Conclusion

There are few solution-phase studies of M–cyclopentadienyl bond strengths.[8] In contrast, a number of studies have been made on complexes with cyclopentadienyl ligands in which this ligand is essentially a spectator. Calorimetric data in this and an earlier paper indicate that cyclopentadiene and pentamethylcyclopentadiene have similar heats of binding in these complexes. This is in contrast to binding of arene ligands where the methyl-substituted complexes are more stable.[8] On the other hand, complexes of the indenyl ligand have been shown to be 10–15 kcal/mol less stable. It seems likely that this contributes to the "indenyl effect", which probably includes a large ground-state destabilization of these complexes.

Surprisingly facile solvolytic reductive elimination of CpH and related ligands occurs for all three group 6 metals when it is thermodynamically allowed. The entropy of this reaction has been measured for the molybdenum complex in acetonitrile. Its value, −51.3 cal/(mol °C), can be used to predict which ligands are capable of forcing reductive elimination. Additional studies of ligand-substitution-induced oxidative addition and reductive elimination are in progress.

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Reactions of Molecular Hydrogen Complexes $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ with Alkynes: Preparation and Crystal Structure of the $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]BPh_4$ Derivative[1]

Gabriele Albertin,*,† Paola Amendola,† Stefano Antoniutti,† Sandra Ianelli,‡ Giancarlo Pelizzi,‡
and Emilio Bordignon*,†

Dipartimento di Chimica dell'Università di Venezia, Dorsoduro 2137, 30123 Venice, Italy, and
Istituto di Chimica Generale, Centro Strutturistica CNR, Università di Parma, 43100 Parma, Italy

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Complexes $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ [P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$] react with terminal alkynes $HC{\equiv}CR$ (R = Ph, *p*-tolyl, CMe_3, $SiMe_3$) to yield alkenes $H_2C{=}CHR$ and $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ derivatives. Selective hydrogenation of the alkyne to alkene by the η^2-H_2 ruthenium catalyst precursor in mild conditions was also observed. The structure of the compound $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt_2\}_4]BPh_4$ was determined crystallographically: space group $P2_1$, a = 12.497 (5) Å, b = 24.407 (8) Å, c = 12.763 (5) Å, β = 96.89 (2)°, Z = 2; final R = 0.057 and R_w = 0.074. The ruthenium atom has a pseudooctahedral coordination with four phosphite groups and the η^3-RC_3CHR ligand. The $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ derivatives react with acetylacetone to afford $[Ru(acac)P_4]^+$ cations and organic compounds (*Z*)-$R(H)C{=}C(H)C{\equiv}CR$. The reaction of other alkynes [$MeO_2CC{\equiv}CCO_2Me$, $RC{\equiv}CR$ (R = Me, Ph)] toward the $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ complexes was also investigated and the synthesis of the vinyl derivatives $[Ru\{C(CO_2Me){=}C(H)CO_2Me\}\{PhP(OEt)_2\}_4]PF_6$ achieved. Characterization of the complexes by IR and ^1H and $^{31}P\{^1H\}$ NMR spectra is also discussed.

Introduction

The reaction of transition-metal hydrides with 1-alkynes represents an important process in organometallic chemistry,[2] and in recent years, a number of studies[3-5] have been reported in this field. Besides simple insertion of the alkyne into the M–H bond to give alkenyl derivatives,[3,4] oxidative additions to the central metal of the C–H group affording alkynyl complexes can also take place,[5] as well as subsequent reaction of these derivatives with alkyne.[6] The factors governing the course of the reaction, i.e. experimental conditions, the nature of the M–H bond, and the alkyne substituent, were extensively investigated and in part rationalized; however, the nature of the resulting product is still poorly predictable owing to the delicate balance of factors that affect this reaction.

Table I. Catalytic Hydrogenation[a] of Alkynes by the Catalyst Precursor $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ at 25 °C

substrate	time	product	conv, %
$HC{\equiv}CPh$	3 min	$H_2C{=}C(H)Ph$	30
$HC{\equiv}CCMe_3$	20 min	$H_2C{=}C(H)CMe_3$	25
$HC{\equiv}CSiMe_3$	60 min	$H_2C{=}C(H)SiMe_3$	30
$HC{\equiv}CPh$[b]	6 min	$H_2C{=}C(H)Ph$	50
$MeO_2C{\equiv}CCO_2Me$	24 h	*cis*- and *trans*-(MeO_2C)-$HC{=}CHCO_2Me$[c]	5
$MeC{\equiv}CPh$	36 h	*cis*-$Me(H)C{=}C(H)Ph$	10

[a] Reaction conditions: H_2 pressure, 1 atm; alkyne, 4 mmol; catalyst, 0.04 mmol; solvent (CH_2Cl_2 or CD_2Cl_2), 3 mL. [b] Using $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$ as catalyst. [c] cis and trans isomers in about 6:4 ratio.

Despite the number of studies on metal hydrides, very few data are available[7] on the reactivity with alkynes of molecular hydrogen complexes containing the $MH(\eta^2\text{-}H_2)$ fragment, although the presence of both H^- and H_2 ligands can give insight both on the interaction of acetylenes with nonclassical hydrides and on possible catalytic hydrogen-

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† Università di Venezia.
‡ Università di Parma.

[1] Presented, in part, at the Congresso Interdivisionale Società Chimica Italiana (CISCI 89), Perugia, Italy, 1989; p 378.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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ation reactions of the triple bond.

As part of our studies on the chemistry of molecular hydrogen complexes,[8] we report here an investigation on the reactions of $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ complexes with both terminal and disubstituted alkynes bearing either electron-releasing or electron-withdrawing substituents. The X-ray crystal structure of one of the new resulting complexes containing the η^3-RC_3CHR ligand is also reported.

Experimental Section

All operations were performed under an inert atmosphere (Argon) by using standard Schlenk techniques or a Vacuum Atmosphere drybox. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;[9] triethyl and trimethyl phosphite were Ega Chemie products purified by distillation under nitrogen. Acetylenes were Aldrich products and used without any further purification. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained by using Varian FT-80A and Bruker AC 200 spectrometers at temperatures varying between −85 and +34 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[10]

Synthesis of Complexes. Molecular hydrogen complexes $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ [P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$] were prepared according to the procedures previously reported.[8b]

Many reactions were carried out in a sealed NMR tube and monitored by NMR spectroscopy. A typical example is the reaction of $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ with alkynes: 0.02 mmol of the Ru complex in 1 mL of CD_2Cl_2 was placed in a Wilmad Omnifit NMR tube system. The tube was cooled to −80 °C, degassed, Ar or H_2 was admitted, and the appropriate amount of alkyne was added by means of a syringe. The hydrogenation reaction was also carried out in 5-mL Schlenk flasks charged with 0.04 mmol of $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ in 3 mL of CH_2Cl_2 or CD_2Cl_2. The solution was cooled to −80 °C, degassed, and connected to a large source of H_2. A 100-fold excess of the appropriate alkyne was added, and the reaction mixture was slowly brought to room temperature. The composition of the mixture during or at the end of the reaction was determined by ^1H NMR or GC techniques.

$[Ru(\eta^3\text{-}RC_3CHR)\{PhP(OEt)_2\}_4]PF_6$ (1) [R = Ph (a), *p*-tolyl (b), CMe_3 (c)]. An excess of the appropriate alkyne (3 mmol) was added to a solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.5 g, 0.51 mmol) in 15 mL of CH_2Cl_2 cooled to −80 °C. The reaction mixture was brought to room temperature in 10–15 min, and then stirred for 1 h. The solvent was removed under reduced pressure to give a brown oil, which was treated with ethanol (10 mL). Addition of an excess of $NaPF_6$ (0.5 g, 3 mmol) in ethanol (5 mL) to the resulting solution afforded a yellow solid, which was crystallized by slow cooling to −30 °C of its saturated solution in ethanol/dichloromethane (15/3 mL); yield ≥70%.

Anal. Calcd for **1a**: C, 54.15; H, 5.76. Found: C, 54.00; H, 5.79. Mp: 165 °C dec. $\Lambda_M = 81.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2), δ: 8.09, 7.59, 7.23, 7.01 (m, 30 H, Ph), 5.56 (dm, 1 H, CH), 3.82, 3.65 (m, 16 H, CH_2), 1.35, 1.21, 1.12 (t, 24 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: spin system ABC_2, $\delta_A = 165.5$, $\delta_B = 162.4$, $\delta_C = 150.2$, $J_{AB} = 36.8$ Hz, $J_{AC} = 43.0$ Hz, $J_{BC} = 47.0$ Hz.

