# Preparation, Structure, and Reactivity of New Bis(acetylide) and Acetylide−Vinylidene Ruthenium(II) Complexes Stabilized by Phosphite Ligands

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*Received December 8, 1994*[⊗]

Bis(alkynyl) complexes $Ru(C{\equiv}CR)_2P_4$ (**1**−**3**) (R = Ph, *p*-tolyl, $^tBu$; P = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**), $PPh(OEt)_2$ (**3**)) were prepared by reacting $RuCl_2P_4$ with excess $Li^+$ $RC{\equiv}C^-$, and a *trans* geometry was established both in solids (X-ray) and in solution. The reaction of these alkynyls (**1**−**3**) with electrophilic reagent depends on the nature of the phosphite ligand. Vinylidene−acetylide derivatives $[Ru(C{\equiv}CR)\{{=}C{=}C(R_1)R\}P_4]^+$ ($R_1$ = H (**4**, **5**), $CH_3$ (**7**, **8**), ArN=N (**10**), I (**12**), 2,3-$(NO_2)_2C_6H_3S$ (**14**)) were prepared with $P(OMe)_3$ and $P(OEt)_3$ ligand by treatment of **1** and **2** with $HBF_4$, $CF_3SO_3Me$, $ArN_2{}^+BF_4{}^-$, $I_2$, and 2,3-$(NO_2)_2C_6H_3SCl$, respectively. Instead, only the diazo- and iodovinylidenes $[Ru(C{\equiv}CR)\{{=}C{=}C(R_1)R\}P_4]^+$ ($R_1$ = *p*-tolN=N (**11**), I (**13**)) were obtained with the $PPh(OEt)_2$ phosphite ligand. These vinylidene compounds were fully characterized by IR, $^1H$, $^{31}P$, and $^{13}C$ NMR spectra, and a single-crystal X-ray structure determination of complex $[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt)_3\}_4]CF_3SO_3$ (**8a**) is reported. The alkynyl−vinylidene $[Ru(C{\equiv}CR)\{{=}C{=}C(H)R\}P_4]^+$ cations (**4**, **5**) rearrange in solution to enynyl $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ derivatives, and the reaction is inhibited by the presence of free alkyne. Kinetic data support a mechanism involving a pentacoordinate intermediate formed by loss of the vinylidene ligand. Substitution of the ${=}C{=}C(H)R$ ligand by phosphite, isocyanide, and nitrile is easy in **4** and **5** and leads to $[Ru(C{\equiv}CPh)\{P(OMe)_3\}P_4]^+$ (**17**), $[Ru(C{\equiv}CPh)(p\text{-tolNC})P_4]^+$ (**18**), and $[Ru(p\text{-tolCN})_2P_4]^{2+}$ (**19**) (P = $P(OEt)_3$), derivatives. Deprotonation with a base of the vinylidene ligand in **4** and **5**, giving $Ru(C{\equiv}CR)_2P_4$, was also detected.

## Introduction

A large number of studies on the chemistry of transition-metal vinylidene complexes has been reported during the last decade,[1−3] and it now seems certain that the properties of vinylidene ligands are a function of the nature of the $C{=}CRR_1$ substituents, the central metal, and its ancillary ligands. Interest in these studies arises not only from the unique and diverse reactivity modes and structural properties that complexes containing the metal−carbon double bond exhibit,[1−3] but also because vinylidene species seem to play an important role in Fischer−Tropsch chemistry,[4] in alkyne polymerization,[5] and in C−C bond formation in the condensation of alkynes with other substrates.[6] Closely related to vinylidene complexes are transition-metal alkynyl derivatives which are common precursors to, and reaction products of, $C{=}CRR_1$ vinylidene derivatives.[7] These compounds are also of interest as precur-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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sors of molecules containing a linear array and delocalizable $\pi$-systems[7f,8] or polymeric materials[8] in the search for $\pi$-interactions through the metal center and new properties.[9]

Despite the large number of vinylidene complexes with cyclopentadienyl and arene rings and mono-, bi-, and polydentate phosphines as supporting ligands,[1-3] very few of them are reported with phosphite ($P(OR)_3$, $PPh(OR)_2$) ligands,[1,10] although it may be expected[11] that the steric and electronic properties of these ligands will reveal new properties of vinylidene and acetylide derivatives.

In this paper we report the synthesis of a series of bis(acetylide) and acetylide–vinylidene ruthenium(II) complexes containing phosphite ligands of the type $Ru(C{\equiv}CR)_2P_4$ and $[Ru(C{\equiv}CR)({=}C{=}CRR_1)P_4]^+$ together with some studies on the reactivity of the new vinylidene derivatives and an X-ray crystal-structure determination.

## Experimental Section

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere drybox. Once isolated, the complexes turned out to be quite air-stable and were stored at −20 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Trimethyl and triethyl phosphite were Aldrich products purified by distillation under nitrogen; diethoxyphenyl phosphine was prepared by the method of Rabinowitz and Pellon.[12] Alkynes were Aldrich products, used without any further purification. Lithium acetylides $Li^+RC{\equiv}C^-$ (R = Ph or *p*-tol) were prepared by reacting a slight excess of the appropriate acetylene (40 mmol) with lithium (35 mmol, 0.24 g) in 10 mL of THF. *tert*-Butylacetylide $Li^{+t}BuC{\equiv}C^-$ was prepared by adding a solution of $Li^nBu$ 2.5 *M* in hexane (8 mmol, 3.2 mL) to a solution of $^tBuC{\equiv}CH$ (10 mmol, 1.23 mL) in 10 mL of THF cooled to −80 °C. The reaction mixture was stirred for 20–30 min at −80 °C and was then used. Diazonium salts were obtained in the usual way described in the literature.[13] The labeled diazonium salt $PhN{\equiv}{}^{15}N^+BF_4^-$ was prepared from $Na^{15}NO_2$ (99% enriched, CIL) and aryl amine. *p*-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*[14] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Perkin-Elmer Model 683 or Digilab BioRad FTS-40 spectrophotometers. NMR spectra ($^1H$, $^{13}C$, $^{31}P$) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. $^1H$ and $^{13}C$ spectra are referenced to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% $H_3PO_4$, with downfield shifts considered positive. IR and NMR data are collected in Table 1. The conductivity of $10^{-3}$ M solutions of the complexes in $CH_3NO_2$ at 25 °C was measured with a Radiometer CDM 83 instrument.

**Synthesis of Complexes.** The dichlorotetrakis(triethyl phosphite)ruthenium(II) complex was prepared as previously reported.[15] The related $RuCl_2[P(OMe)_3]_4$ and $RuCl_2[PPh(OEt)_2]_4$ were also prepared as follows by slight modification of this method.

$RuCl_2[P(OMe)_3]_4$ was prepared by adding an excess of $P(OMe)_3$ (0.15 mol, 19 mL) to ruthenium trichloride trihydrate (0.01 mol, 2.6 g). The mixture was stirred for 1 h at room temperature, and then $NaBH_4$ (0.026 mol, 1 g) was added. After 30 min of stirring, a yellow suspension formed, which was cooled to −20 °C and then filtered. The solid obtained was dissolved in 20 mL of $CH_2Cl_2$, filtered, and evaporated at reduced pressure. The resulting yellow solid was crystallized by slowly cooling to −30 °C its saturated solution in $CH_3OH$ prepared at 20 °C; yield: ≥45%. Anal. Calcd: C, 21.57; H, 5.43. Found: C, 21.42; H, 5.50. $^1H$ NMR ($CDCl_3$), $\delta$: 3.85 (m, 36H, $CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), $\delta$: 129.9 s.

$RuCl_2[PPh(OEt)_2]_4$ was obtained by adding an excess of $PPh(OEt)_2$ (0.15 mol, 30 mL) to solid $RuCl_3{\cdot}3H_2O$ (0.01 mol, 2.6 g) and heating the mixture under vigorous stirring until a reaction took place, giving a yellow suspension (about 1 h at 70–80 °C). After the mixture was cooled to 20 °C, 1 g (0.026 mol) of $NaBH_4$ was added and the suspension was stirred for about 5 h. The solid that formed was filtered, washed with ethanol, and dissolved in $CH_2Cl_2$. The resulting solution was filtered, and removal of the solvent gave an oil, which was treated with ethanol, affording the $RuCl_2[PPh(OEt)_2]_4$ complex as a yellow microcrystalline solid; yield: ≥75%. Anal. Calcd: C, 49.80; H, 6.27. Found: C, 49.96; H, 6.19. $^1H$ NMR ($CD_2Cl_2$), $\delta$: 7.77–7.05 (m, 20H, Ph); 3.99, 3.63 (m, 16H, $CH_2$); 1.15 (t, 24H, $CH_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$), $\delta$: 146.4 s.

