Synthesis and Reactivity of Ruthenium Hydride Complexes of Chelating Triphosphines. 5.[1] Reactions of Acetylenes with RuHCl(Cyttp) and RuH_4(Cyttp) (Cyttp = $C_6H_5P(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$)

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Treatment of RuHCl(Cyttp) with PhC≡C—C≡CPh in benzene produced *syn,mer*-RuCl(η^3-PhC_3CHPh)(Cyttp), which isomerizes into *anti,mer*-RuCl(η^3-PhC_3CHPh)(Cyttp) in dichloromethane or methanol. Reaction of RuHCl(Cyttp) with $MeO_2CC{\equiv}CCO_2Me$ yielded RuCl($MeO_2CC{=}CHCO_2Me$)(Cyttp). Acetylide complexes RuCl(C≡CR)(Cyttp) (R = Ph, $(CH_2)_5CH_3$)) were produced when RuHCl(Cyttp) was treated with HC≡CR. Reactions of RuH_4(Cyttp) with $MeO_2CC{\equiv}CCO_2Me$ and PhC≡CPh gave *fac*-Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp) and Ru(PhC≡CPh)(Cyttp), respectively. Reaction of RuH_4(Cyttp) with 1-octyne produced Ru(C≡C$(CH_2)_5CH_3)_2$(Cyttp). Reaction of RuH_4(Cyttp) with excess phenylacetylene produced Ru(C≡CPh)(η^3-PhC_3CHPh)(Cyttp).

Introduction

The reactivity of transition-metal hydride complexes toward acetylenes has been under active investigation.[2] The interest in this area stems from the fact that transition-metal complexes catalyze various reactions involving acetylenes, such as hydrogenation, oligomerization, and polymerization of acetylenes, and coupling reactions of acetylenes with olefins.[3]

Reactions of acetylenes with ruthenium hydride complexes including $RuHCl(PPh_3)_3$,[4] $RuHCl(CO)(PPh_3)_3$,[5] $RuHCl(CO)(P(i\text{-}Pr)_3)_2$,[6] $RuHCl(CO)(Me_2Hpz)(PR_3)_2$ (R = Ph,[2g,7] *p*-tolyl[2g]), $RuH(O_2CCF_3)(CO)(PPh_3)_2$,[8] $RuH(NO)(PPh_3)_3$,[9] and CpRuH(LL') (LL' = $(PPh_3)_2$,[2e,10] $(CO)(PPh_3)$,[2e,11] dppe,[2e] dppm,[2e] $(CO)_2$[12]) have been examined. With a few exceptions, insertion of acetylenes into Ru–H bonds is the most common reaction.

To compare the chemical and catalytic properties of ruthenium hydride complexes of chelating triphosphines with those of monophosphines/diphosphines, the reactions of acetylenes with the electron-rich hydride complexes RuHCl(Cyttp) and RuH_4(Cyttp) were investigated. The reaction of RuH_4(Cyttp) with excess phenylacetylene has been previously reported.[13]

Experimental Section

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Air-sensitive solids were handled and transferred in a Vacuum 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.

Reagent-grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Sodium tetrahydroborate was obtained from Fisher Scientific Co. Ruthenium trichloride hydrate was loaned by Johnson Matthey Inc. The hydride complexes[14] RuHCl(Cyttp) and RuH_4(Cyttp) were prepared as described in the literature.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1}, as pressed potassium bromide pellets. Spectra were calibrated against the sharp 1601-cm^{-1} peak of polystyrene film. A Bruker AM-250 spec-

Table I. $^{31}P\{^1H\}$ NMR Data for the Ruthenium Complexes[a]

compd	$\delta(P_1)$	$\delta(P_2)$	$J(P_1P_2)$
syn,mer-RuCL(η^3-PhC_3CHPh)-(Cyttp)	21.2 (br)	−1.0	38.0
anti,mer-RuCl(η^3-PhC_3CHPh)-(Cyttp)	13.0	−2.2	37.4
RuCl($MeO_2CC{=}CHCO_2Me$)-(Cyttp)	49.7 (br)	11.4	40.5
Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)-(Cyttp)	43.7	23.0, 19.5	*b*
Ru(PhC≡CPh)(Cyttp)	5.3	13.0	35.5
RuCl(C≡CPh)(Cyttp)	70.6	16.6	35.6
RuCl(C≡C$(CH_2)_5CH_3$)(Cyttp)	73.1	18.5	36.7
Ru(C≡C$(CH_2)_5CH_3)_2$(Cyttp)	79.4	20.8	39.6
Ru(C≡CPh)$_2$(Cyttp)	77.6	19.7	38.4
Ru(C≡CPh)(η^3-PhC_3CHPh)-(Cyttp)	19.6	2.5	37.0[c]

[a] Spectra were obtained in benzene unless stated otherwise. Chemical shifts are in δ with respect to extrnal 85% H_3PO_4 (δ 0.0); positive values are downfield; coupling constants are in Hz. P_1 represents the central phosphorus atom and P_2 the two terminal phosphorus atoms in Cyttp. br = broad. [b] $J(P_1P_2)$ = 31.5 Hz, $J(P_1P_2')$ = 43.0 Hz, $J(P_2P_2')$ = 6.2 Hz. [c] In CD_2Cl_2.

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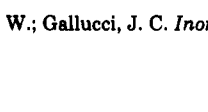
trometer was used to obtain proton (250.13 MHz), phosphorus-31 (101.25 MHz), and carbon-13 (62.9 MHz) NMR spectra in 5-mm tubes. Residual solvent proton or carbon-13 resonances were used as internal standards for the ^1H or ^{13}C NMR spectra. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. The $^{31}P\{^1H\}$ NMR data for the ruthenium complexes are presented in Table I. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

***syn,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)·$^1/_2$C$_6$H$_6$.** A mixture of 0.20 g of RuHCl(Cyttp) (0.28 mmol) and 0.07 g of PhC≡C—C≡CPh (0.4 mmol) in 20 mL of benzene was stirred overnight at room temperature to give a deep orange solution. The solvent was then removed completely under vacuum, and 8 mL of Et_2O was added. The resulting mixture was set in a freezer (ca. −10 °C) overnight to give an orange solid. The orange solid was collected on a filter frit, washed with cold Et_2O, and dried under vacuum overnight. Yield: 0.16 g, 60%. X-ray-quality crystals were obtained by slow diffusion of Et_2O into a saturated benzene solution. ^1H NMR (C_6D_6): δ 0.9–2.8 (m, 6 CH_2 and 4 C_6H_{11}), 6.74 (s, =CH), 7.0–8.6 (m, 3 Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.8–34.5 (m, 26 CH_2), 35.5 (t, J(PC) = 6.9 Hz, 2 P–CH), 36.1 (t, J(PC) = 9.1 Hz, 2 P–CH), 124.7–139.6 (m, C≡C—C=CH and 3 Ph). Anal. Calcd for $C_{55}H_{75}ClP_3Ru$: C, 68.41; H, 7.81; Cl, 3.67. Found: C, 68.24; H, 7.74; Cl, 3.56.