Calcd for **1b**: C, 54.84; H, 5.95. Found: C, 54.69; C, 6.10. Mp: 171 °C dec. $\Lambda_M = 81.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR [$(CD_3)_2CO$], δ: 8.21, 7.92, 7.67, 7.12, 6.84 (m, 28 H, Ph), 5.62 (dm, 1 H, CH), 3.81 (m, 16 H, CH_2), 2.33, 2.26 (s, 6 H, *p*-tolyl CH_3), 1.39 1.28, 1.13 (t, 24 H, phos CH_3). ^{13}C NMR [$(CD_3)_2CO$], δ: 142.3 (dm, $J_{CPtrans} = 53$ Hz, C_γ), 141.8–125.1 (m, Ph), 115.0 (dm, $J_{CPtrans} = 37$ Hz, C_β or C_α), 65.5 (m, phos CH_2), 21.4, 21.2 (qm, $^1J_{CH} = 130$ Hz, *p*-tolyl CH_3), 16.7 (m, phos CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$], δ: spin system ABC_2, $\delta_A = 165.2$, $\delta_B = 161.6$, $\delta_C = 149.3$, $J_{AB} = 36.5$ Hz, $J_{AC} = 42.6$ Hz, $J_{BC} = 47.4$ Hz.

Calcd for **1c**: C, 51.95; H, 6.62. Found: C, 51.91; H, 6.55. Mp: 145 °C dec. $\Lambda_M = 83.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR [$(CD_3)_2CO$], δ: 8.07, 7.61, 7.42 (m, 20 H, Ph), 4.94 (dm, 1 H, CH), 3.78 (m, 16 H, CH_2), 1.48, 1.44, 1.22 (t, 24 H, phos CH_3), 1.02, 0.64 (s, 18 H, *tert*-butyl CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$], δ: spin system ABC_2, $\delta_A = 166.8$, $\delta_B = 162.8$, $\delta_C = 149.1$, $J_{AB} = 27.9$ Hz, $J_{AC} = 43.8$ Hz, $J_{BC} = 50.0$ Hz.

$[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]BPh_4$ (1b′). This compound was prepared exactly like **1b**, using $NaBPh_4$ as a precipitating agent; yield ≥90%. Suitable crystals for X-ray analysis were obtained by slow cooling from +20 to −25 °C of its saturated solution in ethanol.

Anal. Calcd: C, 68.18; H, 6.63. Found: C, 67.83; H, 6.62. Mp: 184 °C dec. $\Lambda_M = 51.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR [$(CD_3)_2CO$], δ: 8.19, 7.90, 7.61, 7.32, 7.10, 6.86 (m, 48 H, Ph), 5.61 (dm, 1 H, CH), 3.78 (m, 16 H, CH_2), 2.32, 2.25 (s, 6 H, *p*-tolyl CH_3), 1.37, 1.25, 1.11 (t, 24 H, phos CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$], δ: spin system ABC_2, $\delta_A = 165.2$, $\delta_B = 161.6$, $\delta_C = 149.3$, $J_{AB} = 36.5$ Hz, $J_{AC} = 42.6$ Hz, $J_{BC} = 47.4$ Hz.

$[Ru\{\eta^3\text{-}(SiMe_3)C_3CH(SiMe_3)\}\{PhP(OEt)_2\}_4]BPh_4$ (1d′). This compound was prepared exactly like 1 using $NaBPh_4$ as a precipitating agent; yield ≥80%.

Anal. Calcd: C, 63.10; H, 7.08. Found: C, 62.88; H, 7.25. Mp: 128 °C. $\Lambda_M = 53.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR [$(CD_3)_2CO$], δ: 8.23, 7.38, 6.85 (m, 40 H, Ph), 5.77 (dm, 1 H, CH), 3.84 (m, 16 H, CH_2), 1.43, 1.40, 1.25, 1.12 (t, 24 H, phos CH_3), 0.17, −0.32 (s, 18 H, $SiMe_3$). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$], δ: spin system ABC_2, $\delta_A = 171.3$, $\delta_B = 162.5$, $\delta_C = 149.2$, $J_{AB} = 30.8$ Hz, $J_{AC} = 41.3$ Hz, $J_{BC} = 49.8$ Hz.

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(3) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245 and references therein.

(4) (a) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. (b) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508. (c) Longato, B.; Bresadola, S. *Inorg. Chem.* **1982**, *21*, 168. (d) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E. *J. Organomet. Chem.* **1983**, *249*, 371. (e) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2449. (f) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (g) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. (h) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, M. *Organometallics* **1986**, *5*, 72. (i) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. (j) Cariou, M.; Etienne, M.; Guerchais, J. E.; Kergoat, R.; Kubicki, M. M. *J. Organomet. Chem.* **1987**, *327*, 393. (k) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801. (l) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 297. (m) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091. (n) Herberich, G. E.; Barlage, W. *Organometallics* **1987**, *6*, 1924. (o) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988. (p) Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917. (q) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589. (r) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (s) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146.

(5) (a) Brown, C. K.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 70. (b) Appleton, T. G.; Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1972**, *11*, 2074. (c) Buang, N. A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1987**, *323*, C47. (d) Hills, A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1988**, *350*, C4.

(6) (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. (b) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (c) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 906. (d) Van Abu Bakar, W. A.; Carlton, L.; Davidson, J. L.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1988**, *352*, C54. (e) Jones, S. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 966.

(7) (a) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediani, P. *Organometallics* **1989**, *8*, 2080. (c) Field, L. D.; George, A. V.; Hambley, T. W.; Malouf, E. Y.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 931. (d) Bianchini, C. *The XIVth ICOC*; Detroit, MI, Aug 19–24, 1990; p 12.

(8) (a) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072. (b) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318.

(9) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623.

(10) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Bailey, R. A. *J. Chem. Educ.* **1972**, *49*, 297.

[Ru(η^3-RC$_3$CHR){P(OEt)$_3$}$_4$]PF$_6$ (2) [R = *p*-Tolyl (b), CMe$_3$ (c)]. A stoichiometric amount of HBF$_4$·Et$_2$O (54% solution, 1 mmol, ca. 0.14 mL) was added to a solution of RuH$_2$[P(OEt)$_3$]$_4$ (0.8 g, 1 mmol) in 40 mL of diethyl ether cooled to −80 °C; the reaction mixture was brought to about −30 °C and stirred at this temperature until a white precipitate of [RuH(η^2-H$_2$){P(OEt)$_3$}$_4$]BF$_4$ separated out. The suspension was again cooled to −80 °C, and then 10 mL of CH$_2$Cl$_2$ and an excess of the appropriate alkyne (6 mmol) were added. The reaction mixture was slowly brought to room temperature and stirred for about 20 min. The solvent was evaporated under reduced pressure to give an oil, which was treated with ethanol (10 mL). The addition of NaPF$_6$ (1 g, 6 mmol) in 5 mL of ethanol to the resulting solution caused the precipitation of a white solid, which was crystallized by slow cooling to −30 °C of its saturated solution in ethanol/dichloromethane (15/3 mL); yield ≥55%.

Anal. Calcd for **2b**: C, 44.17; H, 6.62. Found: C, 44.02; H, 6.71. Mp: 158 °C dec. Λ_M = 81.2 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 8.01 (d), 7.66 (d), 7.28 (m, 8 H, Ph), 4.27, 3.86 (m, 24 H, CH$_2$), 2.40, 2.34 (s, 6 H, *p*-tolyl CH$_3$), 1.45, 1.34, 1.05 (t, 36 H, phos CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system ABC$_2$, δ_A = 138.3, δ_B = 136.1, δ_C = 121.3, J_{AB} = 48.7 Hz, J_{AC} = 56.5 Hz, J_{BC} = 62.5 Hz.

Calcd for **2c**: C, 40.26; H, 7.41. Found: C, 40.08; H, 7.37. Mp: 173 °C dec. Λ_M = 88.3 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 6.11 (dm, 1 H, CH), 4.27, 3.97 (m, 24 H, CH$_2$), 1.52, 1.20 (s, 18 H, *tert*-butyl), 1.39, 1.37, 1.23 (t, 36 H, phos CH$_3$). ^{13}C NMR [(CD$_3$)$_2$CO], δ: 139.4 (dm, $^1J_{CH}$ = 159 Hz, C$_\delta$), 131.9 (dm, $J_{CPtrans}$ = 64 Hz, C$_\gamma$), 115.6 (dm, $J_{CPtrans}$ = 41 Hz, C$_\beta$ or C$_\alpha$), 62.2 (m, phos CH$_2$), 44.6, 36.3 (m, *C*Me$_3$), 32.3, 30.0 (qm, C*Me*$_3$), 16.1 (m, phos CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system ABC$_2$, δ_A = 139.6, δ_B = 137.4, δ_C = 119.3, J_{AB} = 43.4 Hz, J_{AC} = 56.5 Hz, J_{BC} = 67.0 Hz.