**$Ru(C{\equiv}CR)_2P_4$ (1–3) [R = Ph (a), *p*-Tol (b), $^t$Bu (c); P = $P(OMe)_3$ (1), $P(OEt)_3$ (2), $PPh(OEt)_2$ (3)].** To a solution of $RuCl_2P_4$ (1.0 mmol) in 10 mL of THF was added an excess of the appropriate $Li^+RC{\equiv}C^-$ in THF solution (4 mmol), and the resulting mixture was refluxed for about 15 min. Removal of the solvent at reduced pressure gave a brown oil, which was triturated with methanol or ethanol (15 mL). The resulting solution was stirred until a yellow solid separated out, which was filtered and crystallized by slowly cooling at −20 °C its saturated solution in ethanol/hexane (10/25 mL); yield: ≥35%. Anal. Calcd for **1a**: C, 42.06; H, 5.80. Found: C, 41.93; H, 5.82. Mp: 122 °C decomp. Calcd for **1b**: C, 43.53; H, 6.09. Found: C, 43.40; H, 5.98. Mp: 131 °C decomp. Calcd for **1c**: C, 37.94; H, 7.17. Found: C, 37.72; H, 7.02. Mp: 106 °C decomp. Calcd for **2a**: C, 49.63; H, 7.29. Found: C, 49.45; H, 7.45. Mp: 152 °C decomp. Calcd for **2b**: C, 50.65; H, 7.49. Found: C, 50.71; H, 7.40. Mp: 142 °C decomp. Calcd for **2c**: C, 46.59; H, 8.47. Found: C, 46.45; H, 8.65. Mp: 175–177 °C decomp. Calcd for **3a**: C, 61.36; H, 6.44. Found: C, 61.19; H, 6.53. Mp: 93–95 °C decomp. Calcd for **3b**: C, 61.97; H, 6.64. Found: C, 61.79; H, 6.53. Mp: 110 °C decomp. Calcd for **3c**: C, 59.13; H, 7.44. Found: C, 59.22; H, 7.38. Mp: 123–126 °C decomp.

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**Table 1. Infrared and NMR Data for Ruthenium Complexes**

| compd | IR[a,b] ($cm^{-1}$) | $^1H$ NMR[c,d] ($\delta$) | $^{13}C$ NMR[c,d] ($\delta$) | spin system | $^{31}P\{^1H\}$ NMR[c,e] ($\delta$) |
|---|---|---|---|---|---|
| **1a** | $\nu_{C\equiv C}$ 2078 (s)[b] | 3.85 (m, $CH_3$) | 114.8 (qi, $^3J_{CP}$ = 1.6, ≡C–Ph)<br>114.4 (qi, $^2J_{CP}$ = 20, ≡C–Ru)<br>52.9 (qm, $CH_3$) | $A_4$ | 140.1 (s) |
| **1b** | $\nu_{C\equiv C}$ 2081 (s)[b] | 3.91 (m, $CH_3$ phos)[f]<br>2.16 (s, $CH_3$ *p*-tol) | | $A_4$[f] | 141.1 (s) |
| **1c** | $\nu_{C\equiv C}$ 2088 (s)[b] | 3.88 (m, $CH_3$ phos)[f]<br>1.24 (s, $CH_3$ $^t$Bu) | | $A_4$[f] | 142.9 (s) |
| **2a** | $\nu_{C\equiv C}$ 2076 (s)[b] | 4.52 (m, $CH_2$)[f]<br>1.28 (t, $CH_3$) | 117.2 (qi, $^2J_{CP}$ = 20, ≡C–Ru)<br>113.8 (qi, $^3J_{CP}$ = 1.6, ≡C–Ph)<br>61.3 (t, $CH_2$)<br>16.6 (q, $CH_3$) | $A_4$ | 138.1 (s) |
| **2b** | $\nu_{C\equiv C}$ 2077 (s)[b] | 4.54 (m, $CH_2$)[f]<br>2.14 (s, $CH_3$ *p*-tol)<br>1.30 (t, $CH_3$ phos) | 114.8 (qi, $^2J_{CP}$ = 20, ≡C–Ru)<br>113.4 (qi, $^3J_{CP}$ = 1.6, ≡C–Ph)<br>61.2 (t, $CH_2$)<br>21.2 (q, $CH_3$ *p*-tol)<br>16.6 (q, $CH_3$ phos) | $A_4$[f] | 138.3 (s) |
| **2c** | $\nu_{C\equiv C}$ 2085 (s)[b] | 4.54 (m, $CH_2$)<br>1.21 (t, $CH_3$ phos)<br>1.04 (s, $CH_3$ $^t$Bu) | 117.8 (qi, br, ≡C–Ph)<br>88.2 (qi, $^2J_{CP}$ = 20, ≡C–Ru)<br>61.0 (t, $CH_2$)<br>32.9 (q, $CH_3$ $^t$Bu)<br>29.9 (s, $C-(CH_3)_3$)<br>16.5 (q, $CH_3$ phos) | $A_4$ | 138.7 (s) |
| **3a** | $\nu_{C\equiv C}$ 2069 (s)[b] | 4.28, 3.77 (m, $CH_2$)<br>1.12 (t, $CH_3$) | 125.0 (qi, $^2J_{CP}$ = 18, ≡C–Ru)<br>115.6 (qi, br, ≡C–Ph)<br>62.1 (t, $CH_2$)<br>16.5 (q, $CH_3$) | $A_4$[f] | 153.0 (s) |
| **3b** | $\nu_{C\equiv C}$ 2077 (s)[b] | 4.35, 3.83 (m, $CH_2$)[f]<br>2.77 (s, $CH_3$ *p*-tol)<br>1.19 (t, $CH_3$ phos) | | $A_4$[f] | 153.0 (s) |
| **3c** | $\nu_{C\equiv C}$ 2076 (s)[b] | 4.19, 3.65 (m, $CH_2$)<br>1.09 (t, $CH_3$ phos)<br>1.09 (s, $CH_3$ $^t$Bu) | | $A_4$ | 151.7 (s) |
| **4a**[i] | $\nu_{C\equiv C}$ 2100 (s)<br>$\nu_{C=C}$ 1668 (s), 1633 (m) | 5.98 (qi, $J_{PH}$ = 1.5, CH vinyl)<br>3.95 (m, $CH_3$ phos) | 379.8 (qi, $^2J_{CP}$ = 17, Ru=C=)<br>125.5 (br, ≡C–Ph)<br>112.9 (dm, $^1J_{CH}$ = 150, =C(H)Ph)<br>97.1 (qi, $^2J_{CP}$ = 25, ≡C–Ru)<br>54.5 (q, $CH_3$) | $A_4$ | 124.5 (s) |
| **5a**[i] | $\nu_{C\equiv C}$ 2102 (s)<br>$\nu_{C=C}$ 1666 (s), 1634 (w) | 5.32 (qi, br, CH vinyl)<br>4.23 (m, $CH_2$)<br>1.27 (t, $CH_3$) | 377.4 (qi, $^2J_{CP}$ = 17, Ru=C=)<br>112.6 (dm, $^1J_{CH}$ = 150, =C(H)Ph)<br>120.3 (qi, $^3J_{CP}$ = 2.0, ≡C–Ph)<br>99.5 (qi, $^2J_{CP}$ = 25, ≡C–Ru)<br>62.7 (t, $CH_2$)<br>15.9 (q, $CH_3$) | $A_4$<br>$A_2B_2$[h] | 118.6 (s)<br>$\delta_A$ = 124.1; $\delta_B$ = 115.4; $J_{AB}$ = 57.6 |
| **5a$_1$**[i] | $\nu_{C\equiv C}$ 2097 (s)<br>$\nu_{C=C}$ 1662 (s), 1630 (m) | 5.29 (qi, br, CH vinyl)<br>4.25 (m, $CH_2$)<br>1.29 (t, $CH_3$) | | $A_4$ | 119.1 (s) |
| **5b**[i] | $\nu_{C\equiv C}$ 2101 (s)<br>$\nu_{C=C}$ 1664 (s) | 5.25 (qi, $^1J_{CH}$ = 1.6, CH vinyl)<br>4.24 (m, $CH_2$)<br>2.34, 2.36 (s, $CH_3$ *p*-tol)<br>1.28 (t, $CH_3$ phos) | | $A_4$ | 119.2 (s) |
| **5c**[i] | $\nu_{C\equiv C}$ 2097 (m)<br>$\nu_{C=C}$ 1685 (s), 1652 (w) | 5.37 (qi, br, CH vinyl)<br>4.22 (m, $CH_2$)<br>1.14, 1.09 (s, $CH_3$ $^t$Bu)<br>1.28 (t, $CH_3$ phos) | 367.8 (qi, $^2J_{CP}$ = 17, Ru=C=)<br>117.6 (dm, $^1J_{CH}$ = 150, =C(H)$^t$Bu)<br>78.4 (qi, $^2J_{CP}$ = 25, ≡C–Ru)<br>62.4 (t, $CH_2$)<br>33.3, 32.6 (s, br, $C-(CH_3)_3$)<br>31.9, 31.7 (q, $CH_3$ $^t$Bu)<br>15.8 (q, $CH_3$ phos) | $A_4$ | 119.3 (s) |
| **7a** | $\nu_{C\equiv C}$ 2095 (m)<br>$\nu_{C=C}$ 1648 (s) | 3.83 (m, $CH_3$ phos)<br>2.15 (s, $CH_3$ vinyl) | 383.1 (qi of q, $^2J_{CP}$ = 17, $^3J_{CH}$ = 4, Ru=C=)<br>119.8 (br, ≡C–Ph)<br>118.2 (br, =C(Me)Ph)<br>97.8 (qi, $^2J_{CP}$ = 25, ≡C–Ru)<br>53.8 (q, $CH_3$ phos)<br>8.0 (q, $CH_3$ vinyl) | $A_4$ | 123.1 (s) |
| **8a** | $\nu_{C\equiv C}$ 2096 (s)<br>$\nu_{C=C}$ 1671 (s), 1645 (m) | 4.22 (m, $CH_2$)<br>2.20 (s, $CH_3$ vinyl)<br>1.26 (t, $CH_3$ phos) | 379.4 (qi of q, $^2J_{CP}$ = 17, $^3J_{CH}$ = 4.5, Ru=C=)<br>124.2 (qi, $^3J_{CP}$ = 2.5, ≡C–Ph)<br>119.6 (qi, $^3J_{CP}$ = 2.5, =C(Me)Ph)<br>100.4 (qi, $^2J_{CP}$ = 25, ≡C–Ru)<br>62.9 (t, $CH_2$)<br>16.0 (q, $CH_3$ phos)<br>8.68 (q, $CH_3$ vinyl) | $A_4$<br>$A_2B_2$[h] | 118.9 (s)<br>$\delta_A$ = 125.0; $\delta_B$ = 116.4; $J_{AB}$ = 58.4 |