***anti,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp). Method 1.** A mixture of 0.20 g of RuHCl(Cyttp) (0.28 mmol) and 0.10 g of PhC≡C—C≡CPh (0.49 mmol) in 20 mL of benzene was stirred overnight to give a deep orange solution. The solvent was removed completely, and 8 mL of MeOH was added. The resulting mixture was stirred for an additional 1 h to give an orange solid. The solid was collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.21 g, 81%. ^1H NMR (C_6D_6): δ 0.5–3.3 (m, 6 CH_2 and 4 C_6H_{11}), 6.45 (s, =CH), 7.0–8.6 (m, 3 Ph). Anal. Calcd for $C_{52}H_{72}ClP_3Ru$: C, 67.41; H, 7.83; Cl, 3.83. Found: C, 67.15; H, 7.81; Cl, 4.03.

Method 2. The isolated *syn,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was set at room temperature overnight. The ^{31}P NMR spectrum in situ showed that all the syn isomer has converted into the anti isomer.

RuCl(MeO$_2$CC=CHCO$_2$Me)(Cyttp). A mixture of 0.30 g of RuHCl(Cyttp) (0.41 mmol) and 0.3 mL of $C_2(CO_2Me)_2$ (2 mmol) in 20 mL of benzene was stirred at room temperature for 2 h to give a red solution. The liquids of the reaction mixture were then removed completely, and 5 mL of Et_2O was added. The resulting mixture was set in a freezer (ca. −10 °C) overnight to give a yellow brownish powder. The powder was collected on a filter frit, washed with cold Et_2O, and dried under vacuum overnight. Yield: 0.18 g, 51%. (The product is soluble in common organic solvents). ^1H NMR (CD_2Cl_2): δ 1.0–2.5 (m, 6 CH_2 and 4 C_6H_{11}), 3.44 (s, CH_3), 3.66 (s, CH_3), 5.19 (s, =CH), 7.44 (m, *p*- and *m*-Ph), 7.63 (m, *o*-Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; please refer to the numbering scheme (I)



I

for the ^{13}C NMR assignments): δ 14.8–30.7 (m, 26 CH_2), 35.6 (t, J(PC) = 8.3 Hz, 2 P–CH), 37.1 (t, J(PC) = 9.3 Hz, 2 P–CH), 50.3 (s, CH_3), 51.3 (s, CH_3), 122.4 (s, C_3), 128.5 (d, ^3J(PC) = 8.4 Hz, *m*-Ph), 129.6 (s, *p*-Ph), 131.3 (d, ^2J(PC) = 7.8 Hz), 140.0 (d, ^1J(PC) = 37.4 Hz, ipso-Ph), 169.2 (s, C_4), 174.4 (s, C_1), 183.4 (br, C_2, $^3J(C_1H_a)$ = 16.5 Hz). IR(KBr): ν(CO) 1750 (s), 1730 (sh), 1705 (s) cm^{-1}; ν(C=C) 1550 (s) cm^{-1}. Anal. Calcd for $C_{42}H_{68}ClO_4P_3Ru$: C, 58.22; H, 7.91; Cl, 4.09. Found: C, 58.37; H, 7.74; Cl, 4.19.

Ru(η^4-MeO$_2$CCH=CHCO$_2$Me)(Cyttp). A mixture of 4.0 mL of 0.26 M benzene solution of $C_2(CO_2Me)_2$ (1.0 mmol) and RuH_4(Cyttp) (ca. 0.53 mmol, prepared from 0.40 g of $RuCl_2$(Cyttp) with excess NaH) in ca. 30 mL of benzene was stirred at room temperature for 3 h. The liquids of the reaction mixture were then removed completely under vacuum, and 10 mL of Et_2O was added to give a yellow precipitate. The precipitate was collected on a filter frit, washed with small amounts of Et_2O and acetone, and dried under vacuum overnight. Yield: 0.22 g, 51%. ^1H NMR (CD_2Cl_2): δ 0.9–2.7 (m, 6 CH_2, 4 C_6H_{11}, and =CH), 3.27 (s, CH_3), 3.47 (s, CH_3), 4.81 (s, =CH), 7.26 (m, *p*- and *m*-Ph), 8.06 (t, J = 7.9 Hz, *o*-Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.3–32.9 (m, 26 CH_2), 34.1 (d, J(PC) = 26.9 Hz, CH), 36.9 (d, J = 13.1 Hz, CH), 40.6 (d, J = 17.5 Hz, CH), 41.3 (d, J = 6.3 Hz, CH), 43.5 (d, J = 14.0 Hz, 2 CH), 49.6 (s, CH_3), 54.3 (s, CH_3), 127.0 (d, ^3J(PC) = 9.0 Hz, *m*-Ph), 128.8 (s, *p*-Ph), 132.9 (d, ^2J(PC) = 10.7 Hz, *o*-Ph), 139.6 (d, ^1J(PC) = 28.4 Hz, ipso-Ph), 161.5 (s, C=O), 179.7 (s, C=O). IR (KBr): ν(C=O) 1670 (s) cm^{-1}. Anal. Calcd for $C_{42}H_{69}O_4P_3Ru$: C, 60.62; H, 8.36. Found: C, 60.70; H, 8.30.

Ru(PhC≡CPh)(Cyttp). A mixture of 0.20 g of PhC≡CPh (1.1 mmol) and RuH_4(Cyttp) (ca. 0.53 mmol prepared from 0.40 g of $RuCl_2$(Cyttp) with excess NaH) in ca. 40 mL of benzene was stirred at room temperature for 3 h to give a deep red solution. The solvent was then removed completely, and 10 mL of Et_2O was added to give a small amount of red solid. The mixture was set in a freezer (ca. −10 °C) overnight. The red solid was then collected on a filter frit, washed with cold Et_2O, and dried under vacuum overnight. Yield: 0.21 g, 46%. (The compound is soluble in acetone, hexane, and Et_2O, and reacts with MeOH to form $RuH_2(CO)$(Cyttp)). ^1H NMR (CD_2Cl_2): δ 0.6–2.5 (m, 6 CH_2 and 4 C_6H_{11}), 6.4–7.6 (m, 3 Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.9–31.8 (m, 26 CH_2), 32.0 (t, J(PC) = 6.9 Hz, 2 P-CH), 38.3 (t, J(PC) = 7.2 Hz, 2 P–CH), 118.8–160.9 (m, 3 Ph), 160.1 (td, ^2J(PC) = 10.1, 4.8 Hz, ≡C), 195.7 (dt, ^{2}J(PC) = 64.8, 12.8 Hz, ≡C).