[Ru(η^3-PhC$_3$CHPh){P(OEt)$_3$}$_4$]BPh$_4$ (2a′). This compound was prepared exactly like **2b** or **2c**, using NaBPh$_4$ as a precipitating agent; yield ≥60%.

Anal. Calcd: C, 59.67; H, 7.12. Found: C, 59.46; H, 7.27. Mp: 169 °C dec. Λ_M = 53.8 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 8.07, 7.73, 7.35, 6.88 (m, 30 H, Ph), 4.29, 3.85 (m, 24 H, CH$_2$), 1.43, 1.32, 1.03 (t, 36 H, phos CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system ABC$_2$, δ_A = 137.9, δ_B = 136.0, δ_C = 121.0, J_{AB} = 49.4 Hz, J_{AC} = 58.0 Hz, J_{BC} = 64.0 Hz.

[Ru(η^3-RC$_3$CHR){P(OMe)$_3$}$_4$]PF$_6$ (3) [R = Ph (a), *p*-tolyl (b), CMe$_3$ (c)]. An excess of the appropriate alkyne (3 mmol) was added to a solution of [RuH(η^2-H$_2$){P(OMe)$_3$}$_4$]BF$_4$ (0.34 g, 0.5 mmol) in 15 mL of CH$_2$Cl$_2$ cooled to −80 °C. The reaction mixture was brought to 0 °C and then stirred at this temperature for 1 h. The solvent was removed under reduced pressure to give a pale yellow oil, which was treated with methanol (10 mL) containing an excess of NaPF$_6$ (0.5 g, 3 mmol). The white solid that separated out after stirring at 0 °C was filtered and crystallized from CH$_2$Cl$_2$/methanol (3/15 mL); yield ≥40%.

Anal. Calcd for **3a**: C, 35.56; H, 5.01. Found: C, 35.46; H, 5.07. Mp: 180 °C dec. Λ_M = 78.5 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.78, 7.66, 7.40 (m, 10 H, Ph), 3.87 (d), 3.70 (d, J_{PH} = 10.6 Hz), 3.46 (t, J_{PH} = 5.3 Hz, 36 H, CH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$), δ: spin system ABC$_2$, δ_A = 143.0, δ_B = 142.3, δ_C = 124.9, J_{AB} = 47.9 Hz, J_{AC} = 62.7 Hz, J_{BC} = 58.7 Hz.

Calcd for **3b**: C, 37.01; H, 5.28. Found: C, 36.65; H, 5.43. Mp: 166 °C dec. Λ_M = 90.2 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 7.83 (d), 7.65 (d), 7.27 (m, 8 H, Ph), 3.96 (d), 3.80 (d, J_{PH} = 10.6 Hz), 3.52 (t, J_{PH} = 5.3 Hz, 36 H, phos CH$_3$), 2.39, 2.33 (s, 6 H, *p*-tolyl CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system ABC$_2$, δ_A = 142.4, δ_B = 142.1, δ_C = 124.7, J_{AB} = 47.9 Hz, J_{AC} = 68.4 Hz, J_{BC} = 52.5 Hz.

Calcd for **3c**: C, 31.83; H, 6.12. Found: C, 31.60; H, 5.93. Mp: 166 °C. Λ_M = 90.2 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 6.04 (dm, 1 H, CH), 3.84 (d), 3.59 (t, 36 H, phos CH$_3$), 1.45, 1.19 (s, 18 H, *tert*-butyl). ^{13}C NMR (CD$_2$Cl$_2$), δ: 140.0 (dm, $^1J_{CH}$ = 161 Hz, C$_\delta$), 131.8 (dm, $J_{CPtrans}$ = 61 Hz, C$_\gamma$), 114.7 (dm, $J_{CPtrans}$ = 36 Hz, C$_\beta$ or C$_\alpha$), 53.5 (m, phos CH$_3$), 43.1, 36.1 (m, *C*Me$_3$), 32.4, 30.2 (qm, C*Me*$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system ABC$_2$, δ_A = 144.3, δ_B = 143.5, δ_C = 125.6, J_{AB} = 44.5 Hz, J_{AC} = 56.6 Hz, J_{BC} = 66.6 Hz.

[RuC(CO$_2$Me)=CH(CO$_2$Me){PhP(OEt)$_2$}$_4$]PF$_6$ (4). An excess of MeO$_2$CC≡CCO$_2$Me (0.43 g, 3 mmol) was added to a solution of [RuH(η^2-H$_2$){PhP(OEt)$_2$}$_4$]BF$_4$ (0.5 g, 0.51 mmol) in 15 mL of CH$_2$Cl$_2$ cooled to −80 °C, and the reaction mixture was brought to room temperature and stirred for about 10 h. The solvent was removed under reduced pressure to give a brown oil, which was treated with ethanol (10 mL). The slow addition of a solution containing an excess of NaPF$_6$ (2 g, 12 mmol) caused the precipitation of a pale yellow solid, which was repeatedly crystallized from CH$_2$Cl$_2$/ethanol (3/15 mL); yield ≥40%.

Anal. Calcd: C, 46.74; H, 5.71. Found: C, 46.54; H, 5.59. Mp: 197 °C. Λ_M = 79.6 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.60, 7.32 (m, 20 H, Ph), 5.31 (s, 1 H, CH), 3.85 (m, 16 H, CH$_2$), 3.56, 2.39 (s, 6 H, OMe), 1.35, 1.21, 1.18 (t, 24 H, phos CH$_3$). ^{13}C NMR [(CD$_3$)$_2$CO], δ: 209.1 (dm, $J_{CPtrans}$ = 78 Hz, Ru—C=), 180.6, 175.9 (m, CO), 139.9–126.2 (m, Ph), 65.1 (m, phos CH$_2$), 53.5, 50.8 (q, $^1J_{CH}$ = 148 Hz, OMe), 16.6 (m, phos CH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$), δ: spin system ABC$_2$, δ_A = 165.2, δ_B = 164.4, δ_C = 148.1, J_{AB} = 22.1 Hz, J_{AC} = 45.3 Hz, J_{BC} = 47.2 Hz. IR [ν(CO), KBr]: 1723 (m), 1630 (s) cm^{-1}.

[Ru(acac){PhP(OEt)$_2$}$_4$]BPh$_4$ (5a′). An excess of acetylacetone (Hacac, 0.16 mL, 1.6 mmol) was added to a solution of complex [Ru{η^3-(*p*-tolyl)C$_3$CH(*p*-tolyl)}{PhP(OEt)$_2$}$_4$]PF$_6$ (0.5 g, 0.4 mmol) in 15 mL of CH$_2$Cl$_2$, and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the oil obtained was triturated with ethanol (10 mL). The addition of NaBPh$_4$ (0.14 g, 0.4 mmol) to the resulting solution afforded a pale yellow solid, which was crystallized from ethanol; yield ≥80%.

Anal. Calcd: C, 63.16; H, 6.68. Found: C, 62.95; H, 6.57. Mp: 180 °C. Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 7.80, 7.33, 6.86 (m, 40 H, Ph), 4.91 (s, 1 H, CH), 3.90 (m, 16 H, CH$_2$), 1.38, 1.22 (t, 24 H, phos CH$_3$), 1.24 (s, 6 H, acac CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system A$_2$B$_2$, δ_A = 164.3, δ_B = 148.6, J_{AB} = 46.0 Hz. IR [ν(CO), KBr]: 1587 (s) cm^{-1}.

[Ru(acac){P(OEt)$_3$}$_4$]PF$_6$ (5b) and [Ru(acac){P(OMe)$_3$}$_4$]PF$_6$ (5c). These compounds were prepared exactly like **5a′**, using NaPF$_6$ as precipitating agent; yield ≥70%.

Anal. Calcd for **5b**: C, 34.49; H, 6.69. Found: C, 34.53; H, 6.55. Mp: 215 °C. Λ_M = 91.0 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 5.39 (s, 1 H, CH), 4.15 (m, 24 H, phos CH$_2$), 1.90 (s, 6 H, acac CH$_3$), 1.31, 1.28 (t, 36 H, phos CH$_3$). ^{13}C NMR [(CD$_3$)$_2$CO], δ: 187.7 (m, acac CO), 100.3 (d, $^1J_{CH}$ = 157 Hz, CH), 62.4 (m, phos CH$_2$), 27.9 (qm, $^1J_{CH}$ = 127 Hz, acac CH$_3$), 16.5 (m, phos CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system A$_2$B$_2$, δ_A = 136.6, δ_B = 120.8, J_{AB} = 60.1 Hz. IR [ν(CO), KBr]: 1590 (s) cm^{-1}.