**Table 1 (Continued)**

| compd | IR[a,b] ($cm^{-1}$) | $^1H$ NMR[c,d] ($\delta$) | $^{13}C$ NMR[c,d] ($\delta$) | spin system | $^{31}P\{^1H\}$ NMR[c,e] ($\delta$) |
|---|---|---|---|---|---|
| **8b** | $\nu_{C\equiv C}$ 2099 (s) | 4.22 (m, $CH_2$) | 380.5 (qi of q, $^2J_{CP} = 17$, $^3J_{CH} = 4.5$, Ru=C=) | $A_4$ | 119.2 (s) |
| | $\nu_{C=C}$ 1672 (s), 1648 (s) | 2.34, 2.30 (s, $CH_3$ *p*-tol) | 124.5 (qi, $^3J_{CP} = 2.5$, ≡C−Ph) | $A_2B_2$[h] | $\delta_A = 125.2$; $\delta_B = 116.5$; $J_{AB} = 58.1$ |
| | | 2.17 (s, $CH_3$ vinyl) | 119.8 (qi, $^3J_{CP} = 2.5$, =C(Me)*p*-tol | | |
| | | 1.26 (t, $CH_3$ phos) | 99.0 (qi, $^2J_{CP} = 25$, ≡C−Ru) | | |
| | | | 63.3 (tm, $CH_2$) | | |
| | | | 21.3, 21.1 (q, $CH_3$ *p*-tol) | | |
| | | | 16.4 (q, $CH_3$ phos) | | |
| | | | 9.1 (q, $CH_3$ vinyl) | | |
| **8c** | $\nu_{C\equiv C}$ 2096 (s) | 4.20 (m, $CH_2$) | | $A_4$ | 119.2 (s) |
| | $\nu_{C=C}$ 1671 (s) | 1.76 (qi, $J_{PH} = 1.1$, $CH_3$ vinyl) | | $A_2B_2$[h] | $\delta_A = 122.5$; $\delta_B = 118.7$; $J_{AB} = 57.0$ |
| | | 1.29 (t, $CH_3$ phos) | | | |
| | | 1.12 (s, $CH_3$ $^t$Bu) | | | |
| **10aa** | $\nu_{C\equiv C}$ 2104 (s) | 4.18 (m, $CH_2$) | 382.2 (qi, $^2J_{CP} = 17$, Ru=C=) | $A_4$ | 115.3 (s) |
| | $\nu_{C=C}$ 1593 (s) | 1.23 (t, $CH_3$ phos) | 126.7 (qi, $^3J_{CP} = 3.0$, ≡C−Ph) | $A_2B_2$[h] | $\delta_A = 120.2$; $\delta_B = 114.1$; $J_{AB} = 57.0$ |
| | $\nu_{N=N}$ 1574 (m) | | 98.8 (qi, $^2J_{CP} = 26$, ≡C−Ru) | | |
| | | | 63.6 (t, $CH_2$) | | |
| | | | 16.2 (q, $CH_3$) | | |
| **10ab** | $\nu_{C\equiv C}$ 2107 (s) | 4.18 (m, $CH_2$) | | $A_4$ | 115.5 (s) |
| | $\nu_{C=C}$ 1595 (s) | 2.38 (s, $CH_3$ *p*-tol) | | | |
| | $\nu_{N=N}$ 1573 (m) | 1.30 (t, $CH_3$ phos) | | | |
| **10ac** | $\nu_{C\equiv C}$ 2104 (s) | 4.18 (m, $CH_2$) | 382.2 (qi of d, $^2J_{CP} = 17$, $^2J_{C^{15}N} = 7$, Ru=C=) | $A_4$ | 115.3 (s) |
| | $\nu_{C=C}$ 1592 (s) | 1.22 (t, $CH_3$) | 126.7 (qi, $^3J_{CP} = 3.0$, ≡C−Ph) | | |
| | | | 98.8 (qi, $^2J_{CP} = 26$, ≡C−Ru) | | |
| | | | 63.6 (t, $CH_2$) | | |
| | | | 16.2 (q, $CH_3$) | | |
| **10ad** | $\nu_{C\equiv C}$ 2103 (s) | 4.18 (m, $CH_2$) | 381.9 (qi of d, $^2J_{CP} = 17$, $^2J_{C^{15}N} = 7$, Ru=C=) | $A_4$ | 115.2 (s) |
| | $\nu_{C=C}$ 1593 (s) | 1.22 (t, $CH_3$) | 126.7 (qi, $^3J_{CP} = 3.0$, ≡C−Ph) | | |
| | | | 98.9 (qi, $^2J_{CP} = 25$, ≡C−Ru) | | |
| | | | 63.6 (t, $CH_2$) | | |
| | | | 16.2 (q, $CH_3$) | | |
| **11ab** | $\nu_{C\equiv C}$ 2096 (s) | 3.82 (m, $CH_2$)[g] | | $A_4$[g] | 142.6 (s) |
| | $\nu_{C=C}$ 1582 (s) | 2.40 (s, $CH_3$ *p*-tol) | | | |
| | $\nu_{N=N}$ 1565 (m) | 1.20 (t, $CH_3$ phos) | | | |
| **12a** | $\nu_{C\equiv C}$ 2104 (s) | 4.22 (m, $CH_2$) | 336.1 (qi, $^2J_{CP} = 17$, Ru=C=) | $A_4$ | 117.1 (s) |
| | $\nu_{C=C}$ 1673 (m), 1626 (m) | 1.16 (t, $CH_3$) | 124.3 (br, ≡C−Ph) | | |
| | | | 100.2 (qi, $^2J_{CP} = 25$, ≡C−Ru) | | |
| | | | 91.3 (br, =C(I)Ph) | | |
| | | | 62.8 (t, $CH_2$) | | |
| | | | 16.0 (q, $CH_3$) | | |
| **13a** | $\nu_{C\equiv C}$ 2083 (s) | 3.71 (m, $CH_2$)[g] | | $A_4$[g] | 141.6 (s) |
| | $\nu_{C=C}$ 1658 (m), 1633 (m) | 1.18 (t, $CH_3$) | | | |
| **14a** | $\nu_{C\equiv C}$ 2101 (s) | 4.36 (m, $CH_2$)[g] | 349.6 (qi, $^2J_{CP} = 17$, Ru=C=) | $A_4$[g] | 116.2 (s) |
| | $\nu_{C=C}$ 1620 (s) | 1.31 (t, $CH_3$) | 116.5 (qi, br, ≡C−Ph) | | |
| | | | 109.4 (br, =C($SR_1$)Ph) | | |
| | | | 99.4 (qi, $^2J_{CP} = 25$, ≡C−Ru) | | |
| | | | 64.0 (t, $CH_2$) | | |
| | | | 16.5 (q, $CH_3$) | | |
| **16** | | 6.37 (dm, CH vinyl)[g] | | $ABC_2$[g] | $\delta_A = 142.5$; $\delta_B = 137.3$; $\delta_C = 124.0$ |
| | | 4.25, 3.90 (m, $CH_2$) | | | $J_{AB} = 47.3$; $J_{AC} = 55.7$; $J_{BC} = 65.7$ |
| | | 1.28 (t, $CH_3$ $^t$Bu) | | | |
| | | 1.42, 1.31, 1.13 (t, $CH_3$ phos) | | | |
| **17** | $\nu_{C\equiv C}$ 2105 (s)[b] | 4.28 (m, $CH_2$ of $P(OEt)_3$)[g] | | $AB_4$[g] | $\delta_A = 134.3$; $\delta_B = 127.4$; $J_{AB} = 53.6$ |
| | | 3.77 (d, $CH_3$ of $P(OMe)_3$) | | | |
| | | 1.28 (t, $CH_3$ of $P(OEt)_3$) | | | |
| **18** | $\nu_{CN}$ 2134 (s)[b] | 4.22 (m, $CH_2$) | | $A_4$ | 127.3 (s) |
| | $\nu_{C\equiv C}$ 2100 (s) | 2.38 (s, $CH_3$ *p*-tol) | | | |
| | | 1.27 (t, $CH_3$ phos) | | | |
| **19** | $\nu_{CN}$ 2262 (w)[b] | 4.34 (m, $CH_2$)[g] | | $A_2B_2$[g] | $\delta_A = 126.6$; $\delta_B = 118.5$; |
| | | 2.45 (s, $CH_3$ *p*-tol) | | | |
| | | 1.39, 1.35 (t, $CH_3$ phos) | | | $J_{AB} = 60.0$ |

[a] In Nujol mull. [b] In KBr pellets. [c] At 25 °C in $CD_2Cl_2$, coupling constants in Hz. [d] Phenyl group signals are omitted. [e] Positive shift downfield from 85% $H_3PO_4$. [f] In $C_6D_6$. [g] In $(CD_3)_2CO$. [h] At −100 °C. [i] NMR data obtained at −30 °C.