RuCl(C≡CPh)(Cyttp). Method A. A mixture of 0.15 g of RuHCl(Cyttp) (0.21 mmol) and 0.5 mL of phenylacetylene (5 mmol) in 15 mL of benzene was stirred at room temperature for 1 h to give a purple solution. The liquids of the reaction mixture were removed completely, and 10 mL of hexane was added to give a purple powder. The powder was then collected by filtration, washed with hexane, and dried under vacuum overnight. Yield: 0.12 g, 69%. ^1H NMR (C_6D_6): δ 0.3–1.9 (m, 6 CH_2 and 4 C_6H_{11}), 6.4–7.4 (m, 2 Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.5–31.2 (m, 26 CH_2), 34.4 (t, J(PC) = 9.2 Hz, 2 P-CH), 38.1 (d, J(PC) = 10.1 Hz, 2 P-CH), 114.4 (s, C_β), 122.3 (dt, ^2J(PC) = 35.3, 13.8 Hz, C_α), 123.3–133.7 (m, 3 Ph). IR (KBr): ν(C≡C) 2060 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{66}ClP_3Ru$: C, 64.10; H, 8.07; Cl, 4.30. Found: C, 64.36; H, 7.92; Cl, 4.12.

Method B. The exact same procedure as in method A was used except a 1:1 molar ratio of phenylacetylene and RuHCl(Cyttp) was employed. The same product RuCl(C≡CPh)(Cyttp) was isolated.

RuCl(C≡C(CH$_2$)$_5$CH$_3$)(Cyttp). A mixture of 0.20 g of RuHCl(Cyttp) (0.28 mmol) and 0.3 mL of 1-octyne (2 mmol) in 20 mL of benzene was stirred at room temperature for 3 h to give a purple solution. The solvent was then removed completely, and 10 mL of MeOH was added to the residue to give a purple solid. The solid was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.13 g, 56%. ^1H NMR (CD_2Cl_2): δ 0.9–2.4 (m, CH_3, 11 CH_2 and 4 C_6H_{11}), 7.35 (m, *p*- and *m*-Ph), 8.01 (m, *o*-Ph). $^{13}C\{^1H\}$ NMR (CH_2Cl_2/$CDCl_2CDCl_2$): δ 14.3 (s, CH_3), 17.9–31.8 (m, 31 CH_2), 33.9 (t, J(PC) = 9.0 Hz, 2 P-CH), 37.0 (t, J(PC) = 10.8 Hz, 2 P–CH), 94.8 (dt, ^2J(PC) = 32.3, 14.1 Hz, C_α), 115.3 (s, C_β), 127.3 (d, ^3J(PC) = 9.1 Hz, *m*-Ph), 129.5 (s, *p*-Ph), 133.2 (d, ^2J(PC) = 9.8 Hz, *o*-Ph), 133.5 (d, ^1J(PC) = 40.2 Hz, ipso-Ph). IR (KBr): ν(C≡C) 2080 (m) cm^{-1}. Anal. Calcd for $C_{44}H_{74}ClP_3Ru$: C, 63.48; H, 8.96; Cl, 4.26. Found: C, 63.60; H, 8.79; Cl, 4.02.

Ru(C≡C(CH$_2$)$_5$CH$_3$)$_2$(Cyttp). A 0.3-mL volume of 1-octyne (2 mmol) was added to a benzene solution of RuH_4(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH). The color of the reaction mixture turned deep blue im-

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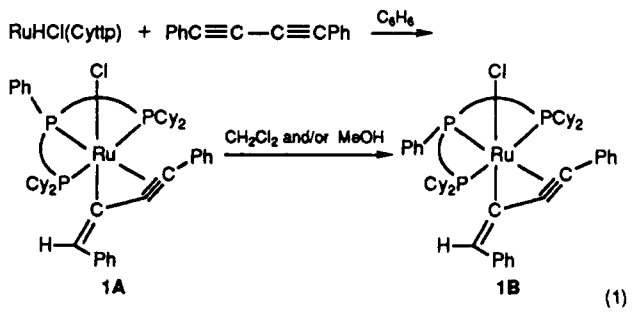
mediately. The liquids were then removed under vacuum. The spectroscopic data were collected by using the residue. ^{1}H NMR (C_6H_6): δ 0.4–3.6 (m, 2 CH_3, 16 CH_2 and 4 C_6H_{11}), 7.28 (m, *p*-Ph), 7.47 (t, J = 7.2 Hz, *m*-Ph), 8.57 (t, J = 8.6 Hz, *o*-Ph). ^{13}C{^{1}H} NMR (C_6H_6): δ 14.3 (s, CH_3), 14.4 (s, CH_3), 20.0–32.4 (m, 36 CH_2), 37.0 (t, J(PC) = 10.7 Hz, 2 P-CH), 38.7 (t, J(PC) = 10.0 Hz, 2 P-CH), 114.0 (s, C_β), 115.1 (dt, ^2J(PC) = 24.0, 13.5 Hz, C_ϵ), 121.5 (td, ^2J(PC) = 15.8, 7.4 Hz, C_α), 126.3 (s, C_β), 127.2 (d, ^3J(PC) = 9.1 Hz, *m*-Ph), 129.4 (s, *p*-Ph), 133.9 (d, ^2J(PC) = 10.2 Hz, *o*-Ph), 135.8 (d, ^1J(PC) = 35.7 Hz, ipso-Ph). IR (KBr): ν(C≡C) 2060 (m) cm^{-1}.

Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp). A mixture of 0.3 mL of phenylacetylene (3 mmol) and RuH_4(Cyttp) (ca. 0.40 mmol, prepared from 0.30 g of $RuCl_2$(Cyttp) with excess NaH) in 30 mL of benzene was stirred at room temperature for 3 h to give a deep red solution. The reaction mixture was then pumped to dryness. The residue was washed with 10 mL of MeOH to give a red powder. The powder was then collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.34 g, 86% based on $RuCl_2$(Cyttp). X-ray-quality crystals were obtained by slowly evaporating solvents from a saturated solution in CH_2Cl_2/MeOH with a stream of argon. ^{1}H NMR (CD_2Cl_2): δ 0.5–3.0 (m, 6 CH_2 and 4 C_6H_{11}), 6.80 (s, =CH), 7.0–8.4 (m, 4 Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.3–30.1 (m, 26 CH_2), 35.7 (t, J(PC) = 8.3 Hz, 2 P–CH), 37.7 (t, J(PC) = 7.7 Hz, 2 P-CH), 118.3–158.5 (m, C≡C—C=CH and 4 Ph). Anal. Calcd for $C_{60}H_{77}P_3Ru$: C, 72.63; H, 7.82. Found: C, 72.57; H, 7.83.