Calcd for **5c**: C, 24.26; H, 5.15. Found: C, 24.02; H, 5.23. Mp: >200 °C. Λ_M = 86.3 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR [(CD$_3$)$_2$CO], δ: 5.43 (s, 1 H, CH), 3.82 (d), 3.75 (t, 36 H, phos CH$_3$), 1.92 (s, 6 H, acac CH$_3$). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$CO], δ: spin system A$_2$B$_2$, δ_A = 140.6, δ_B = 126.0, J_{AB} = 60.1 Hz. IR [ν(CO), KBr]: 1588 (s) cm^{-1}.

X-ray Data Collection and Reduction. A yellow well-shaped parallelepiped crystal with dimensions 0.19 × 0.31 × 0.51 mm was mounted on an ENRAF-NONIUS CAD4 fully automated four-circle diffractometer, used to measure cell dimensions and diffraction intensities by means of graphite-monochromatized Mo Kα radiation. Automatic routines to search for, center, and index reflections in conjunction with a cell reduction program yielded a primitive monoclinic cell. Systematic absences in 0*k*0 for *k* odd agreed with centric space group $P2_1/m$ or acentric space group $P2_1$. The assumption that the space group was acentric was based on convincing intensity statistics and later confirmed by successful refinement of the structure.

Crystal data: *M* = 2892.88, monoclinic, space group $P2_1$, *a* = 12.497 (5) Å, *b* = 24.407 (8) Å, *c* = 12.763 (5) Å, β = 96.89 (2)°, *V* = 3865 (3) Å^3, *Z* = 2, D_c = 2.486 g cm^{-3}, Mo Kα radiation (λ = 0.71069 Å), *F*(000) = 3048, μ(Mo Kα) = 6.61 cm^{-1}.

The unit-cell parameters were determined and refined from the setting angles of 25 intense reflections, accurately measured. Data were collected by the ω–2θ scan technique for one quadrant of reciprocal space to a 2θ limit of 46, with a ω scan range of (0.80 + 0.35 tan θ)° centered about the calculated Mo Kα peak position. The scan area was actually extended an extra 25% on both sides of the peak for background measurement. Scan rates ranged from 0.9 to 3.3° min^{-1}, the rate to be used for each reflection being determined by a prescan. The intensity for each reflection is given by $I = (FF/S)[P - 2(B_1 + B_2)]$, where *P* represents the counts picked up over the peak area, B_1 and B_2 are the left and right

Table II. Selected Bond Distances (Å) and Angles (deg)

Ru-P(1)	2.375 (4)	P(2)-C(11)	1.822 (11)
Ru-P(2)	2.266 (4)	P(3)-O(5)	1.622 (11)
Ru-P(3)	2.321 (4)	P(3)-O(6)	1.609 (10)
Ru-P(4)	2.355 (4)	P(3)-C(21)	1.814 (11)
Ru-C(50)	2.145 (14)	P(4)-O(7)	1.589 (12)
Ru-C(49)	2.244 (12)	P(4)-O(8)	1.594 (10)
Ru-C(48)	2.430 (14)	P(4)-C(31)	1.826 (11)
Ru-C(489)[a]	2.256 (12)	C(45)-C(48)	1.48 (2)
P(1)-O(1)	1.599 (10)	C(48)-C(49)	1.23 (2)
P(1)-O(2)	1.619 (11)	C(49)-C(50)	1.39 (2)
P(1)-C(1)	1.832 (9)	C(50)-C(51)	1.33 (2)
P(2)-O(3)	1.567 (10)	C(51)-C(52)	1.47 (2)
P(2)-O(4)	1.622 (12)		
P(1)-Ru-P(2)	89.8 (2)	Ru-P(2)-O(4)	111.4 (5)
P(1)-Ru-P(3)	93.4 (1)	Ru-P(2)-C(11)	121.6 (4)
P(1)-Ru-P(4)	170.0 (2)	O(3)-P(2)-O(4)	107.8 (5)
P(2)-Ru-P(3)	96.2 (2)	O(3)-P(2)-C(11)	101.5 (5)
P(2)-Ru-P(4)	90.9 (2)	O(4)-P(2)-C(11)	103.1 (6)
P(3)-Ru-P(4)	96.4 (2)	Ru-P(3)-O(5)	119.7 (5)
P(1)-Ru-C(50)	84.5 (4)	Ru-P(3)-O(6)	108.4 (4)
P(2)-Ru-C(50)	99.8 (4)	Ru-P(3)-C(21)	122.9 (4)
P(3)-Ru-C(50)	163.8 (4)	O(5)-P(3)-O(6)	104.3 (6)
P(4)-Ru-C(50)	85.6 (4)	O(5)-P(3)-C(21)	95.9 (6)
P(1)-Ru-C(489)	87.1 (3)	O(6)-P(3)-C(21)	103.1 (5)
P(2)-Ru-C(489)	152.4 (4)	Ru-P(4)-O(7)	122.9 (5)
P(3)-Ru-C(489)	111.3 (4)	Ru-P(4)-O(8)	108.5 (4)
P(4)-Ru-C(489)	87.7 (3)	Ru-P(4)-C(31)	117.9 (4)
C(50)-Ru-C(489)	52.6 (5)	O(7)-P(4)-O(8)	105.6 (6)
Ru-P(1)-O(1)	107.2 (4)	O(7)-P(4)-C(31)	95.8 (6)
Ru-P(1)-O(2)	116.5 (4)	O(8)-P(4)-C(31)	104.0 (5)
Ru-P(1)-C(1)	117.0 (4)	C(45)-C(48)-C(49)	148.1 (14)
O(1)-P(1)-O(2)	109.1 (6)	C(48)-C(49)-C(50)	150.9 (13)
O(1)-P(1)-C(1)	104.7 (5)	C(49)-C(50)-C(51)	136.0 (13)
O(2)-P(1)-C(1)	101.6 (5)	C(50)-C(51)-C(52)	127.3 (13)
Ru-P(2)-O(3)	110.3 (4)		

[a] C(489) is the midpoint between atoms C(48) and C(49).

background counts, S is an integer inversely proportional to the scan rate, and FF is either a unit or a multiplier, to account for occasional attenuation of the diffracted beam.

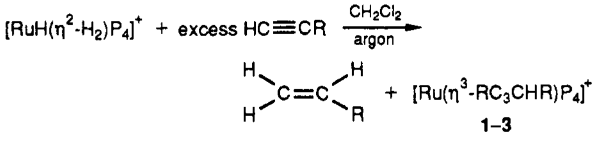
Two intensity check reflections were measured every 2.5 h of X-ray exposure time, and two orientation check reflections were measured every 200 reflections. There was no evidence of crystal decomposition or loss of alignment. Of a total of 5493 independent reflections (5767 measured) those having $I < 2\sigma(I)$ were considered unobserved, leaving 3332 independent reflections that were used in structure analysis. Intensities were corrected for Lorentz and polarization factors. Corrections for absorption effects were applied after isotropic refinement according to the empirical method of Walker and Stuart.[11]

Structure Determination and Refinement. Coordinates for ruthenium and phosphorus atoms were obtained by using the automatic PATT routine in the SHELX 86 program package.[12] A difference map phased on the refined positions of these atoms led to the location of the remaining non-hydrogen atoms. The structure was refined by full-matrix least-squares techniques to minimize the quantity $\sum w|\Delta F^2|$. Ru, P, and O atoms were refined anisotropically, and the remaining atom isotropically. Initially unit weights were used, while during the final stages of refinement a weighting scheme of the type $k/[\sigma^2(F_o) + gF^2_o]$ was applied (0.2941 and 0.006 271 being the values of k and g, respectively, for the last cycle). The phenyl rings bonded to the P atoms and those of the anion were refined as rigid groups of D_{6h} symmetry. Due to the large number of parameters to be refined, the atoms were divided into two groups that were allowed to vary alternately. No attempt was made to locate the hydrogen atoms.

Structure polarity was determined by parallel refinement, the resulting final residual indices R and R_w being 0.0567 and 0.0735, and 0.0572 and 0.0742, respectively. The atomic coordinates given in Table III, together with their estimated standard deviations, are those of the correct enantiomer. The data-to-variable ratio was 9.4. The final difference Fourier map was essentially featureless. Neutral scattering factors were employed, and anomalous dispersion terms were included in F_c. Computation was performed on a GOULD 6040 computer using SHELX 76[13] and SHELX 86 package programs. Other computer programs used have been cited elsewhere.[14] Selected bond distances and angles are listed in Table II. Supplementary material includes thermal parameters, observed and calculated structure factors, and a complete list of bonding parameters.

Results and Discussion

Terminal alkynes HC≡CR (R = Ph, *p*-tolyl, CMe$_3$, SiMe$_3$) react under inert atmosphere with molecular hydrogen complexes [RuH(η^2-H$_2$)P$_4$]BF$_4$ to give alkenes H$_2$C=CHR (about 1.8 equiv) and the new compounds [Ru(η^3-RC$_3$CHR)P$_4$]$^+$ (1–3), which can be isolated in high yields as PF$_6$ or BPh$_4$ salts (eq 1).