**[Ru(C≡CR){=C=C(H)R}$P_4$]$BF_4$ (4,5) [R = Ph (a), *p*-Tol (b), $^t$Bu (c); P = $P(OMe)_3$ (4), $P(OEt)_3$ (5)].** To a solution of the appropriate $Ru(C\equiv CR)_2P_4$ complex (0.25 mmol) in 10 mL of $Et_2O$ cooled to −80 °C was added $HBF_4 \cdot Et_2O$ (0.25 mmol, 36 $\mu$L of 54% solution), and the reaction mixture was brought to 20 °C under stirring. A pink solid separated out, which was filtered and dried under vacuum; yield: ≥80%. Anal. Calcd for **4a**: C, 37.89; H, 5.34. Found: C, 37.72; H, 5.28. $\Lambda_M$ = 89.4 $\Omega^{-1}$ $mol^{-1}$ $cm^2$. Calcd for **5a**: C, 45.50; H, 6.78. Found: C, 45.38; H, 6.72. Mp: 137 °C decomp. $\Lambda_M$ = 92.3 $\Omega^{-1}$ $mol^{-1}$

cm$^2$. Calcd for **5b**: C, 46.54; H, 6.98. Found: C, 46.65; H, 6.83. Mp: 106 °C decomp. $\Lambda_M = 88.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **5c**: C, 42.57; H, 7.84. Found: C, 42.44; H, 7.77. Mp: 143–145 °C decomp. $\Lambda_M = 90.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]CF_3SO_3$ (5a$_1$).** Triflic acid ($CF_3SO_3H$; 0.25 mmol, 22 $\mu$L) was added to a solution of $Ru(C{\equiv}CPh)_2\{P(OEt)_3\}_4$ (0.25 mmol, 0.24 g) in 15 mL of diethyl ether cooled to −80 °C. The reaction mixture was brought to 20 °C under stirring, and, as the temperature increased, a pink solid began to separate out, which, after 1 h, was filtered and dried under vacuum; yield: ≥70%. Anal. Calcd: C, 44.04; H, 6.40. Found: C, 43.89; H, 6.29. Mp: 112–115 °C decomp. $\Lambda_M = 76.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(\eta^3\text{-}RC_3CHPh)\{PPh(OEt)_2\}_4]BF_4$ (6a).** This compound was obtained following a procedure similar to that used for the synthesis of **4** and **5** by reacting the bis(acetylide) $[Ru(C{\equiv}CPh)_2\{PPh(OEt)_2\}_4]$ (0.25 mmol, 0.27 g) with $HBF_4{\cdot}Et_2O$ (0.25 mmol, 36 $\mu$L of a 54% solution) in 10 mL of diethyl ether cooled to −80 °C. The reaction mixture was brought to 20 °C while stirring, and, as the temperature increased, an oil separated out, which slowly gave a yellow solid by addition of 1–2 mL of ethanol. After filtration, the product was crystallized from $CH_2Cl_2$ (5 mL)/diethyl ether (10 mL); yield: ≥90%. Anal. Calcd: C, 56.81; H, 6.04. Found: C, 56.72; H, 6.11.

**$[Ru(C{\equiv}CR)\{{=}C{=}C(Me)R\}P_4]CF_3SO_3$ (7,8) [R = Ph (a), *p*-Tol (b), $^t$Bu (c); P = $P(OMe)_3$ (7), $P(OEt)_3$ (8)].** Methyl triflate ($CF_3SO_3Me$) was added to a solution of the appropriate bis(acetylide) $Ru(C{\equiv}CR)_2P_4$ (0.25 mmol) in 10 mL of $Et_2O$ previously cooled to −80 °C. The mixture was brought to room temperature and was stirred until a purple solid separated out, which was filtered and dried under vacuum; yield: ≥80%. Anal. Calcd for **7a**: C, 37.39; H, 5.12. Found: C, 37.26; H, 5.04. Mp: 114–116 °C decomp. $\Lambda_M = 77.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **8a**: C, 44.56; H, 6.50. Found: C, 44.64; H, 6.49. Mp: 122 °C decomp. $\Lambda_M = 82.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **8b**: C, 45.55; H, 6.69. Found: C, 45.63; H, 6.55. Mp: 116 °C decomp. $\Lambda_M = 73.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **8c**: C, 41.79; H, 7.48. Found: C, 41.66; H, 7.51. Mp: 127 °C decomp. $\Lambda_M = 72.9\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}C(N{=}NR)Ph\}\{P(OEt)_3\}_4]BPh_4$ (10) [R = Ph, (aa); *p*-tol, (ab)].** A solid sample of the acetylide $Ru(C{\equiv}CPh)_2\{P(OEt)_3\}_4$ (0.25 mmol, 0.24 g) and solid arenediazonium tetrafluoroborate $RN_2^+BF_4^-$ (0.25 mmol) were mixed together and cooled to about −196 °C. Dichloromethane (10 mL) was added, and the resulting mixture was slowly brought to room temperature and stirred for 1 h. Removal of the solvent at reduced pressure gave an oil, which was treated with ethanol (10 mL) containing an excess of $NaBPh_4$ (0.5 mmol, 0.17 g). The resulting solution slowly yielded a green solid, which was filtered and crystallized from $CH_2Cl_2$/ethanol (5/15 mL); yield: ≥80%. Anal. Calcd for **10aa**: C, 60.38; H, 6.88; N, 2.01. Found: C, 60.23; H, 6.94; N, 1.97. $\Lambda_M = 50.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **10ab**: C, 60.64; H, 6.95; N, 1.99. Found: C, 60.43; H, 6.98; N, 1.96. Mp: 125–127 °C decomp. $\Lambda_M = 53.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}C(^{15}N{=}NPh)Ph\}\{P(OEt)_3\}_4]BPh_4$ (10ac).** The complex was prepared exactly as **10aa** using the labeled $PhN{\equiv}^{15}N^+BF_4^-$ arenediazonium salt; yield: ≥80%. Anal. Calcd: C, 60.34; H, 6.87; N, 2.08. Found: C, 60.19; H, 6.80; N, 1.99. $\Lambda_M = 49.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}C(^{15}N{=}NPh)Ph\}\{P(OEt)_3\}_4]BF_4$ (10ad).** This complex, too, was prepared like **10aa** by mixing together solid samples of $Ru(C{\equiv}CPh)_2[P(OEt)_3]_4$ (0.15 mmol, 0.145 g) and $PhN{\equiv}^{15}N^+BF_4^-$ (0.15 mmol, 0.031 g), cooling to about −196 °C, and adding 10 mL of $CH_2Cl_2$. After the reaction mixture had reached room temperature, it was stirred for 1 h and the solvent was removed at reduced pressure. The oil obtained was triturated with $Et_2O$ (10 mL) and THF (2 mL), giving, after 3–4 h of stirring, a green solid which was crystallized from $CH_2Cl_2$ and $Et_2O$ (3/10 mL); yield: ≥80%. Anal. Calcd: C, 47.59; H, 6.51; N, 2.50. Found: C, 47.38; H, 6.64; N, 2.42. $\Lambda_M = 91.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}(N{=}N\text{-}p\text{-}tol)Ph\}\{PPh(OEt)_2\}]BPh_4$ (11ab).** This compound was prepared exactly like the related **10** by reacting $Ru(C{\equiv}CPh)_2\{PPh(OEt)_2\}_4$ with *p*-toluenediazonium tetrafluoroborate at −196 °C in $CH_2Cl_2$; yield ≥70%. Anal. Calcd: C, 68.09; H, 6.37; N, 1.83. Found: C, 67.88; H, 6.22; N, 1.90. Mp: 73–75 °C. $\Lambda_M = 52.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{{=}C{=}C(I)Ph\}\{P(OEt)_3\}_4]I_3$ (12a) and $[Ru(C{\equiv}CPh)\{{=}C{=}C(I)Ph\}\{PPh(OEt)_2\}_4]I_3$ (13a).** An excess of $I_2$ (0.5 mmol, 4.17 mL of a 0.12 M solution in $Et_2O$) was added to a solution of the appropriate $Ru(C{\equiv}CPh)_2P_4$ acetylide (0.2 mmol) in 10 mL of diethyl ether, and the reaction mixture was stirred at room temperature for 2 h. The brown solid that formed was filtered and dried under vacuum; yield: ≥60%. Anal. Calcd for **12a**: C, 32.56; H, 4.78; I, 34.40. Found: C, 32.39; H, 4.50; I, 33.20. Mp: 92 °C decomp. $\Lambda_M = 69.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **13a**: C, 41.94; H, 4.40; I, 31.65. Found: C, 41.72; H, 4.47; I, 30.50. Mp: 81 °C decomp. $\Lambda_M = 64.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)[{=}C{=}C\{2,4\text{-}(NO_2)_2C_6H_3S\}Ph]\{P(OEt)_3\}_4]Cl$ (14a).** A solution of $2,4\text{-}(NO_2)_2C_6H_3SCl$ (0.20 mmol, 0.047 g) in 3 mL of $Et_2O$ was added via syringe to a solution of $Ru(C{\equiv}CPh)_2[P(OEt)_3]_4$ (0.20 mmol, 0.19 g) in 10 mL of $Et_2O$ cooled to −80 °C, and the reaction mixture was brought to room temperature. A purple oil began to separate out after 10 min of stirring, which slowly gave a microcrystalline solid in about 2 h. After filtration, the sample was dried under vacuum; yield: ≥55%. Anal. Calcd: C, 45.94; H, 6.12; N, 2.33. Found: C, 45.70; H, 5.97; N, 2.51. Mp: 98 °C decomp. $\Lambda_M = 65.2\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(\eta^3\text{-}PhC_3CHPh)\{P(OEt)_3\}_4]BF_4$ (15).** A solid sample of $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.25 g, 0.24 mmol) was placed in a 25-mL three-necked flask, and 10 mL of $CH_2Cl_2$ was added. The solution was vigorously stirred for 2 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with 10 mL of diethyl ether containing 2 mL of ethanol until a white solid separated out. By crystallization from ethanol (2 mL)/diethyl ether (10 mL) white microcrystals of the complex were obtained. Yield: ≥85%. Anal. Calcd: C, 45.50; H, 6.78. Found: C, 45.39; H, 6.82.