Results and Discussion

Reactions of PhC≡CPh and PhC≡C—C≡CPh with RuHCl(Cyttp). It has been reported that $RuHCl(PPh_3)_3$ reacts with excess internal acetylenes such as diphenylacetylene or 2- or 3-hexyne to give the orthometalated complex $RuCl(PPh_2C_6H_4)(PPh_3)_2$.[4b] The Cyttp analogue RuHCl(Cyttp), however, failed to react with diphenylacetylene in benzene solution. In contrast, treatment of RuHCl(Cyttp) in benzene with excess 1,4-diphenylbutadiyne (PhC≡C—C≡CPh) overnight produced cleanly the cis insertion product *syn,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (**1A**). The compound **1A** is very soluble in aromatic solvents, fairly soluble in hexane and ether, and completely isomerizes into its isomer *anti,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp), (**1B**) when treated with polar solvents such as MeOH or dichloromethane (eq 1).



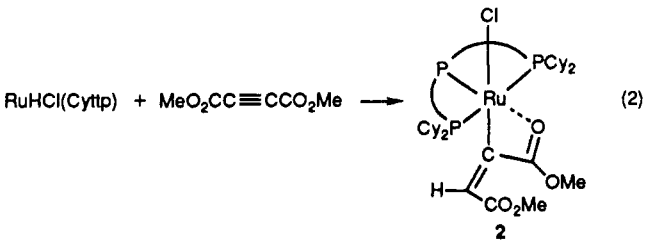
(1)

The molecular structures[15] of both isomers **1A** and **1B** show that both isomers contain a meridional Cyttp and an η^3-PhC$_3$CHPh ligand. The C≡C group is more strongly bonded on ruthenium in isomer **1A** than that in **1B**. The phenyl group on the central phosphorus atom is on the same side of chloride in isomer **1A** and on the opposite side in **1B**. In both isomers, the vinyl proton is cis to the metal, indicating a cis insertion mode for the PhC≡C—C≡CPh reaction.

In the ^{1}H NMR spectra, the vinyl proton signal appears at 6.74 ppm for isomer **1A** and at 6.45 ppm for isomer **1B**. In their ^{31}P NMR spectra in benzene, the chemical shifts of the terminal PCy_2 groups are similar (−1.0 ppm for isomer **1A**, −2.2 ppm for isomer **1B**). However, the signal for the central PPh group in **1A** appears as a broad peak at 21.2 ppm, whereas a sharp triplet at 13.0 ppm, which stays sharp even at 70 °C, is observed in **1B**. The A_2B ^{31}P NMR pattern is consistent with a meridional geometry of Cyttp in both isomers. The broad nature of the resonance for the central phosphorus atom in **1A** is probably caused by a rapid chemical exchange process involving dissociation and association of the weakly bound acetylene ligand. No infrared bands assignable to ν(C≡C) were observed in the region 1600–2200 cm^{-1} for both **1A** and **1B**.

The insertion reactions of 1,4-diphenylbutadiyne into the M–H bonds in $MH(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru, Os) have been reported previously.[8] In the above reactions, the diyne is also cis inserted into the M–H bonds to form $M(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$. Although the overall reaction pattern is similar, the acetylenic group is not bonded to the metal centers.

Reactions of $C_2(CO_2Me)_2$ with RuHCl(Cyttp) and RuH_4(Cyttp). Treatment of RuHCl(Cyttp) with excess $C_2(CO_2Me)_2$ in benzene at room temperature yielded the cis insertion product $RuCl(MeO_2CC{=}CHCO_2Me)$(Cyttp) (**2**) (eq 2). In the ^{1}H NMR spectrum, the vinyl proton



(2)

signal was observed at 5.19 ppm, which is comparable with the value 5.00 ppm in $CpRu(dppm)(MeO_2CC{=}CHCO_2Me)$ and 5.33 ppm in $CpRu(CO)(PPh_3)(MeO_2CC{=}CHCO_2Me)$.[2e] The ^{13}C NMR chemical shifts for the $Ru(MeO_2CC{=}CHCO_2Me)$ group in **2** are comparable to those observed in other $M(MeO_2CC{=}CHCO_2Me)$ complexes.[2f,16,17]

In a refocused ^{13}C INEPT experiment, the long-range $^3J(^{13}C_1{-}^1H_a)$ coupling (see the numbering scheme in the Experimental Section) was determined to be 16.5 Hz. It has been reported that such $^3J(^{13}C{-}^1H)_{trans}$ coupling ranges from 14 to 16 Hz, while $^3J(^{13}C{-}^1H)_{cis}$ ranges from 8.5 to 10 Hz.[16] This argument has previously been used to deduce the configuration of similar alkenyl groups.[2f,16] Thus, the insertion mode is also cis. The signals for the ipso carbon atoms of the cyclohexyl groups appear as virtual triplets, which confirms the meridional geometry of the triphosphine around ruthenium.

Consistent with a meridional geometry of Cyttp, the ^{31}P NMR spectrum in dichloromethane at room temperature shows a doublet at 11.4 ppm for the two terminal phosphorus atoms and a broad signal at 49.7 ppm for the central phosphorus atom. The broad signal became a triplet at 250 K. The ^{31}P NMR spectrum of **2** is similar to that of isomer **1A** of RuCl(η^3-PhC$_3$CHPh)(Cyttp) in that the signals for the central phosphorus atom in both isomers are broad at room temperature. In isomer **1a** of RuCl(η^3-PhC$_3$CHPh)(Cyttp), the acetylenic group is weakly bound to ruthenium as confirmed by its X-ray structure. Therefore, the broad nature of the resonance for the central phosphorus atom in **2** is probably caused by a rapid chemical exchange process involving dissociation and as-

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sociation of the ketonic oxygen atom.