(1)

P = PhP(OEt)$_2$, P(OEt)$_3$, or P(OMe)$_3$

Under hydrogen (1 atm) the reaction is catalytic and the alkynes are selectively converted to alkenes at room temperature in the presence of the catalyst precursor [RuH(η^2-H$_2$)P$_4$]$^+$. Also under H$_2$, however, the butenylnyl complex 1 is formed, and its formation probably causes interruption of the catalytic cycle. Studies on this reaction did show that hydrogenation is fast and stops after about 30 turnovers, just when the formation of the η^3-RC$_3$CHR derivative becomes quantitative (Table I).

In order to obtain information on the reaction path and the nature of probable intermediates, we monitored the progress of the reaction[15] by infrared and ^{1}H and ^{31}P NMR spectra, by adding successive small amounts of alkyne and changing the molar ratio between the alkyne and the η^2-H$_2$ complex in the range 0.5–10. When HC≡CR was added under argon, in ratios below 1:1, the reaction was virtually instantaneous and the ^{1}H NMR spectra showed only the presence of the alkene H$_2$C=CHR and the unreacted [RuH(η^2-H$_2$)P$_4$]$^+$ complex (about 90%). Further addition of alkyne (to a ratio of 2:1) caused an increase in the amount of H$_2$C=CHR and the gradual appearance of η^3-complex 1.

The ^{31}P NMR spectra did not give any further information, showing only some new signals of arduous attribution, besides the resonances of the known compounds. In the 2300–1600-cm^{-1} region, the infrared spectra of the reaction mixture did not show new signals when the HC≡CR/Ru complex ratio was below 1:1, but a new weak band at 2096 cm^{-1} (R = CMe$_3$) appeared when further alkyne was added (ratio 2:1). This absorption may reasonably be attributed to the ν(C≡C) of an alkynyl complex[4p,r] formed as an intermediate during the reaction course. When an excess of alkyne was used, the reaction proceeded in the same way, but the formation of the η^3-complex was fast and almost quantitative. Operating under H$_2$, the formation of alkene alone was observed for HC≡CR/Ru complex ratios below 1:3, whereas when the amount of alkyne was increased, butenynyl complex 1 also began to be produced; the hydrogenation reaction stopped

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[11] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[12] Sheldrick, G. M. SHELX-86, A program for structure solution. University of Gottingen, 1986.

[13] Sheldrick, G. M. SHELX-76, A program for crystal structure determination. University of Cambridge, 1976.

[14] Delledonne, D.; Pelizzi, G.; Pelizzi, C. *Acta Crystallogr.* **1987**, *C43*, 1502.

[15] The reaction was studied by starting from [RuH(η^2-H$_2$){PhP(OEt)$_2$}$_4$]BF$_4$ complex and using HC≡CPh or HC≡CCMe$_3$ acetylenes.

Table III. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2$)[a]

atom	x	y	z	B_{eq}	atom	x	y	z	B_{eq}
Ru	-154.4 (8)	0.0 (0)	-3714.0 (8)	3.08 (3)	C(36)	797 (8)	-639 (4)	-6426 (8)	5.25 (35)
P(1)	584 (3)	716 (2)	-2591 (3)	3.73 (11)	C(37)	-2529 (17)	-1159 (9)	-4575 (17)	8.10 (52)
P(2)	-1764 (3)	438 (2)	-3913 (3)	3.91 (11)	C(38)	-2846 (17)	-1756 (10)	-4468 (17)	8.39 (53)
P(3)	-514 (3)	-551 (2)	-2316 (3)	4.13 (11)	C(39)	-2027 (17)	-607 (9)	-6921 (17)	8.13 (51)
P(4)	-767 (3)	-623 (2)	-5062 (3)	4.04 (11)	C(40)	-1745 (23)	-232 (11)	-7893 (22)	12.45 (84)
O(1)	390 (7)	1277 (4)	-3234 (8)	4.27 (28)	C(41)	4663 (17)	-2054 (9)	-2343 (16)	8.07 (50)
O(2)	114 (8)	777 (5)	-1469 (8)	5.30 (34)	C(42)	3893 (13)	-1582 (7)	-2725 (12)	5.28 (34)
O(3)	-1850 (7)	835 (4)	-2961 (7)	4.10 (27)	(C43)	3603 (14)	-1481 (7)	-3816 (14)	6.33 (40)
O(4)	-2759 (6)	8 (6)	-3962 (8)	5.88 (29)	C(44)	2885 (11)	-1054 (6)	-4151 (11)	4.28 (30)
O(5)	-584 (9)	-1210 (4)	-2469 (9)	5.51 (34)	C(45)	2473 (10)	-746 (5)	-3423 (10)	3.37 (26)
O(6)	429 (8)	-464 (4)	-1357 (7)	4.63 (31)	C(46)	2677 (13)	-831 (7)	-2343 (12)	5.10 (34)
O(7)	-1413 (9)	-1166 (4)	-4855 (10)	6.08 (38)	C(47)	3472 (14)	-1258 (8)	-2001 (14)	6.40 (41)
O(8)	-1509 (8)	-300 (4)	-5962 (7)	4.96 (31)	C(48)	1675 (11)	-320 (6)	-3799 (11)	4.10 (30)
C(1)	2039 (6)	696 (5)	-2179 (8)	4.23 (29)	C(49)	1383 (9)	36 (7)	-4457 (9)	3.43 (22)
C(2)	2443 (6)	519 (5)	-1169 (8)	6.58 (42)	C(50)	623 (10)	412 (5)	-4900 (10)	3.51 (27)
C(3)	3553 (6)	512 (5)	-864 (8)	7.48 (46)	C(51)	577 (12)	791 (6)	-5658 (11)	4.20 (30)
C(4)	4258 (6)	681 (5)	-1568 (8)	7.92 (49)	C(52)	1453 (11)	962 (6)	-6262 (11)	4.07 (29)
C(5)	3854 (6)	858 (5)	-2577 (8)	7.32 (46)	C(53)	2477 (13)	704 (7)	-6145 (12)	5.24 (35)
C(6)	2744 (6)	866 (5)	-2883 (8)	5.08 (35)	C(54)	3266 (14)	888 (7)	-6743 (13)	5.87 (38)
C(7)	880 (14)	1827 (8)	-2977 (14)	6.18 (40)	C(55)	3033 (14)	1317 (8)	-7477 (14)	6.01 (39)
C(8)	979 (15)	2103 (8)	-4003 (15)	7.28 (47)	C(56)	3987 (18)	1515 (9)	-8107 (17)	8.61 (54)
C(9)	362 (17)	1247 (9)	-736 (18)	8.04 (51)	C(57)	2122 (17)	1584 (8)	-7561 (16)	7.82 (50)
C(10)	-28 (25)	1105 (13)	290 (25)	12.83 (86)	C(58)	1275 (15)	1393 (8)	-6923 (15)	6.54 (42)
C(11)	-2157 (10)	888 (4)	-5034 (9)	5.41 (35)	B	-5286 (12)	2864 (7)	-1867 (12)	4.14 (32)
C(12)	-1707 (10)	1411 (4)	-5031 (9)	5.22 (36)	C(59)	-4329 (8)	2542 (4)	-1005 (7)	5.34 (33)
C(13)	-1961 (10)	1758 (4)	-5894 (9)	7.75 (49)	C(60)	-3355 (8)	2786 (4)	-607 (7)	6.34 (38)
C(14)	-2665 (10)	1581 (4)	-6759 (9)	9.16 (58)	C(61)	-2613 (8)	2497 (4)	88 (7)	9.29 (56)
C(15)	-3114 (10)	1058 (4)	-6762 (9)	11.15 (73)	C(62)	-2845 (8)	1964 (4)	385 (7)	8.15 (48)
C(16)	-2860 (10)	711 (4)	-5899 (9)	8.88 (56)	C(63)	-3819 (8)	1720 (4)	-13 (7)	8.73 (52)
C(17)	-2711 (15)	1252 (8)	-2805 (15)	6.90 (43)	C(64)	-4562 (8)	2009 (4)	-708 (7)	5.95 (36)
C(18)	-2168 (17)	1754 (10)	-2315 (17)	8.45 (54)	C(65)	-6489 (6)	2849 (4)	-1408 (7)	3.79 (26)
C(19)	-3870 (23)	205 (11)	-3751 (21)	11.48 (74)	C(66)	-6634 (6)	2673 (4)	-395 (7)	6.12 (37)
C(20)	-4600 (23)	-317 (12)	-3904 (22)	11.56 (74)	C(67)	-7649 (6)	2705 (4)	-49 (7)	7.16 (43)
C(21)	-1733 (8)	-487 (5)	-1683 (8)	4.99 (34)	C(68)	-8520 (6)	2913 (4)	-717 (7)	6.39 (38)
C(22)	-2433 (8)	-926 (5)	-1594 (8)	8.06 (51)	C(69)	-8376 (6)	3089 (4)	-1730 (7)	6.04 (36)
C(23)	-3319 (8)	-862 (5)	-1037 (8)	11.47 (74)	C(70)	-7360 (6)	3057 (4)	-2076 (7)	5.16 (32)
C(24)	-3506 (8)	-360 (5)	-570 (8)	10.76 (68)	C(71)	-5254 (7)	2521 (4)	-3000 (6)	4.20 (28)
C(25)	-2807 (8)	79 (5)	-659 (8)	7.99 (46)	C(72)	-6104 (7)	2196 (4)	-3454 (6)	5.55 (34)
C(26)	-1920 (8)	15 (5)	-1215 (8)	5.16 (28)	C(73)	-6016 (7)	1917 (4)	-4394 (6)	6.15 (37)
C(27)	332 (15)	-1503 (8)	-2757 (14)	6.13 (41)	C(74)	-5077 (7)	1962 (4)	-4879 (6)	6.52 (38)
C(28)	64 (18)	-2105 (10)	-2665 (17)	8.77 (56)	C(75)	-4226 (7)	2287 (4)	-4424 (6)	5.49 (33)
C(29)	306 (16)	-733 (8)	-307 (15)	6.76 (44)	C(76)	-4315 (7)	2566 (4)	-3485 (6)	5.07 (32)
C(30)	1315 (28)	-967 (15)	99 (25)	14.16 (96)	C(77)	-4953 (9)	3508 (4)	-1960 (9)	4.97 (31)
C(31)	237 (8)	-960 (4)	-5768 (8)	4.83 (34)	C(78)	-4871 (9)	3771 (4)	-2918 (9)	6.33 (38)
C(32)	445 (8)	-1520 (4)	-5676 (8)	5.48 (36)	C(79)	-4593 (9)	4325 (4)	-2931 (9)	8.77 (53)
C(33)	1211 (8)	-1760 (4)	-6241 (8)	6.96 (44)	C(80)	-4398 (9)	4615 (4)	-1986 (9)	10.26 (60)
C(34)	1770 (8)	-1440 (4)	-6899 (8)	6.35 (43)	C(81)	-4480 (9)	4353 (4)	-1028 (9)	11.57 (71)
C(35)	1563 (8)	-879 (4)	-6991 (8)	6.29 (40)	C(82)	-4757 (9)	3799 (4)	-1015 (9)	7.26 (44)