The related $BPh_4^-$ salt can easily be obtained using $NaBPh_4$ (0.16 g; 0.48 mmol) as a precipitating agent and crystallizing the product from ethanol. Anal. Calcd for $[Ru(\eta^3\text{-}PhC_3CHPh)\{P(OEt)_3\}_4]BPh_4$: C, 59.67; H, 7.12. Found: C, 59.43; H, 6.97.

**$[Ru\{\eta^3\text{-}(Ph)C_3C(H)^tBu\}\{P(OEt)_3\}_4]BF_4$ (16).** A solid sample of $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.20 mmol, 0.21 g) was added to a $CH_2Cl_2$ solution containing an excess of $^tBuC{\equiv}CH$ (2 mmol, 0.25 mL) cooled to −20 °C. The reaction mixture was first brought to 0 °C and stirred for 1 h and then to room temperature and stirred again for 30 min. Removal of solvent gave a white solid, which was triturated with $Et_2O$ and filtered. Crystallization from $CH_2Cl_2/Et_2O$ (1/10 mL) gave white microcrystals of the product; yield: ≥80%. Anal. Calcd: C, 44.06; H, 7.30. Found: C, 43.82; H, 7.38. Mp: 187 °C decomp. $\Lambda_M = 89.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)\{P(OMe)_3\}\{P(OEt)_3\}_4]BF_4$ (17).** A dichloromethane solution (10 mL) containing an excess of $P(OMe)_3$ (2 mmol, 0.25 mL) was cooled to −20 °C, and solid $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.20 mmol, 0.21 g) was added. The reaction mixture was brought to 0 °C in about 10 min and was stirred for 2 h. Removal of the solvent under reduced pressure gave an oil, which was triturated with diethyl ether. A pale yellow solid was obtained after vigorous stirring, which was filtered and crystallized from $CH_2Cl_2/Et_2O$ (1/10 mL); yield: ≥70%. Anal. Calcd: C, 39.01; H, 6.92. Found: C, 38.88; H, 6.98. Mp: 197–199 °C decomp. $\Lambda_M = 89.9\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(C{\equiv}CPh)(p\text{-}tolNC)\{P(OEt)_3\}_4]BPh_4$ (18).** A solid sample of $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.21 g, 0.20 mmol) was placed in a three-necked flask cooled to −20 °C and treated with 10 mL of $CH_2Cl_2$. An excess of *p*-tolyl isocyanide (2 mmol, 0.23 mL) was added to the resulting

**Table 2. Crystallographic Data for $[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt)_3\}_4]CF_3SO_3$ (8a)**

| | |
|---|---|
| formula | $C_{42}H_{73}F_3O_{15}P_4RuS$ |
| fw | 1132.05 |
| cryst syst | orthorhombic |
| space group | $P2_12_12_1$ |
| $a$, Å | 23.362(8) |
| $b$, Å | 12.072(4) |
| $c$, Å | 20.350(6) |
| $V$, Å$^3$ | 5739(3) |
| $Z$ | 4 |
| $D_{calcd}$, g/cm$^3$ | 1.310 |
| temp, °C | 22 |
| $2\theta$ range, deg | 6–54 |
| $\mu$, cm$^{-1}$ | 4.9 |
| no. of unique data collcd | 12491 |
| no. params refined | 514 |
| R1 (on $F$) | 0.0717 (6604 $4\sigma$ data),<br>0.1559 (12 491 data) |
| wR2 (on $F^2$) | 0.2284 (12 491 data) |

solution, and the reaction mixture was slowly brought to 0 °C and was stirred for 1 h. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (5 mL) containing an excess of $NaBPh_4$ (0.4 mmol, 0.14 g). When the resulting solution, cooled to 0 °C, was stirred vigorously, a yellow solid separated out, which was filtered and crystallized from ethanol; yield: ≥70%. Anal. Calcd: C, 58.98; H, 7.12; N, 1.08; Found: C, 59.12; H, 7.00; N, 1.12. Mp: 197 °C decomp. $\Lambda_M = 49.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**$[Ru(p\text{-}tolCN)_2\{P(OEt)_3\}_4](BPh_4)_2$ (19).** A dichloromethane solution (10 mL) containing an excess of *p*-toluonitrile (2 mmol, 0.24 mL) was cooled to −20 °C, and solid $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.2 mmol, 0.21 g) was added. The reaction mixture was slowly brought to 0 °C, was stirred for 2 h, and was then evaporated to dryness. The oil obtained was treated with 5 mL of ethanol containing an excess of $NaBPh_4$ (0.4 mmol, 0.14 g), and the resulting solution was cooled to −25 °C. After 1−2 days, yellow microcrystals separated out, which were filtered and dried under vacuum. Yield: ≥70%. Anal. Calcd: C, 64.51; H, 7.01; N, 1.71. Found: C, 64.32; H, 6.88; N, 1.85. Mp: 178 °C decomp. $\Lambda_M = 118.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

**Reactions with $Cl^-$ and $Br^-$.** A solution containing an excess of the appropriate lithium halogenide (2 mmol) in ethanol/dichloromethane (7:3 mL) was cooled to −20 °C, and solid $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (0.2 mmol, 0.21 g) was added. The reaction mixture was slowly brought to 0 °C and then to room temperature. After 1 h of stirring, the solvent was removed under reduced pressure to give an oil, which was treated with 3 mL of ethanol. When the resulting solution was stirred vigorously, a little amount of a yellow solid separated out, which was filtered and identified as the bis(acetylide) complex $Ru(C{\equiv}CPh)_2[P(OEt)_3]_4$ (**2a**) by IR and NMR. The yield was about 20%. The bis(acetylide) compound was also obtained (in low yield) by treatment of $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OMe)_3\}_4]BF_4$ with an excess of LiCl in ethanol/dichloromethane solution.

**X-ray Structure Determination of $[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt)_3\}_4]CF_3SO_3$ (8a).** X-ray work was carried out with a Philips PW 1100 diffractometer using Mo Kα ($\lambda$ = 0.710 69 Å) radiation. The crystallographic data are summarized in Table 2. No loss of intensity of standard reflections was detected during data collection. Data were processed with the peak profile analysis procedure and corrected for Lorentz, polarization, and absorption effects.

The structure was solved by automated Patterson and difference Fourier techniques. Full-matrix least-squares refinement on $F^2$ was used with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of most terminal methyl groups and anion atoms. The hydrogen atoms were refined isotropically in their calculated riding positions. Complex neutral-atom scattering factors were used, and anomalous dispersion corrections were applied to all non-hydrogen atoms. Calculations were carried out on GOULD POWERNODE 6040 and ENCORE 91 computers using SHELXS86[16] and SHELXL92[17] programs. Other crystallographic programs used have been cited elsewhere.[18] Fractional atomic coordinates are listed in Table 3, and selected bond distances and angles are given in Table 4.

**Kinetic Measurements.** The kinetics of the reaction of vinylidene $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (**5a**) to enynyl $[Ru(\eta^3\text{-}PhC_3CHPh)\{P(OEt)_3\}_4]BF_4$ (**15**) derivative was studied by $^{31}P\{^1H\}$ NMR, monitoring the intensity decrease of the signal of compound **5a**. No significant signals other than those of **5a** (sharp singlet near 118 ppm) and **15** ($ABC_2$ multiplet: $\delta_A$ 137.9 ppm, $\delta_B$ 136.0 ppm, $\delta_C$ 121.1 ppm, $J_{AB}$ = 49.0 Hz, $J_{AC}$ = 57.9 Hz, $J_{BC}$ = 63.1 Hz) could be observed during the course of reaction. In typical kinetic runs, the initial concentration of **5a** was $2.0 \times 10^{-2}$ mol/L in $CDCl_3$, and the NMR tube was thermostated to 15 °C; the $[PhC{\equiv}CH]$:[**5a**] ratio varied from 0 to about 15. Preliminary measurements were made at different initial concentrations of **5a** and/or temperatures to establish both the kinetic order of the reaction and the best $t_{1/2}$ conditions for following the reaction. First-order rate constants ($s^{-1}$) were obtained by a linear least-squares fitting of ln[**5a**] plotted against time using standard computer software.