The cis insertion mode observed in the reaction of RuHCl(Cyttp) with $C_2(CO_2Me)_2$ is consistent with the observations in other ruthenium monohydride systems such as RuHCl(CO)$(PPh_3)_3$,[5a] RuHCl(CO)$(Me_2Hpz)(PR_3)_2$ (R = Ph, *p*-tolyl),[2g] CpRuH(CO)(PPh_3),[2e,11] CpRuH$(PPh_3)_2$,[2e,10a] and CpRuH(L_2) (L_2 = dppe, dppm).[2e] The trans insertion mode of $C_2(CO_2Me)_2$ into M–H bonds is known, for example, in the reaction of $C_2(CO_2Me)_2$ with Cp_2ReH,[16] Cp_2WH_2,[16] Cp_2MoH_2,[16] *trans*-$PtH_2(PR_3)_2$ (PR_3 = PCy_3, $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_2(n\text{-}Bu)$, $P(t\text{-}Bu)_2Me$).[17] The reaction of $C_2(CO_2Me)_2$ with $Cp_2NbH(CO)$ produces a mixture of cis and trans insertion products.[2f]

The reaction of RuH_4(Cyttp) with excess $C_2(CO_2Me)_2$ produced intractable products and with 1 equiv of $C_2(CO_2Me)_2$ yielded a complicated mixture. However, treatment of RuH_4(Cyttp) with 2 equiv of $C_2(CO_2Me)_2$ in benzene for 2 h at room temperature gave a yellow compound as the predominant product, which can be formulated as Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp) (**3**) on the basis of analytical and spectroscopic data (eq 3). The ^{31}P NMR parameters for the yellow compound are very similar to those for Ru(η^4-$CH_2{=}CHCO_2Me$)(triphos) (triphos = Cyttp, ttp; ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$).[1]

$RuH_4(Cyttp) + MeO_2CC{\equiv}CCO_2Me \longrightarrow$ **3** (3)

The presence of a π-bonded $MeO_2CCH{=}CHCO_2Me$ ligand is inferred from the ^{13}C NMR spectra. In the aromatic region, only resonances assignable to the phenyl group of the triphosphine were observed. In the aliphatic region, however, there are resonances corresponding to six CH carbon atoms ranging from 34.1 to 43.5 ppm, as indicated by its broad-band decoupled ^{13}C DEPT spectra. The chemical shift range is in the region for resonances of olefinic carbon nuclei of π-bonded dimethyl fumarate or dimethyl maleate of ruthenium complexes, for example, 37.1 ppm in Ru(*E*-$MeO_2CCH{=}CHCO_2Me$)$(CO)_4$ and 38.7 ppm in Ru(*Z*-$MeO_2CCH{=}CHCO_2Me$)$(CO)_4$.[18] Thus, in the aliphatic region of the ^{13}C NMR spectrum of Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp), four of the six CH signals are due to the ipso CH groups of the four cyclohexyl groups of the triphosphine; the other two signals must be due to the π-bonded olefinic CH groups. In the ^{13}C NMR spectrum, the resonances for carboxylate C=O groups were observed at 179.7 and 161.5 ppm. The former is assigned to the uncoordinated C=O, while the later is assigned to the π-bonded C=O. In fact, the value 161.5 ppm is very similar to the chemical shifts of π-bonded C=O in η^4-$RCH{=}CR'COMe$ tungsten complexes,[19] for example, 164.5 ppm in $[CpW(CO)_2(\eta^4\text{-}PhCH{=}CHCOMe)]BF_4$ and 157.9 ppm in $[CpW(CO)_2(\eta^4\text{-}MeCH{=}CMeCOMe)]BF_4$. The two methyl groups in Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp) are also inequivalent in the ^{13}C NMR spectrum and appear at 54.34 and 49.63 ppm.

In the ^1H NMR spectrum, a broad signal at 4.81 ppm (one proton on the basis of integration) was observed, which is assigned to the central olefinic proton of the η^4 ligand. The chemical shift is comparable to those observed for the CH proton of η^4-$CH_2{=}CHCOMe$ in the complexes Ru(η^4-$CH_2{=}CHCOMe$)(triphos) (4.23 ppm, triphos = ttp; 4.11 ppm, triphos = Cyttp)[1] and very similar to the value 4.88 ppm for the CH proton in the η^4-$CH_2{=}CH{-}CH{=}CH_2$ complex Ru(η^4-$CH_2{=}CH{-}CH{=}CH_2$)$(CO)_3$.[20] For comparison, the chemical shifts for the two CH protons of η^2-$MeO_2CCH{=}CHCO_2Me$ are usually of the same value and appear at relatively higher field, for example, 2.18 ppm in $Cp_2W(\eta^2\text{-}Z\text{-}MeO_2CCH{=}CHCO_2Me)$,[16] 2.83 ppm in $Cp_2W(\eta^2\text{-}E\text{-}MeO_2CCH{=}CHCO_2Me)$,[16] 3.05 ppm in Ru($\eta^2$-*Z*-$MeO_2CCH{=}CHCO_2Me$)$(CO)_4$, and 3.73 ppm in Ru($\eta^2$-*E*-$MeO_2CCH{=}CHCO_2Me$)$(CO)_4$.[18] The two methyl signals in **3** were observed at 3.48 and 3.27 ppm. The signal for the open-end olefinic proton of the η^4 ligand was not located, but is presumably buried in the resonances of the triphosphine in the aliphatic region (0.9–2.8 ppm).

In the infrared spectrum, only one strong band at 1670 cm^{-1} assignable to ν(C=O) was observed above 1500 cm^{-1}. The presence of only one ν(C=O) above 1500 cm^{-1} in Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp) is in agreement with the structural assignment that one of the C=O double bonds is π-bonded to ruthenium. The ν(C=O) frequencies for π-bonded C=O are usually below 1500 cm^{-1}.[19,21] For example, ν(C=O) in W(η^4-$CH_2{=}CHCOMe)_3$[21] was observed at 1495 cm^{-1}. Unfortunately, ν(C=O) for the π-bonded C=O in Ru(η^4-$MeO_2CCH{=}CHCO_2Me$)(Cyttp) cannot be assigned confidently, since triphosphine absorbs in the region 1400–1500 cm^{-1}.

Reaction of PhC≡CPh with RuH_4(Cyttp). In contrast to the reaction of $C_2(CO_2Me)_2$ with RuH_4(Cyttp), treatment of RuH_4(Cyttp) with 2 equiv or large excess of PhC≡CPh produced a red compound that can be formulated as the acetylene complex Ru(PhC≡CPh)(Cyttp) (**4**) on the basis on its spectroscopic data (eq 4).