[a] B values are equal to one-third of the trace of the orthogonalized matrix.

when its formation was about quantitative. In this case too, the appearance of the weak ν(C≡C) band attributable to an alkynyl intermediate was detected.

All these data do not allow us to define a mechanism for the reaction unambiguously. However, the nature of the product, catalytic hydrogenation, and spectroscopic studies on the reaction allow us to propose the reaction path shown in Scheme I.

The molecular hydrogen complex can quickly react with alkynes to give the 16-electron vinyl complex (B) through a probable π-acetylene complex (A). Although the σ-alkenyl derivative (B) was not detected by spectroscopic methods, its formation is reasonable when it is taken into account that several ruthenium hydrides are known to react with HC≡CR to give σ-alkenyl complexes[3,6d,m,o,p] and that we observed that the dimethyl acetylenedicarboxylate reacts with $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ to give the vinyl species 4 (see below). The reaction of the pentacoordinate compounds B with hydrogen can yield the olefin and monohydride C, which, in the presence of H_2, regenerates the η^2-H_2 complexes. The catalytic cycle probably involves several other intermediates in a series of elementary steps that remain to be elucidated.

However, the alkenyl complex B can also react[16] with HC≡CR to give the alkene and σ-acetylide complex D, which, by further reaction with alkyne, affords the $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ as final product. The formation of an acetylide derivative may also follow a different path involving oxidative addition of HC≡CR to ruthenium followed by H_2 elimination, giving a Ru—C≡CR derivative (D) (Scheme II).

This pathway needs the reaction of a vacant site at a certain stage, a heptacoordinate Ru intermediate being unlikely. Such a vacant site can be provided by phosphite dissociation. In every case, whatever the mechanism may be, an acetylide intermediate seems to be plausible and the 2096-cm^{-1} IR band confirms its presence. The further reaction of this Ru—C≡CR complex with alkyne yields η^3-derivatives 1–3, and this insertion reaction probably involves an intermediate containing one alkynyl and one π-alkyne ligand such as E (Scheme III), which rearranges into F followed by the coupling of the vinylidene group and the acetylide ligand.

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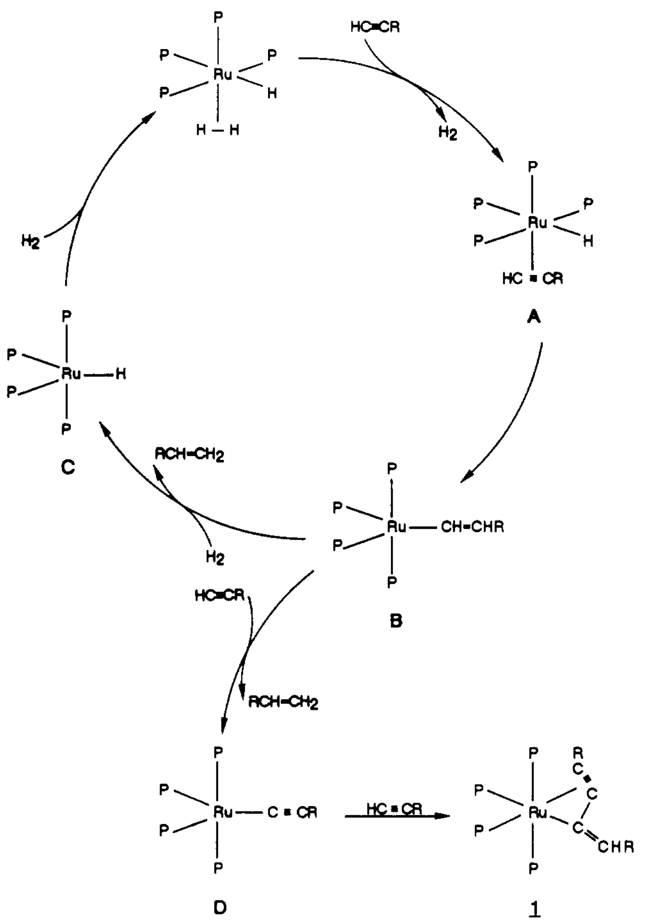
(16) An example of a reaction between an alkenyl complex and alkynes affording alkene and an acetylide derivative has recently been reported (see ref 4s).

Scheme I



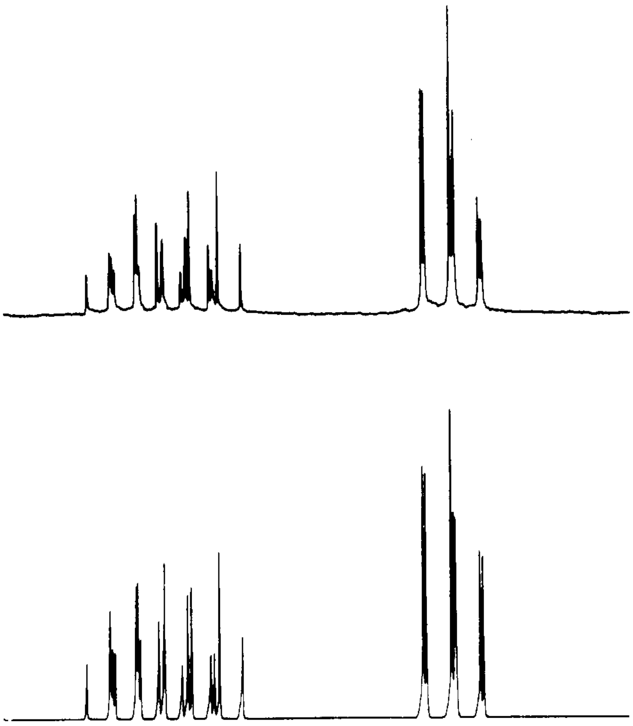


Figure 1. Observed (top) and calculated (bottom) ^{31}P{^{1}H} NMR spectra of [Ru{η^3-(*p*-tolyl)C$_3$CH(*p*-tolyl)}{PhP(OEt)$_2$}$_4$]PF$_6$ (**1b′**) in (CD$_3$)$_2$CO at 30 °C. The simulated spectrum was obtained with the following parameters: spin system ABC$_2$, δ_A = 165.2, δ_B = 161.6, δ_C = 149.3, J_{AB} = 36.5 Hz, J_{AC} = 42.6 Hz, J_{BC} = 47.4 Hz.