## Results and Discussion

**Preparation of Bis(acetylide) Complexes.** Dichloro complexes $RuCl_2P_4$ (P = $P(OMe)_3$, $P(OEt)_3$, and $PPh(OEt)_2$) quickly reacted with excess lithium acetylides $Li^+RC{\equiv}C^-$ (R = Ph, *p*-tol, $^tBu$) in THF to give the bis(alkynyl) derivatives $Ru(C{\equiv}CR)_2P_4$ (**1**−**3**) as yellow powders in 30−40% yield (eq 1). Subsequent crystallization afforded analytically pure, air-stable crystals of the complexes, which were characterized by IR, $^1H$, $^{31}P$, and $^{13}C$ NMR data (Table 1). The reaction between $RuCl_2\{P(OEt)_3\}_4$ and phenyl acetylide at room temperature was also followed by IR spectra in the 2200−2000 $cm^{-1}$ region. A $\nu_{C\equiv C}$ band at 2040 $cm^{-1}$ initially appeared which was predominant for the low $Ru:PhC{\equiv}C^-$ ratio (1:1) and was reasonably attributed to the mono(acetylide) $RuCl(C{\equiv}CPh)P_4$ complex. As the reaction proceeded in excess $Li^+PhC{\equiv}C^-$, the band at 2040 $cm^{-1}$ was substituted by two bands at 2073 and 2051 $cm^{-1}$, which were of comparable intensity and always present for all $Ru:RC{\equiv}C^-$ ratios. From this solution only the bisacetylide complex **2** with a $\nu_{C\equiv C}$ band at 2073 $cm^{-1}$ (THF) was isolated as a solid, and therefore no formulation of the other acetylide species with $\nu_{C\equiv C}$ at 2051 $cm^{-1}$ could be proposed.

$$RuCl_2P_4 \xrightarrow[\text{THF}]{RC\equiv C^-,\ \text{excess}} \underset{\mathbf{(1{-}3)}}{Ru(C{\equiv}CR)_2P_4} \qquad (1)$$

$$P = P(OMe)_3,\ \mathbf{1};\ P(OEt)_3,\ \mathbf{2},\ PPh(OEt)_2,\ \mathbf{3}$$

$$R = Ph,\ \mathbf{a};\ p\text{-tolyl},\ \mathbf{b};\ {}^tBu,\ \mathbf{c}$$

The infrared spectra of alkynyl complexes **1**−**3** showed only one $\nu_{C\equiv C}$ band at 2088−2069 $cm^{-1}$, suggesting a mutually *trans* arrangement of the two acetylide ligands. This geometry was confirmed by $^{31}P\{^1H\}$ NMR spectra, which gave a sharp singlet between +30 and −90 °C.

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[16] Sheldrick, G. M. *SHELXS86, A Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

[17] Sheldrick, G. M. *SHELXL92, A Program for Structure Refinement*; University of Göttingen: Göttingen, Germany, 1992.

[18] Bacchi, A.; Ferranti, F.; Pelizzi, G. *Acta Crystallogr.* **1993**, *1163*, C49.

**Table 3. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters (Å × $10^4$) (One-Third Trace of the Diagonalized Matrix) for Non-Hydrogen Atoms**

| atom | *x*/*a* | *y*/*b* | *z*/*c* | $U_{eq}$ |
|---|---|---|---|---|
| Ru | 9155.7(2) | 3858.7(5) | 94.4(3) | 513(2) |
| P1 | 9907(1) | 4725(2) | −468(1) | 636(7) |
| P2 | 8569(1) | 2628(2) | 675(1) | 740(8) |
| P3 | 9421(1) | 4685(2) | 1090(1) | 736(8) |
| P4 | 8810(1) | 3119(2) | −897(1) | 634(7) |
| O1 | 10451(2) | 4842(5) | −4(3) | 853(22) |
| O2 | 9764(3) | 5940(5) | −718(4) | 911(26) |
| O3 | 10141(3) | 4230(6) | −1135(3) | 822(23) |
| O4 | 7929(3) | 3067(7) | 771(4) | 1019(29) |
| O5 | 8519(4) | 1483(7) | 301(4) | 1109(32) |
| O6 | 8731(4) | 2322(7) | 1394(3) | 984(29) |
| O7 | 9718(4) | 5870(7) | 1110(4) | 994(30) |
| O8 | 9831(3) | 4070(7) | 1583(3) | 956(28) |
| O9 | 8856(3) | 4830(6) | 1533(3) | 939(27) |
| O10 | 8154(3) | 2737(6) | −933(4) | 891(26) |
| O11 | 9144(3) | 2089(6) | −1177(3) | 943(26) |
| O12 | 8868(3) | 4025(6) | −1458(3) | 790(22) |
| C1 | 8612(3) | 5016(6) | 2(4) | 614(26) |
| C2 | 8208(4) | 5785(8) | −17(4) | 748(31) |
| C3 | 7816(5) | 5866(10) | 548(6) | 1115(50) |
| C4 | 8098(4) | 6571(7) | −574(5) | 776(34) |
| C5 | 7695(6) | 7385(10) | −523(7) | 1166(54) |
| C6 | 7623(8) | 8048(14) | −1095(12) | 1664(95) |
| C7 | 7874(7) | 7906(14) | −1679(10) | 1445(75) |
| C8 | 8283(8) | 7219(12) | −1667(7) | 1402(71) |
| C9 | 8406(6) | 6519(11) | −1149(7) | 1148(52) |
| C10 | 9752(3) | 2553(6) | 199(4) | 620(26) |
| C11 | 10091(3) | 1802(7) | 256(4) | 665(29) |
| C12 | 10475(4) | 862(7) | 256(5) | 709(31) |
| C13 | 10667(5) | 296(12) | −332(7) | 1147(52) |
| C14 | 11034(7) | −508(11) | −309(7) | 1245(64) |
| C15 | 11241(7) | −897(12) | 247(10) | 1337(70) |
| C16 | 11077(8) | −431(16) | 830(11) | 1660(90) |
| C17 | 10683(7) | 472(11) | 828(7) | 1282(63) |
| C18 | 10980(5) | 5368(15) | −191(7) | 1395(63) |
| C19 | 11431(10) | 5061(21) | 197(13) | 2294(104) |
| C20 | 10039(8) | 6464(12) | −1273(9) | 1515(78) |
| C21 | 9954(11) | 7601(24) | −1312(13) | 2263(102) |
| C22 | 10469(5) | 3193(11) | −1197(5) | 1002(44) |
| C23 | 10607(7) | 3030(17) | −1870(8) | 1597(82) |
| C24 | 7516(7) | 2694(21) | 1189(13) | 2381(136) |
| C25 | 6997(11) | 3168(23) | 1091(13) | 2150(101) |
| C26 | 8223(8) | 566(16) | 530(11) | 1833(103) |
| C27 | 8574(10) | −550(21) | 352(12) | 2011(90) |
| C28 | 9138(9) | 1579(16) | 1629(7) | 1563(80) |
| C29 | 9025(10) | 1563(20) | 2375(11) | 1993(89) |
| C30 | 9453(7) | 6809(11) | 838(8) | 1374(68) |
| C31 | 9715(12) | 7880(28) | 1036(17) | 2580(132) |
| C32 | 10422(7) | 3877(14) | 1493(6) | 1209(57) |
| C33 | 10623(10) | 3442(20) | 2134(12) | 2454(136) |
| C34 | 8897(7) | 5318(15) | 2200(6) | 1409(71) |
| C35 | 8341(11) | 5305(22) | 2461(12) | 2068(91) |
| C36 | 7665(5) | 3386(12) | −865(8) | 1144(55) |
| C37 | 7185(6) | 2794(17) | −934(11) | 1674(94) |
| C38 | 8945(12) | 1071(13) | −1341(9) | 2175(136) |
| C39 | 9313(8) | 366(14) | −1718(10) | 1790(96) |
| C40 | 8713(8) | 3736(15) | −2154(5) | 1433(71) |
| C41 | 8958(7) | 4566(15) | −2547(9) | 1517(56) |
| C42 | 2528(10) | 6201(21) | 7868(11) | 1874(73) |
| F1 | 2383(9) | 6054(19) | 7271(11) | 2985(49) |
| F2 | 2788(8) | 5238(19) | 7851(10) | 2985(49) |
| F3 | 3037(9) | 6350(19) | 8123(10) | 2985(49) |
| S | 1974(2) | 6251(5) | 8434(3) | 1564(15) |
| O13 | 2185(7) | 6320(17) | 9093(9) | 2271(66) |
| O14 | 1434(6) | 6426(12) | 8159(7) | 1838(47) |
| O15 | 1999(12) | 4997(23) | 8301(12) | 3085(106) |

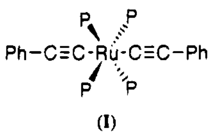
**Table 4. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Ru−P1 | 2.342(2) | P3−O7 | 1.590(8) |
| Ru−P2 | 2.342(3) | P3−O8 | 1.573(8) |
| Ru−P3 | 2.341(3) | P3−O9 | 1.608(8) |
| Ru−P4 | 2.350(2) | P4−O10 | 1.602(7) |
| Ru−C1 | 1.898(7) | P4−O11 | 1.575(8) |
| Ru−C10 | 2.114(8) | P4−O12 | 1.586(7) |
| P1−O1 | 1.590(6) | C1−C2 | 1.323(11) |
| P1−O2 | 1.587(7) | C2−C3 | 1.473(15) |
| P1−O3 | 1.580(7) | C2−C4 | 1.502(14) |
| P2−O4 | 1.598(8) | C10−C11 | 1.209(11) |
| P2−O5 | 1.582(9) | C11−C12 | 1.446(12) |
| P2−O6 | 1.557(7) | | |
| | Angles | | |
| C1−Ru−C10 | 179.2(3) | Ru−P1−O1 | 110.4(2) |
| P4−Ru−C10 | 91.7(2) | Ru−P2−O6 | 118.8(3) |
| P4−Ru−C1 | 88.0(2) | Ru−P2−O5 | 110.7(3) |
| P3−Ru−C10 | 93.2(2) | Ru−P2−O4 | 113.6(3) |
| P3−Ru−C1 | 87.1(2) | Ru−P3−O9 | 108.3(3) |
| P3−Ru−P4 | 174.8(1) | Ru−P3−O8 | 120.8(3) |
| P2−Ru−C10 | 82.1(2) | Ru−P3−O7 | 121.4(3) |
| P2−Ru−C1 | 97.2(2) | Ru−P4−O12 | 109.0(2) |
| P2−Ru−P4 | 89.5(1) | Ru−P4−O11 | 116.1(3) |
| P2−Ru−P3 | 89.4(1) | Ru−P4−O10 | 118.5(3) |
| P1−Ru−C10 | 83.6(2) | Ru−C1−C2 | 174.9(7) |
| P1−Ru−C1 | 97.2(2) | C1−C2−C4 | 126.0(8) |
| P1−Ru−P4 | 90.4(1) | C1−C2−C3 | 117.8(8) |
| P1−Ru−P3 | 91.9(1) | C3−C2−C4 | 116.2(9) |
| P1−Ru−P2 | 165.7(1) | Ru−C10−C11 | 179.6(7) |
| Ru−P1−O3 | 120.7(3) | C10−C11−C12 | 173.8(9) |
| Ru−P1−O2 | 114.2(3) | | |