$RuH_4(Cyttp) + PhC{\equiv}CPh \longrightarrow$ **4** (4)

The ^1H NMR spectrum indicates that there are no hydride ligands in the compound and that there is one PhC≡CPh per Cyttp ligand on the basis of integration. The presence of PhC≡CPh is confirmed by the ^{13}C NMR spectrum. The broad-band-decoupled ^{13}C DEPT spectra show that there are 19 CH carbon atoms and 5 quaternary carbon atoms in the molecule. The CH resonances are assigned to the four ipso CH carbon atoms of the four cyclohexyl groups of the triphosphine and the three phenyl rings. The virtual triplet appearance of the resonances of the ipso carbon atoms of the cyclohexyl groups indicates that the triphosphine is meridional around ruthenium.[22]

The quaternary carbon resonances corresponding to five carbon atoms appear in the region 143.6–195.7 ppm, which are assigned to the one ipso carbon atom of the phenyl group of the triphosphine, the two acetylenic carbon atoms of PhC≡CPh, and the two quaternary carbon atoms of the

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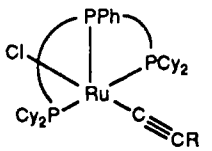
phenyl rings of PhC≡CPh. The signals at 195.6 ppm (dt, ^2J(PC) = 64.8, 12.8 Hz) and at 160.1 ppm (td, ^2J(PC) = 10, 4.8 Hz) are assigned to the two acetylenic carbon atoms. Since the compound is diamagnetic, the diphenylacetylene in the compound is either a 2e donor or a 4e donor. The chemical shifts (δ_{av} = 177.9 ppm) for the acetylenic carbon atoms are at much higher field than those observed for 2e donor acetylenes but are close to those for 4e donor acetylenes. For example, the acetylenic carbon resonances for 2e donor acetylenes were observed at 98.46 ppm in $[Ru(NH_3)_5(DMAD)](PF_6)_2$,[23] 115.3 ppm in $Cp_2Mo(MeC{\equiv}CMe)$,[24] and those for 4e donor acetylenes, at 196.01 ppm in $Cp_2Ti(PhC{\equiv}CPh)$[25] and 192.5 and 187.4 ppm in $CpW(CO)(Me)(HC{\equiv}CH)$.[24] Thus, the diphenylacetylene in Ru(PhC≡CPh)(Cyttp) is a 4e donor to form an 18e complex. The phosphorus–carbon coupling constants indicate that one of the acetylenic carbon atoms is trans to the central phosphorus atom (the one resonating at 195.7 ppm (dt, ^2J(PC) = 64.8, 12.8 Hz), and the other one (resonating at 160.1 ppm (td, ^2J(PC) = 10, 4.8 Hz)) is cis to the three phosphorus atoms of the triphosphine. In the infrared spectrum, no infrared bands assignable to ν(C≡C) were observed above 1600 cm^{-1}; the band might be too weak to be observed.

In an attempt to isolate the organic compounds formed during the reaction, *trans*-stilbene was isolated by sublimation at ca. 100 °C. The formation of *cis*-stilbene from the reaction of diphenylacetylene with Cp_2MoH_2 has been reported previously.[26] It is possible that in our case *cis*-stilbene is formed initially and thermal isomerization occurred during sublimation. Isomerization of *cis*-stilbene into *trans*-stilbene was reported in the thermal decomposition of $Cp_2Ti(PhC{\equiv}CPh)$.[25]

Thus, both RuHCl(Cyttp) and RuH_4(Cyttp) are reactive toward internal acetylenes to give insertion products. In addition, reactions of RuH_4(Cyttp) with internal acetylenes usually result in the transfer of two hydrides to an acetylene to form an olefin.

Reactions of Terminal Acetylenes with RuHCl(Cyttp). Treatment of RuHCl(Cyttp) with 1 equiv or excess phenylacetylene produced the purple compound RuCl(C≡CPh)(Cyttp) (**5**) (eq 5). In the ^{1}H NMR spectrum of the purple compound, no hydride or vinyl proton resonances were observed. In the infrared spectrum, a strong band at 2060 cm^{-1} assignable to ν(C≡C) was observed.

RuHCl(Cyttp) + RC≡CH ⟶  (5)

5: R = Ph
6: R = $(CH_2)_5CH_3$

The structure of compound **5** can be deduced from the ^{13}C and ^{31}P NMR data. In the ^{13}C NMR spectrum, the resonances of the ipso carbon atoms of the cyclohexyl groups of the triphosphine appear as virtual triplets; thus the triphosphine must be meridional around ruthenium so that the two terminal phosphorus atoms are trans to each other.[22] The resonances for C_α (the carbon atom bound directly on ruthenium) and C_β were observed at 122.3 ppm (dt, J = 33.5, 13.8 Hz) and 114.4 ppm (s), respectively. These chemical shifts are comparable with those observed for the acetylide carbon atoms in Ru(C≡CPh)(CH=CHPh)(CO)(P(i-Pr)$_3$)$_2$.[6] The coupling constant between C_α and the two terminal phosphorus atoms (13.8 Hz) is typical for *cis*-phosphorus–^{13}carbon coupling in metal acetylide complexes. The coupling between C_α and the central phosphorus atom (33.5 Hz) is slightly larger than the common cis ^2J(PC) and much smaller than trans ^2J(PC) coupling in acetylide complexes. For example, in several platinum compounds, cis ^2J(PC) coupling was observed to range from 10 to 15 Hz, while the trans ^2J(PC) coupling ranges from 134 to 148 Hz.[27] Thus, the phenylacetylide in RuCl(C≡CPh)(Cyttp) is cis to the three phosphorus atoms of the triphosphine.

Consistent with the meridional arrangement of Cyttp around ruthenium as inferred from its ^{13}C NMR data, the ^{31}P NMR spectrum shows a doublet at 16.6 ppm for the terminal PCy_2 groups and a triplet at 70.6 ppm for the central phosphorus atom (^2J(PP) = 35.6 Hz). Thus, the central phosphorus atom is significantly deshielded compared with the terminal ones. This ^{31}P NMR pattern has been observed for several meridional square-pyramidal complexes with an apical phosphine such as $RuCl_2(PR_3)_3$ (PR_3 = PPh_3, $PEtPh_2$),[28] $RuCl_2(PPh_3)(L_2)$ (L_2 = dppb, dppp),[29] and $Ru_2Cl_4(diop)_3$.[30] For example, the resonance for the apical PPh_3 appeared at 75.0 ppm and for the basal PPh_3 at 23.3 ppm in $RuCl_2(PPh_3)_3$,[28] and that for the apical PPh_2 at 72.9 ppm and for the basal PPh_3 and PPh_2 at 19.6 ppm and 34.3 ppm, respectively, appeared in $RuCl_2(PPh_3)$(dppp).[29] Thus, the acetylide complex RuCl(C≡CPh)(Cyttp) might have a square-pyramidal geometry in which the central phosphorus atom occupies the apical position.

