)CO₂R)(dppe)₂⁵⁷ and Cp(CO)₂Mo(C(Me)=C(Me)COR)⁶³ to explain the downfield chemical shifts for the carbon atoms directly attached to Mo.

It is noted that the two isomers display an interesting trans influence spectral feature. Thus, in the ³¹P NMR spectrum of **3A**, the resonance for the central phosphorus atom appeared upfield (10.4 ppm) from the two terminal phosphorus atoms (28.1 ppm), while the opposite pattern was observed in **3B** (38.5 ppm for the central phosphorus atom and 19.3 ppm for the two terminal phosphorus at-

(58) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. J. *Organomet. Chem.* **1986**, *309*, 169.

(59) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

(60) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(61) Foot, R. J.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1973**, 838.

(62) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. *J. Chem. Soc., Dalton Trans.* **1979**, 1929.

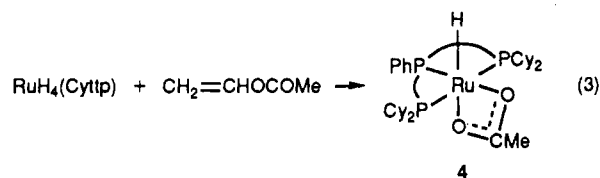
(63) Allen, S. R.; Green, M.; Norman, N. C.; Paddick, K. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1625.

(56) (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347. (b) Schoonover, M. W.; Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1978**, *17*, 3050. (c) Smith, A. E. *Inorg. Chem.* **1972**, *11*, 2306. (d) Lydon, J. E.; Truter, M. R. *J. Chem. Soc. A* **1968**, 362. (e) Colombo, A.; Allegra, G. *Acta Crystallogr., Sect. B* **1971**, *27*, 1653.

(57) Ito, T.; Tosaka, H.; Yoshida, S.; Mita, K.; Yamamoto, A. *Organometallics* **1986**, *5*, 735.

oms). This is consistent with the structural assignments that a strong trans influence ligand (a vinyl or carbenoid carbon atom) is trans to the central phosphorus atom in **3A** and a relatively weak trans influence ligand (pyridine nitrogen atom) is trans to the central phosphorus atom in **3B**. The difference in trans influences of the vinyl group and pyridine is also responsible for the Ru-H bond strength in the isomers. For example, the Ru-H stretching frequencies were observed at 1930 cm^{-1} in **3A** (H trans to the nitrogen atom of pyridine) and 1795 cm^{-1} in **3B** (H trans to the vinyl carbon atom). In addition, the hydride chemical shifts changed from -15.41 ppm in **3A** to relatively downfield at -5.90 ppm in **3B**. This change is consistent with the fact that the hydride is trans to the coordinated pyridine in **3A** and trans to the relatively strong trans influence vinyl carbon atom in **3B**.

Other Reactions. Treatment of $\text{RuH}_4(\text{Cyttp})$ with vinyl acetate gives the ruthenium acetate complex $\text{RuH}(\text{O}_2\text{CMe})(\text{Cyttp})$ (**4**; eq 3). The same complex could also



be obtained from the reaction of $\text{RuCl}_2(\text{Cyttp})$ with excess sodium acetate in refluxing MeOH under a hydrogen atmosphere.⁶⁴ The presence of a chelate O_2CMe group in $\text{RuH}(\text{O}_2\text{CMe})(\text{Cyttp})$ is inferred from the presence of the infrared band at 1560 cm^{-1} characteristic of chelate carboxylate ligands. For example, infrared bands at 1526 and 1451 cm^{-1} were observed for the chelate acetate group in $\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3$,⁷ the structure of which has been confirmed by X-ray diffraction.⁵² In the ^{13}C NMR spectrum, the OCO resonance appeared at 179.6 ppm as a singlet and the methyl resonance at 24.6 ppm as a singlet. These values are comparable with 176.2 and 23.0 ppm for the acetate ligand in $\text{Et}_4\text{N}[\text{W}(\text{CO})_5(\text{O}_2\text{CMe})]$.⁶⁵ In the ^1H NMR spectrum, the resonance for the hydride appeared at -22.41 ppm as a doublet of triplets ($J(\text{PH}) = 38.2, 20.8$ Hz). The lack of large phosphorus-hydride coupling indicates that the hydride is cis to the three phosphorus atoms of the chelating triphosphine.⁶⁶ The resonance for the methyl proton of the acetate appeared at 1.91 ppm as a singlet. The ^{31}P NMR spectrum is an A_2B pattern with $J(\text{PP}) = 38.3$ Hz, and the resonance for the central phosphorus atom (51.7 ppm) is downfield from that of the two terminal phosphorus atoms. This is also consistent