Furthermore, in the $^{13}C\{^1H\}$ spectra, the $C_\alpha$ and $C_\beta$ signals of the two equivalent acetylides were present as quintets: at $\delta$ 125.0−88.2 ppm the $C_\alpha$ had an appreciable $^2J_{CP}$ of about 20 Hz, while the $C_\beta$ at $\delta$ 113.4−117.8 ppm had a $^3J_{CP}$ of about 1.6 Hz. A similar *trans* geometry[19] was observed in the recently reported Ru(II) bis(acetylide) complexes of the type $Ru(C{\equiv}CR)_2(PMe_3)_4$,[7a] $Ru(CO)_2(PEt_3)_2[(C{\equiv}C)_nR]_2$ ($n = 1, 2$),[7f] and $Ru(dppm)_2[(C{\equiv}C{-}C{\equiv}CCPh_2(OSiMe_3)]_2$[20] (dppm = $Ph_2PCH_2PPh_2$), whose $\nu_{C\equiv C}$ frequencies fitted those of our (**1**−**3**) derivatives very well.

The solid-state structure of $Ru(C{\equiv}CPh)_2\{P(OEt)_3\}_4$ (**2a**) was investigated by the X-ray diffraction technique, an experiment that was only partially successful. The compound crystallized in the tetragonal space group $I4_1/acd$, with $a = 20.332(8)$ Å, $c = 24.071(9)$ Å, and $Z = 8$. After many unsuccessful attempts, the structure was solved by application of direct methods and was refined by the full-matrix least-squares procedures to an $R$ value of 0.07. In spite of this quite satisfactory value, structure analysis was greatly hampered by disorder problems involving the phosphite ligands. Because the space group has 32 general positions, the eight molecules per unit cell have to be constrained at special positions.

Although the disorder does not allow a detailed description, there is no doubt that the basic structure is correct and that the complex is monomeric, with the ruthenium atom surrounded by four phosphite molecules and two acetylide groups in a distorted *trans* octahedral geometry (**I**).



(**I**)

**Protonation and Methylation of $Ru(C{\equiv}CR)_2P_4$.** Complexes **1** and **2**, containing $P(OMe)_3$ and $P(OEt)_3$

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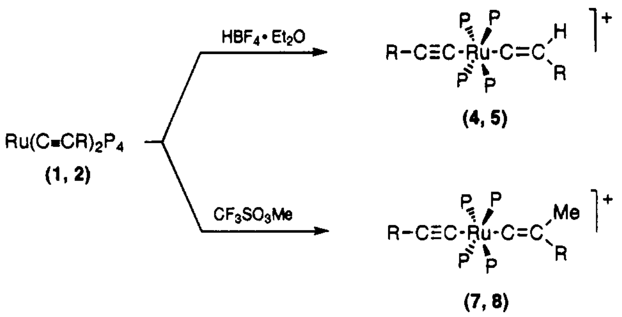
[19] Examples of *cis*-bis(acetylide) Ru(II) complexes that also catalyze the dimerization of alkynes have also recently been reported (refs 7a,b).

[20] Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 651.

**Scheme 1**[a]



[a] Legend: P = $P(OMe)_3$ (**1**, **4**, **7**), and $P(OEt)_3$ (**2**, **5**, **8**); R = Ph (**a**), *p*-tolyl (**b**), ${}^tBu$ (**c**).

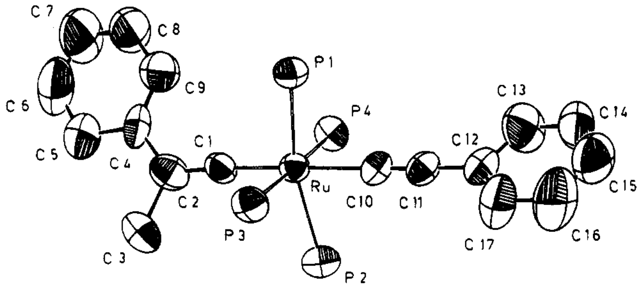


**Figure 1.** ORTEP diagram and numbering scheme for $[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt)_3\}_4]^+$ (cation of **8a**). OEt moieties and H atoms have been omitted for clarity; thermal ellipsoids are drawn at 50% probability level.

ligands, reacted with $HBF_4{\cdot}Et_2O$ and $CF_3SO_3Me$ in diethyl ether to afford the vinylidene–acetylide[21,22] derivatives $[Ru(C{\equiv}CR)\{{=}C{=}C(R_1)R\}P_4]^+$ (**4**, **5**, **7**, **8**) (Scheme 1) as stable pink or purple solids.

In contrast, the protonation reaction of related $PPh(OEt)_2$ derivatives **3** did not afford vinyldene complexes but rather an oily product which, after solidification, turned out to be the already known[11c] $[Ru\{\eta^3\text{-}RC_3C(H)R\}\{PPh(OEt)_2\}_4]^+$ (**6**) derivative (eq 2). Methylation

$$\underset{(\mathbf{3})}{Ru(C{\equiv}CR)_2[PPh(OEt)_2]_4} \xrightarrow{HBF_4{\cdot}Et_2O} \underset{(\mathbf{6})}{[Ru\{\eta^3\text{-}RC_3C(H)R\}\{PPh(OEt)_2\}_4]^+} \quad (2)$$

of **3** with $CF_3SO_3Me$ also did not afford vinylidene species, only an intractable oil whose NMR spectra excluded the presence of enynyl derivativers such as those forming in the protonation reaction.

While vinylidene complexes **4** and **5** were unstable in solution (see below), related methyl–vinylidene derivatives **7** and **8** did yield suitable crystals for X-ray analysis from their solutions. The X-ray analysis carried out on $[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt)_3\}_4]CF_3SO_3$ (**8a**) showed the structure to consist of discrete, clearly separated cations and anions. In the cation, which is shown in the ORTEP diagram of Figure 1, the ruthenium atom lies in a six-coordinated environment comprising four phosphorus atoms from the phosphite molecules and two carbon atoms from the vinylidene and acetylide groups. The donor atoms adopt a distorted octahedral arrangement with the two carbon-donor ligands *trans* to each other. Both of these ligands coordinate to ruthenium in an essentially linear mode, thus giving rise to a somewhat unusual nearly linear array of six atoms, C2–C1–Ru–C10–C11–C12, in which the bond angles range from 173.8 to 179.6°, the greatest deviations from linearity occurring at the two ends. This linkage is nearly orthogonal to the best plane through the four P atoms (88.1°). The distorted octahedral nature is also seen in the least-squares planes drawn through the three sets of donor atoms forming the coordination planes of the octahedron. While the two planes of the $RuP_2C_2$ sets indicate an almost planar arrangement, the plane for the $RuP_4$ set shows a marked deviation from planarity, describing a flattened tetrahedron.

Another parameter also characterizing departure from regular octahedral geometry is the P1–Ru–P2 angle of 165.7(1)°, which should be 180°. The four Ru–P bond distances are nearly equal, and the average value of 2.344(2) Å is somewhat shorter than the single Ru–P value of 2.43 Å calculated from Pauling's covalent radii, but it is almost identical to the value of 2.35(1) Å found in *trans*-bis(acetone hydrazone)tetrakis(trimethyl phosphite)ruthenium(II) bis(tetraphenylborate),[23] the only structurally characterized ruthenium complex containing a pair of mutually *trans* phosphite ligands. The Ru–C1 bond distance to the vinylidene ligand is 1.898(7) Å, only slightly longer than the corresponding bond in related compounds (see below), while the C1–C2 distance of 1.32(1) Å is typical for a vinylidene bond. As pointed out in a recent review[1a] on the organometallic chemistry of vinylidene and related unsaturated carbenes, the metal–carbon bond in mononuclear vinylidene complexes is consistent with a bond order of about 2 and the C=C bond corresponds to an order between 2 and 3, as predicted by theory.

Concerning ruthenium derivatives, the Ru–C and C=C bond distances in the complexes characterized so far range from 1.82 to 1.88 Å and from 1.22 to 1.34 Å, respectively.[1a,2c,f] An Ru–C (vinylidene) bond as short as 1.749(5) Å has also been reported.[24] Like most vinylidene complexes, the ligand is nearly linear, with an Ru–C1–C2 angle of 174.9(7)°. The orientation of the vinylidene ligand with respect to the phosphite moieties can be defined by the angles its least-squares plane forms with the four Ru–P bonds, *i.e.*, −36.3(2)° (P1), 37.1(2)° (P2), −51.6(2)° (P3), and 53.4(2)° (P4). The Ru–C10 bond to the acetylide ligand of 2.114(8) Å is consistent with a single bond from ruthenium(II) to an sp carbon. This value as well as that of the C10–C11 triple bond, 1.21(1) Å, falls at the long end of the range observed for phenylethynyl ruthenium derivatives:[25] Ru–C, 2.01–2.12 Å; C≡C, 1.17–1.21 Å. The Ru–C≡C–C linkage is almost exactly linear at C10

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[21] For theoretical studies on protonation and methylation of vinylidene complexes see: Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

[22] The first alkynyl–vinylidene complex has recently been reported for rhodium: Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315.