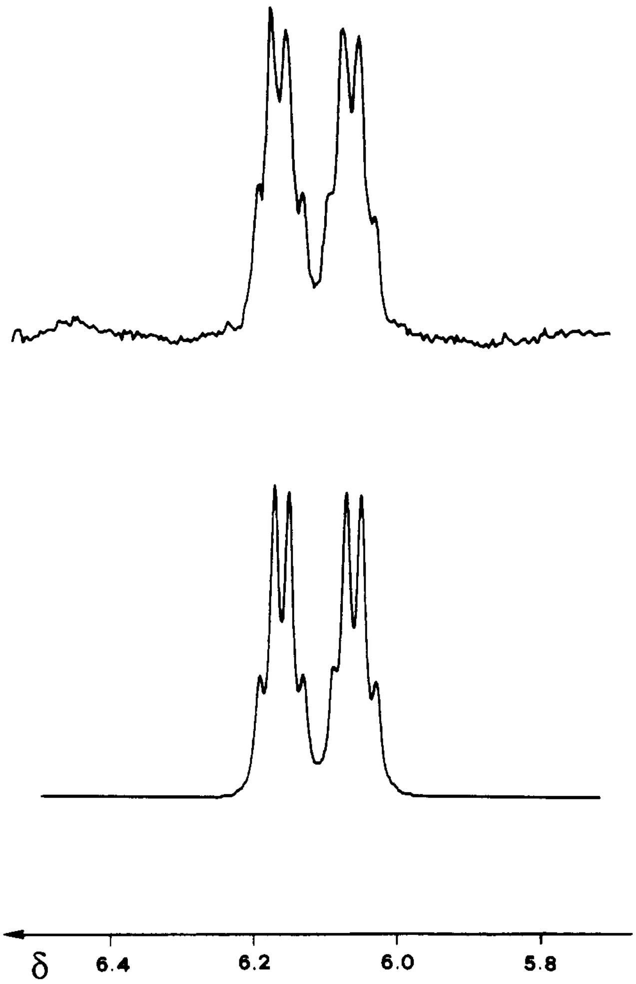


Figure 2. Observed (top) and calculated (bottom) ^{1}H NMR spectra in the vinyl region of [Ru{η^3-(CMe$_3$)C$_3$CH(CMe$_3$)}{P(OEt)$_3$}$_4$]PF$_6$ (**2c**) in (CD$_3$)$_2$CO at 30 °C. The simulated spectrum was obtained with the following parameters: spin system ABC$_2$X (X = H), δ_A = 139.6, δ_B = 137.4, δ_C = 119.3, δ_X = 6.11, J_{AB} = 43.4 Hz, J_{AC} = 56.5 Hz, J_{AX} = 8.5 Hz, J_{BC} = 67.0 Hz, J_{BX} = 1.1 Hz, J_{CX} = 1.5 Hz.

Scheme II

$$\underset{\textbf{A}}{[\mathrm{RuH(HC{\equiv}CR)P_4}]^+} \xrightarrow{-\mathrm{P}} [\mathrm{RuH_2(C{\equiv}CR)P_3}]^+ \xrightarrow[+\mathrm{P}]{-\mathrm{H_2}} \underset{\textbf{D}}{[\mathrm{Ru(C{\equiv}CR)P_4}]^+}$$

Scheme III

$$\underset{\textbf{D}}{[\mathrm{Ru(C{\equiv}CR)P_4}]^+} \xrightarrow{\mathrm{HC{\equiv}CR}} \underset{\textbf{E}}{[\mathrm{Ru(C{\equiv}CR)(HC{\equiv}CR)P_4}]^+} \rightarrow \underset{\textbf{F}}{[\mathrm{Ru(C{\equiv}CR)(C{=}CHR)P_4}]^+} \rightarrow \underset{\textbf{1-3}}{[\mathrm{Ru(\eta^3\text{-}RC_3CHR)P_4}]^+}$$

[Ru(η^3-RC$_3$CHR)P$_4$]$^+$ derivatives **1**–**3** are yellow or orange solids, stable in air, and soluble in polar organic solvents, where they behave as 1:1 electrolytes.[17] In the temperature range −80 to +30 °C the ^{31}P{^{1}H} NMR spectra of **1**–**3** are multiplets of the type shown in Figure 1, which can be simulated by using an ABC$_2$ model. Besides the signals of the phosphite ligands, the ^{1}H NMR spectra show a doublet of multiplets at δ 4.94–6.11, assigned to the vinyl proton of the η^3-RC$_3$CHR ligand. The multiplicity of this signal is probably due to coupling with the four phosphorus

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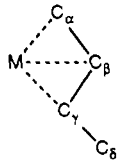
[17] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table IV. Selected Bond Distances (Å) and Angles (deg) for the M–C_4 Group in η^3 Derivatives



	$[Os(\eta^3\text{-}PhC_3CHPh)P_4]PF_6$ (P = PMe_3)	$[Ru(CCPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)]$	$[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}P_4]BPh_4$ [P = $PhP(OEt)_2$]
C(α)–C(β)	1.29 (2)	1.249 (5)	1.23 (2)
C(β)–C(γ)	1.39 (2)	1.379 (5)	1.39 (2)
C(γ)–C(δ)	1.32 (2)	1.339 (5)	1.33 (2)
M–C(α)	2.39 (1)	2.258 (3)	2.430 (14)
M–C(β)	2.21 (1)	2.191 (3)	2.244 (12)
M–C(γ)	2.15 (1)	2.200 (3)	2.145 (14)
C(α)–C(β)–C(γ)	132 (1)	133.0 (3)	136.0 (13)
C(β)–C(γ)–C(δ)	150 (1)	148.7 (3)	150.9 (13)

atoms of the phosphite ligands, as can be demonstrated by simulation of the spectra as the X part of an ABC_2X model, using the parameters reported in Figure 2. Furthermore, the methyl protons of substituent R (*p*-tolyl, CMe_3, and $SiMe_3$) always show the presence of two singlets, indicating the existence of nonequivalent groups. In the ^{13}C NMR spectra, the C_δ vinyl carbon signal of the η^3-RC_3CHR ligand appears as a doublet of multiplets at δ 139.4–140.0 ($^1J_{CH}$ = 159–161 Hz), whereas two signals are observed for the methyl carbon of the CH_3 group present in the R substituent. These data, however, do not allow us to propose a definitive structure for these complexes, and a single-crystal X-ray diffraction study of one of these complexes, $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]BPh_4$ (**1b′**), was therefore undertaken.

The structure of the compound consists of discrete well-separated $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ cations and BPh_4^- anions; Figure 3 shows an ORTEP drawing that emphasizes the coordination geometry around the ruthenium atom in the complex cation as well as the bonding arrangement of the organic molecule. The metal atom has a pseudooctahedral environment that involves the four phosphite groups and the organic molecule with this ligand formally occupying two coordination sites (a carbon atom and the midpoint of the triple bond). The four Ru–P bonds are not equivalent, the two shortest bonds occurring at the sites located approximately trans to the organic ligand, with an average reduction in bond distance of 0.072 Å. This value is significantly larger than 0.007 Å, found in *cis*-$RuH(Et)(PMe_3)_4$[18] and 0.002 Å found in $Ru(DMPE)_2(CN)_2$[19] [DMPE = bis(dimethylphosphino)ethane], in both of which Ru–P bonds are mutually trans and Ru–P bonds are trans to C-containing ligands. All four Ru–P bond distances are typical of such distances for six-coordinate ruthenium complexes containing phosphite ligands.

The only other two structurally characterized compounds containing the η^3-$PhC_3CHPh(L)$ ligand of which we are aware[20] are $[Os(L)(PMe_3)_4]PF_6$[21] and $[Ru(CCPh)(L)(Cyttp)]$[7a] {Cyttp = $PhP[CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2]_2$}. The structural parameters involving the L ligand in the three compounds deserve some comment and are collected in Table IV. While there is very good agreement as far as bond distances and angles in the C_4 chain are concerned, large and unexpected differences occur in the metal–carbon bonds. While bond distances are quite comparable in our **1b′** and in osmium derivatives, large and significant differences are observed in the $[Ru(CCPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)]$ complex. This may in part be attributed to the different charge of the complexes containing the acetylide ligand rather than to different steric or electronic influence of the phosphine ligand. The osmium and our **1b′** complexes are both cationic with four P groups and the η^3-ligand and show comparable M–C bond distances, although the M–C_α and M–C_β are slight longer in our **1b′**, probably owing to the different properties of the phosphite $PhP(OEt)_2$ as compared to the PMe_3 phosphine ligand. The L ligand can be described in terms of two near-planar moieties, containing the C(42)–C(47) ring with the attached methyl carbon C(41) (planar within experimental error) and the rest of the molecule, C(48) through C(58) (with none of the atoms lying more than 0.08 Å out of the least-squares plane), respectively. The two parts are at an angle of 51.9 (4)° to each other.