The analogous acetylide complex RuCl(C≡C-$(CH_2)_5CH_3$)(Cyttp) (**6**) was produced from the reaction of RuHCl(Cyttp) with excess 1-octyne in benzene at room temperature. No hydride or vinyl proton resonances were observed in the ^{1}H NMR spectrum. In the infrared spectrum, the ν(C≡C) frequency was observed at 2080 cm^{-1} as a medium-intensity band. The ^{31}P and ^{13}C NMR parameters for this acetylide complex are similar to those for RuCl(C≡CPh)(Cyttp).

It is noted that RuHCl(Cyttp) is also very reactive toward other terminal acetylenes such as HC≡CH, HC≡CCO_2Et, HC≡CCOMe, $HC{\equiv}CCH_2OH$, and $HC{\equiv}CCH_2$-Cl. However, mixtures were usually produced.

Reactions of Terminal Acetylenes with RuH_4(Cyttp). The hydride RuH_4(Cyttp) reacted instantly with excess 1-octyne to give blue oily products. The spectroscopic data indicate that the predominant compound in the reaction products could be formulated as Ru(C≡C-$(CH_2)_5CH_3)_2$(Cyttp) (**7**) (eq 6). Attempts to isolate solid for the compound failed owing to its high solubility. The diacetylide complex is very air sensitive and is converted into an uncharacterized compound very quickly when exposed to air.

The formulation of the predominant product as Ru-(C≡C$(CH_2)_5CH_3)_2$(Cyttp) is based on spectroscopic data. In the ^{1}H NMR spectrum, no hydride or vinyl proton

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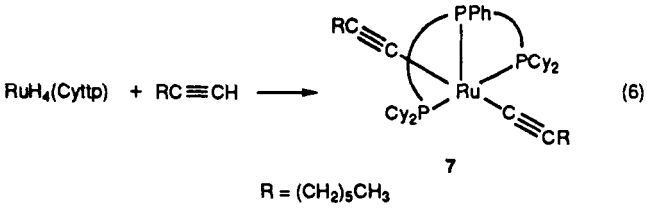

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R = $(CH_2)_5CH_3$

signals were observed. In the ^{13}C NMR spectrum in benzene, the resonances for the two C_β carbon atoms were observed at 126.3 ppm and 114.0 ppm. The resonances for the two methyl groups overlapped at 14.3 ppm. The resonances for the two C_α carbon atoms were observed at 121.5 ppm (td, $^2J(PC)$ = 15.8, 7.4 Hz) and 115.1 ppm (dt, $^2J(PC)$ = 24.0, 13.5 Hz). The magnitude[27] of the $^2J(PC)$ coupling indicates that both of the acetylide groups are cis to the three phosphorus atoms of the triphosphine, which in turn implies that the triphosphine is meridional around ruthenium and that the two acetylide groups are trans to each other. The meridional geometry of the triphosphine around ruthenium is confirmed by the presence of virtual triplet resonances at 38.7 and 37.0 ppm for the ipso carbon atoms of the cyclohexyl groups of the triphosphine in the ^{13}C NMR spectrum. The geometry is consistent with the ^{31}P NMR spectrum, which shows a doublet at 20.8 ppm for the terminal PCy_2 groups and a triplet at 79.4 ppm for the apical PPh group. The ^{31}P NMR pattern is similar to that observed for RuCl(C≡CR)(Cyttp) (R = Ph, $(CH_2)_5CH_3$). The mutually trans arrangement for the two acetylide groups is supported by the infrared spectrum, which shows only one band at 2060 cm^{-1} assignable to the $\nu(C{\equiv}C)$ frequency.[31]

Treatment of RuH_4(Cyttp) with excess phenylacetylene in benzene at room temperature, on the other hand, resulted in the formation of Ru(C≡CPh)(η^3-PhC_3CHPh)(Cyttp) (9) as a red solid (Scheme I). The compound is presumably formed via a coupling reaction between one molecule of phenylacetylene and the diacetylide complex Ru(C≡CPh)$_2$(Cyttp) (8). In fact, when RuH_4(Cyttp) was treated with 2 equiv of phenylacetylene, a purple compound was formed as the predominant product, which was converted into Ru(C≡CPh)(η^3-PhC_3CHPh)(Cyttp) upon treatment with excess phenylacetylene. The resonances corresponding to the purple compound were also observed in the early stage and disappeared eventually during the reaction of RuH_4(Cyttp) with excess phenylacetylene when monitored by ^{31}P NMR spectroscopy in situ. The ^{31}P NMR parameters of the purple compound are very similar to those of Ru(C≡C$(CH_2)_3CH_3)_2$(Cyttp), which implies that this purple compound is probably the diacetylide complex Ru(C≡CPh)$_2$(Cyttp) having a structure similar to that of Ru(C≡C$(CH_2)_5CH_3)_2$(Cyttp). The ^1H NMR and infrared spectra support this formulation. Indeed no hydride or vinyl proton resonances were observed in the ^1H NMR spectrum. The infrared spectrum shows only one strong band at 2015 cm^{-1}, assignable to the $\nu(C{\equiv}C)$ frequency.

The structure of Ru(C≡CPh)(η^3-PhC_3CHPh)(Cyttp) has been clarified by an X-ray diffraction study[13] and is consistent with the spectroscopic data. Its ^1H NMR spectrum in CD_2Cl_2 displays a resonance at 6.8 ppm, which is assigned to the one vinyl proton, in addition to the normal resonances due to phenyl groups (7.0–8.4 ppm) and cyclohexyl and methylene groups (0.6–3.0 ppm) of the triphosphine ligand. The $\nu(C{\equiv}C)$ frequency of the acetylide ligand was observed at 2060 cm^{-1}. Its ^{31}P NMR