with the structure where the triphosphine is meridional around ruthenium and the central phosphorus atom is trans to the weak trans influence acetate ligand. The reactions of vinyl acetate with $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuHCl}(\text{PPh}_3)_3$ to give $\text{RuH}(\text{O}_2\text{CMe})(\text{PPh}_3)_3$ and $\text{RuCl}(\text{O}_2\text{CMe})(\text{PPh}_3)_3$ have been reported previously.²¹ The mechanism proposed there could be applied to the $\text{RuH}_4(\text{Cyttp})$ system.

The products of the reaction of $\text{RuH}_4(\text{Cyttp})$ with excess methyl acrylate are dependent on the reaction time. If the reaction time is over 24 h, the major product from this reaction is *cis-mer*- $\text{RuH}_2(\text{CO})(\text{Cyttp})$,¹ as indicated by its ^1H and ^{31}P NMR spectra. Other intermediate compounds are produced if the reaction time is short. However, these intermediate species could not be purified and fully characterized due to their high solubility in common organic solvents. Cleavage of the C-O bond of alkyl esters and aryl esters by $\text{RuH}_2(\text{PPh}_3)_4$ to give $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ occurred under more severe conditions.⁶⁷

Unlike $\text{RuH}_4(\text{PPh}_3)_3$, the monohydride complex $\text{RuHCl}(\text{Cyttp})$ is unreactive toward olefins such as 1-pentene, methyl vinyl ketone, 2-vinylpyridine, and dimethyl maleate. This result is not surprising, since $\text{RuHCl}(\text{PPh}_3)_3$ is also unreactive toward olefins such as 1-hexene, 1-heptene, and 2-octene, although $\text{RuHCl}(\text{PPh}_3)_3$ is a catalyst for the hydrogenation of terminal olefins.²

In summary, the reactivity of $\text{RuH}_4(\text{Cyttp})$ and $\text{RuHCl}(\text{Cyttp})$ is very similar to that of $\text{RuH}_4(\text{PPh}_3)_3$ or $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuHCl}(\text{Cyttp})$ toward olefins. The products formed from the reactions of olefins with $\text{RuH}_4(\text{Cyttp})$ are very dependent on the olefins used. A slight change in the structures of the olefins will change the ruthenium complexes formed. The hydride complexes $\text{RuH}_4(\text{Cyttp})$ and $\text{RuHCl}(\text{Cyttp})$ might have catalytic properties similar to the catalysts $\text{RuH}_4(\text{PPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_4$, and $\text{RuHCl}(\text{PPh}_3)_3$.

Acknowledgment. We are grateful to the Johnson Matthey Co. for a loan of " $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ". We thank Professors Robert H. Morris and Andrew Wojcicki and Mr. Patrick Blosser for their help in the preparation of this manuscript. We also thank Ms. Susan Reid for her work on the solution and refinement of the X-ray structure.

Supplementary Material Available: Tables (SUP-1-SUP-7) of complete bond distances and angles (involving non-hydrogen and hydrogen atoms), calculated positional parameters and *B* values for hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, and torsion or conformation angles for $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ (12 pages); a table (SUP-8) of observed and calculated structure factors for the non-hydrogen atoms of $\text{Ru}(\eta^4\text{-CH}_2=\text{CHCOMe})(\text{ttp})$ (40 pages). Ordering information is given on any current masthead page.

(64) Jia, G.; Meek, D. W. Unpublished results.

(65) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132.

(66) (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.

(b) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 189.

(67) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808.