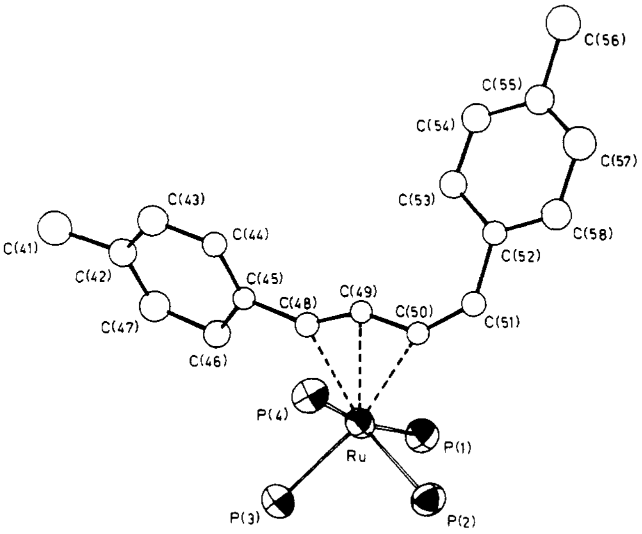


Figure 3. ORTEP diagram and numbering scheme for the $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]^+$ cation. Phenyl rings and ethyl groups in phosphite moieties have been omitted for clarity. Anisotropic thermal parameters were used only for shaded atoms. Thermal ellipsoids are drawn at the 50% probability level.

The torsion angles of interest are C(44)–C(45)–C(48)–C(49) = −38°, C(45)–C(48)–C(49)–C(50) = 171°, C(48)–C(49)–C(50)–C(51) = −176°, and C(49)–C(50)–C(51)–C(52) = −5°.

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[18] Wong, W. K.; Chin, K. W.; Statler, J. A.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1255.

[19] Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823.

[20] Extensive use of the Cambridge Crystallographic Database Files was made for a bibliographic search.

[21] Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247.

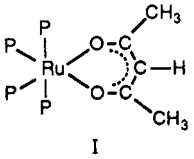
The C_6 fragment, formed of C(45)C(48)C(49)C(50)C(51)C(52), is nearly planar (in agreement with an extended π delocalization), as the atoms are located within 0.07 Å of their common plane; the Ru atom resides 0.06 Å out of this plane on the same side as P(2) (0.08 Å) and P(3) (0.22 Å).

The geometry of the anion is in agreement with that found in other structures, the B–C distances and C–B–C angles averaging 1.68 Å and 109°, respectively. There are no unusual interionic contacts, the closest approach of carbon in the anion to any non-hydrogen atom in the cation being greater than 3.45 Å.

[Ru(η^3-RC_3CHR)P_4]$^+$ derivatives react at room temperature with acetylacetone to give the acetylacetonate derivatives [Ru(acac)P_4]$^+$ (**5**) in almost quantitative yield ($\geq$90%); they were isolated and characterized. The reaction can be followed by ^{1}H NMR spectra, and in the case of the [Ru{η^3-(*p*-tolyl)C_3CH(*p*-tolyl)}{PhP(OEt)$_2$}$_4$]PF_6 starting material, the disappearance of the signals at δ 5.62 (vinyl protons) and δ 2.33 and 2.26 (CH_3 of *p*-tolyl) characteristic of the η^3-ligand and the parallel appearance of the resonance of the [Ru(acac)P_4]$^+$ derivative can all be observed. Furthermore, two doublets at δ 6.65 and 5.84 (AB quartet, J_{AB} = 11.9 Hz) and a singlet at δ 2.35 also appear in the spectra and were attributed[22] to the (*Z*)-(*p*-tolyl)HC=CHC≡C(*p*-tolyl) organic compound formed by protonation of the η^3-(*p*-tolyl)C_3CH(*p*-tolyl) ligand with acetylacetone (eq 2).

$$[\mathrm{Ru}(\eta^3\text{-}\mathrm{RC_3CHR})\mathrm{P_4}]^+ + \mathrm{Hacac} \rightarrow [\mathrm{Ru}(\mathrm{acac})\mathrm{P_4}]^+ + (Z)\text{-}\mathrm{R(H)C{=}C(H)C{\equiv}CR} \quad (2)$$

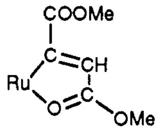
The [Ru(acac)P_4]Y (Y = BPh_4 (**5a′**), PF_6 (**5b**, **5c**)) complexes are pale yellow solids, diamagnetic and 1:1 electrolytes in solutions of polar organic solvents. Their IR spectra show the ν(CO) band of the acac ligand at 1587–1590 cm^{-1}. Besides the signals of the phosphite ligand, the ^{1}H NMR spectra exhibit two singlets at δ 4.91–5.43 and 1.24–1.92, attributable to the CH and CH_3 protons, respectively, of the acac ligand. The ^{13}C NMR spectra revealed the characteristic signals of the acac moiety at δ 187.7 and 27.9 (**5b**) for the carbonyl and methyl groups, respectively, and a doublet at δ 100.3 ($^1J_{CH}$ = 157 Hz) attributable to the methyne carbon atom. The ^{31}P{^{1}H} NMR spectra also support the proposed formulation for the complexes, showing an A_2B_2 pattern, in agreement with a type I geometry.



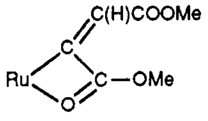
I

Dimethyl acetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$) reacted at room temperature under inert atmosphere with [RuH(η^2-H_2)P_4]BF_4 to give the alkene $MeO_2CC(H){=}C(H)CO_2Me$ as a mixture of dimethyl fumaric and dimethyl maleic esters and the ruthenium alkenyl complex [Ru{C(CO_2Me)=C(H)CO_2Me}P_4]PF_6 (**4**), which could be isolated, with the PhP(OEt)$_2$ ligand, in low yield and characterized. The reaction was slower than that of the terminal alkynes, and monitoring the progress of the reaction by ^{1}H NMR spectra in the presence of excess acetylene also revealed the gradual formation of other products (not characterized). Under hydrogen atmosphere (1 atm) the reaction was catalytic, with selective reduction of the alkyne to alkene, but in contrast to 1-alkynes, it was very slow, with about 5% convertion in 24 h. The slow rate of the reaction of **4** with H_2 and/or the alkyne was probably the cause of the observed low conversion to alkene.

Complex [Ru{C(CO_2Me)=C(H)CO_2Me}{PhP(OEt)$_2$}$_4$]PF_6 (**4**) was a pale yellow air-stable solid, but in solution it slowly decomposed even in an inert atmosphere. It behaved as a 1:1 electrolyte in nitromethane solution. The IR spectra showed two bands at 1630 and 1723 cm^{-1} (KBr), which could be assigned to the ν(CO) of a coordinate carbonyl group and to a free –CO_2Me substituent, respectively.[4r,s,6a] A medium-intensity band at 1540 cm^{-1} was attributed to the ν(C=C) of the alkenyl ligand.[4] Apart from the signals of the phosphite ligand, the ^{1}H NMR spectra showed a singlet at δ 5.31, assigned to the CH vinyl proton, and two singlets at δ 3.56 and 2.39, attributed to the methyl protons of two magnetically nonequivalent carbomethoxy (–CO_2Me) substituents. Two signals for the nonequivalent –CO_2Me groups were also observed in the ^{13}C NMR spectra at δ 180.6 and 175.9 for the CO group and at δ 53.5 and 50.8 for the methyl carbon, whereas a doublet of multiplets at δ 209.1 can be attributed to the carbenoid carbon atom. In the temperature range –80 to +30 °C the ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 was a multiplet, which could be simulated by using an ABC_2 model. On the basis of these data, it is reasonable to propose for our complex a cyclic structure, in which the carbonyl oxygen atom of one of the ester groups coordinates to the ruthenium in structures of types II or III.



II



III

Although the spectroscopic data do not allow us to distinguish between them, it may be observed that a type III geometry has recently been determined by X-ray studies in related ruthenium complexes,[4m,r]

We also studied the interaction of other disubstituted acetylenes such as MeC≡CPh and PhC≡CPh with [RuH(η^2-H_2)P_4]$^+$ derivatives, and although the reaction proceeded with a color change of the solution from pale yellow to red-brown, no stable ruthenium compounds were isolated. However, in mild conditions, the hydrogenation reaction also proceeded, and the slow formation of the *cis*-alkene was observed, with ca. 10% convertion in 36 h.

Acknowledgment. The financial support of MURST and CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan and Andrea Cantoni for their valuable technical assistance.

Supplementary Material Available: Tables of thermal parameters, bonding parameters, and crystal data (7 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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[22] Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley: New York, 1974.