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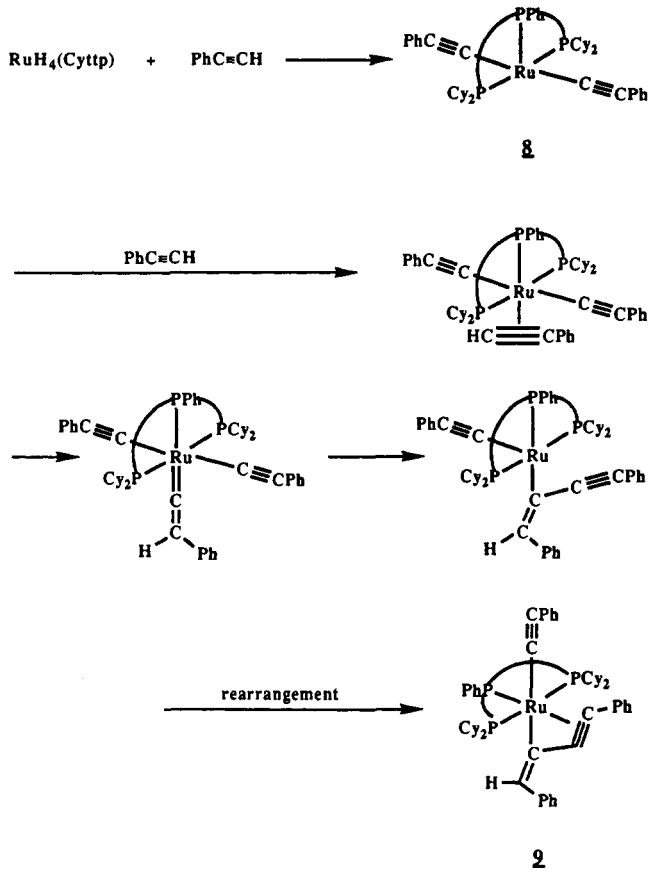
Scheme I. Possible Mechanism for the Formation of Ru(C≡CPHh)(η^3-PhC_3CHPh)(Cyttp)



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spectrum in CD_2Cl_2 exhibits a doublet at 2.5 ppm for the two terminal phosphorus atoms and a triplet at 19.6 ppm ($J(PP)$ = 37.0 Hz) for the central phosphorus atom. Thus, the chelating triphosphine has a meridional arrangement in the coordination sphere. In the ^{13}C NMR spectrum, the resonances for the ipso carbon atoms of the cyclohexyl groups of the triphosphine appear as virtual triplets at 37.7 ppm (t, J = 7.7 Hz) and 35.7 ppm (t, J = 8.3 Hz), which is consistent with a meridional arrangement of the triphosphine around ruthenium.

A possible mechanism for the formation of Ru(C≡CPh)(η^3-PhC_3CHPh)(Cyttp) in the reaction of RuH_4(Cyttp) with excess phenylacetylene is shown in Scheme I. The diacetylide complex Ru(C≡CPh)$_2$(Cyttp) (8) has been detected spectroscopically and is probably formed by sequences of oxidative addition of the sp C–H bond of phenylacetylene on unsaturated ruthenium intermediates such as RuH_2(Cyttp) and RuH(C≡CPh)(Cyttp), followed by reductive elimination of H_2. The unsaturated complex Ru(C≡CPh)$_2$(Cyttp) combines with one phenylacetylene to form an 18e acetylene complex. The π-bonded phenylacetylene might then couple with one phenyl acetylide and rearrange to give the final product, or most likely the π-bonded phenylacetylene isomerizes into the vinylidene complex. Such isomerization is common for octahedral d^6 complexes.[32] The vinylidene may then couple to one of the acetylides to form the final product. Such a coupling reaction was proposed in the mechanism for the formation of [Os(η^3-PhC_3CHPh)$(PMe_3)_4$]PF_6 by treatment of *cis*-Os$(C_2Ph)_2(PMe_3)_4$ with $AgPF_6$.[33] The stereospecific re-

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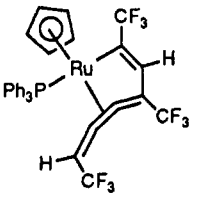
action probably occurred due to the interaction of the triphosphine with the vinylidene group, which causes the vinylidene to orient stereospecifically in space.

The compound $Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)$ formed in the reaction of excess phenylacetylene with $RuH_4(Cyttp)$ can be regarded as an intermediate in catalytic polymerization or oligomerization reactions of terminal acetylenes. Reactions between phenylacetylene and $MH(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru, Os) gave similar coupling compounds $M(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ in which the C≡C triple bond is not bound to the metal centers.[8] The compound $Os(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ is an active oligomerization catalyst for phenylacetylene; thus, it was suggested that it is probably an intermediate in the catalytic oligomerization of phenylacetylene by $OsH(O_2CCF_3)(CO)(PPh_3)_2$.[8] The reaction of $CF_3C{\equiv}CH$ with $CpRuMe(PPh_3)_2$ also gives a C–C coupling product (eq 7).[10c] The product could be viewed as a coupling reaction between $CF_3C{\equiv}CH$ and an intermediate such as $Ru(\eta^3\text{-}CF_3C_3CHCF_3)$, although the authors proposed an alternative mechanism for its formation. The formation of the compound $Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)$ is also related to catalytic dimerization of terminal acetylenes, for example, the head-to-tail dimerization catalyzed by $Pd(OAc)_2 + PPh_3$[34] and $Cp_2YCH(SiMe_3)_2$[35] and the head-to-head dimerization catalyzed by $Pd(PPh_3)_4$.[36]

$$CpRuMe(PPh_3)_2 + \text{excess } CF_3C{\equiv}CH \longrightarrow$$



(7)

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Organo-f-Element Thermochemistry. Actinide–Group 14 Element and Actinide–Transition-Element Bond Disruption Enthalpies and Stoichiometric/Catalytic Chemical Implications Thereof in Heterobimetallic Tris(cyclopentadienyl)uranium(IV) Compounds

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Uranium–metal bond disruption enthalpies have been determined in the series of complexes $Cp_3U\text{–}MPh_3$, where Cp = $\eta^5\text{-}C_5H_5$, Ph = C_6H_5, and M = Si, Ge, Sn, and in $Cp_3U\text{–}M'(CO)_2Cp$, where M′ = Fe, Ru. Thermochemical data were obtained by anaerobic batch-titration solution calorimetry in toluene from enthalpies of solution and iodinolysis of the aforementioned compounds. Derived U–M/U–M′ bond disruption enthalpies in toluene solution are as follows (M/M′ moiety, kcal/mol): $SiPh_3$, 37.3 (4.2); $GePh_3$, 38.9 (4.5); $SnPh_3$, 37.2 (4.0); $Fe(CO)_2Cp$, 30.9 (3.0); $Ru(CO)_2Cp$, 40.4 (4.0). These data fall in a relatively narrow range and indicate comparatively weak heterobimetallic bonding. Chemical implications of the present thermochemical results include the general favorability and marked M/M′ sensitivity of alkane, hydrogen, and amine elimination synthetic routes to these compounds, the existence of favorable pathways for hydrocarbon and olefin activation, and the observation that no steps in plausible f-element-catalyzed dehydrogenative silane polymerization and olefin hydrosilylation cycles are predicted to have major thermodynamic impediments.

Although metal–metal bonding is a ubiquitous feature of contemporary transition-metal chemistry, that involving well-characterized heterobimetallic early-transition-metal–late-transition-metal[1–3] and f-element–late-transition-metal combinations[4,5] as well as early-transition-metal–metalloid[6] and f-element–metalloid[7,8] combinations

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