[23] Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1974**, 2406.

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(179.6(7)°) and only slightly bent at C11 (173.8(9)°). Atoms C10–C17 are coplanar to within 0.02 Å, and their mean plane makes angles of 116.2(4) and 26.0(4)° with the two RuP2C2 coordination planes.

In the absence of chiral elements in the molecule, the chirality of the crystal structure (the space group $P2_12_12_1$ is free of reflective elements) must be ascribed to the spatial arrangement of the molecules. Packing is determined mainly by van der Waals interactions, with normal intermolecular distances. The shortest contact between non-hydrogen atoms is C19···O13 ($x + 1, y, z - 1$), 3.23(3) Å.

The spectroscopic properties of the methyl–vinylidene complexes **7** and **8** are reported in Table 1 and suggest a geometry in solution like that in the solid state. Characteristic features of IR spectra are the $\nu_{C\equiv C}$ band of the alkynyl ligand at 2099–2095 cm$^{-1}$ and those due to $\nu_{C=C}$ of the vinylidene ligand[1-3] at 1672–1645 cm$^{-1}$. In the $^1$H NMR spectra, vinylidenes **7** and **8** show the signal of the =C=C(Me)R methyl group as a sharp singlet at $\delta$ 2.15–2.20 ppm for the Ph and *p*-tol complexes. The $^t$Bu derivative **8c** shows a sharp quintet with a small coupling constant of 1.1 Hz at $\delta$ 1.76 ppm, probably due to coupling with the four phosphorus atoms.

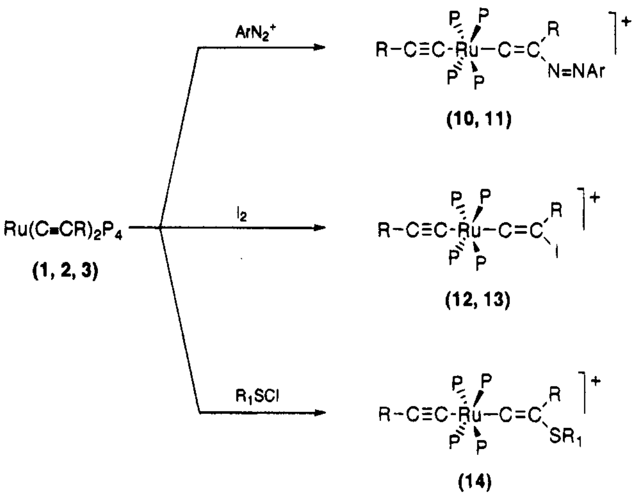
The $^{13}$C spectra of **7** and **8** display the characteristic highly deshielded Ru=*C* carbene carbon resonance at $\delta$ 383.1–379.4 ppm as a quintet of quartets, due to coupling with all of the four phosphorus atoms ($^2J_{CP}$ of 17 Hz) and the three methyl protons of the Me substituent ($^3J_{CH}$ near 4 Hz), and the vinylic =*C*(Me)R carbon resonance in the $\delta$ 120–118 ppm region as a sharp quintet, with a smaller $^3J_{CP}$ coupling constant of 2.5 Hz. Note that both vinylidene carbon atoms Ru=$C_\alpha$=$C_\beta$ should be coupled with the methyl protons of the Me substituent, but coupling is only observed with the carbene Ru=$C_\alpha$= with a $^3J_{CH}$ value of 4.0–4.5 Hz, while in the vinylic carbon atom, =$C_\beta$(Me)R, the $^2J_{CH}$ is probably too small to be detected.

The ethynyl carbons of the RC≡C ligand also appear in the $^{13}$C spectra as quintets due to $^{31}$P coupling at $\delta$ 97.8–100.4 ppm with $J_{CP}$ of 25 Hz for $C_\alpha$ and at $\delta$ 119.8–124.5 ppm with a smaller $^3J_{CP}$ of about 2.5 Hz for $C_\beta$. In the proton-coupled $^{13}$C spectra, the methyl substituent of the vinylidene ligand =C=C(Me)R is also present as a quartet at $\delta$ 8.0–9.1 ppm with a typical $^1J_{CH}$ of 132 Hz.

In the temperature range from +30 to −70 °C, the $^{31}$P{$^1$H} NMR spectra of vinylidenes **7** and **8** appear as sharp singlets at $\delta$ 123.1–118.9 ppm, but at temperatures below −70 °C, the singlet broadens and at −90 °C resolves into two triplets, indicating that each of the two pairs of phosphorous atoms are magnetically equivalent. The spectra can also be simulated using an $A_2B_2$ model with the parameters reported in Table 1. These results may be interpreted on the basis of the existence of a *trans* octahedral geometry in which the inequivalence of the phosphorus atoms at low temperature may be due to a restricted vinylidene rotation which makes each of the two pairs of P atoms magnetically equivalent.

The spectroscopic properties of vinylidenes **4** and **5** were measured in solution, kept below −20 °C to avoid the formation of new species, and are reported in Table 1. These data confirm the formulation proposed for the complexes, showing the $\nu_{C\equiv C}$ of the alkynyl at 2102–2097 cm$^{-1}$ and the $\nu_{C=C}$ of the vinylidene ligand at 1685–1633 cm$^{-1}$ in the infrared spectra. In the $^1$H NMR spectra, the vinylic proton [Ru=C=C(*H*)R] is present at $\delta$ 5.98–5.25 ppm as a quintet due to coupling with the four P atoms ($J_{PH}$ about 1.5 Hz), while in the $^{13}$C spectra the characteristic $C_\alpha$ of the vinylidene ligand is observed as a quintet at $\delta$ 379.8 ppm (**4a**) and at $\delta$ 377.4 ppm (**5a**) with $^2J_{CP}$ = 17 Hz. The vinylic carbon atom =C=$C_\beta$(H)R is also observed as a CH resonance at $\delta$ 112.6–117.6 ppm ($^1J_{CH}$ = 150 Hz), while the $C_\alpha$ and $C_\beta$ of the alkynyl ligand RuC≡CR appear as quintets near $\delta$ 78–100 and $\delta$ 120–125 ppm, with $J_{CP}$ coupling constants of 25 and 2 Hz, respectively. Finally, the $^{31}$P spectra for **4** and **5** suggest a *trans* geometry in solution like that proposed for related methyl–vinylidene derivatives **7** and **8**. In fact, the sharp singlet observed from +30 to −70 °C begins to broaden as the temperature is further lowered and appears at −100 °C as an $A_2B_2$ multiplet, in agreement with a slight distortion of *trans* geometry at low temperatures.

**Scheme 2**[a]



[a] Legend: P = P(OEt)$_3$ (**10**, **12**, **14**) and PPh(OEt)$_2$ (**11**, **13**); R = Ph (**a**); Ar = Ph, *p*-tol; R$_1$ = 2,4-(NO$_2$)$_2$C$_6$H$_3$.

**Reactions with Other Electrophiles.** The reactions of bis(acetylide) Ru(C≡CR)$_2$P$_4$ with other electrophilic reagents were studied. Results are summarized in Scheme 2. Aryldiazonium cations react with **2** and **3** in CH$_2$Cl$_2$ to give diazo–vinylidene [Ru(C≡CR){=C=C(N=NAr)R}P$_4$]$^+$ cations **10** and **11**, which can be isolated as BPh$_4^-$ or BF$_4^-$ salts.[26] The compounds are stable both in solid state and in solution of polar organic solvents, where they behave as 1:1 electrolytes. Their spectroscopic properties, reported in Table 1, confirm the formulation proposed. The IR spectra show the $\nu_{C\equiv C}$ of the alkynyl groups at 2104–2096 cm$^{-1}$, while the two bands at 1593–1582 and 1574–1565 cm$^{-1}$ are reasonably assigned to the $\nu_{C=C}$ and $\nu_{N=N}$ modes of the =C=C(N=NAr)R ligand.[27,28] Diagnostic for the pres-

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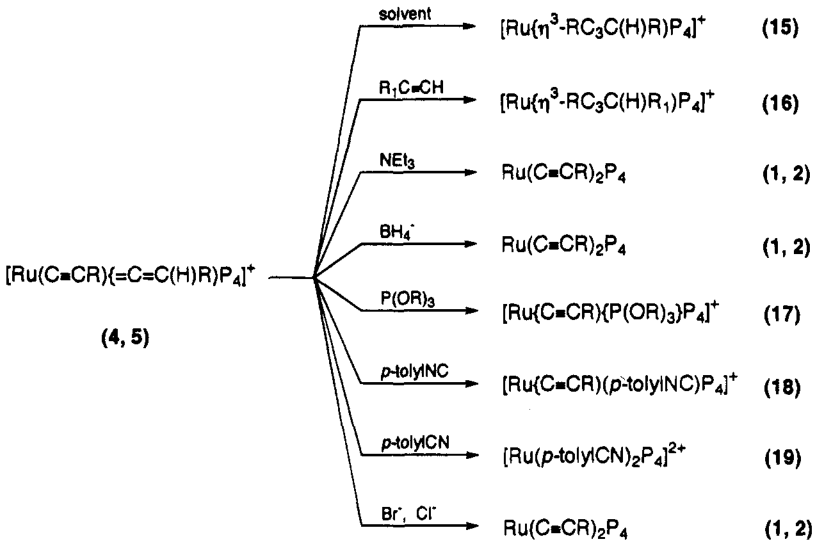
[26] P(OMe)$_3$ derivative **1** also reacted with aryldiazonium cations to give diazo–vinylidene, but the oily nature of the product prevented its complete characterization.

[27] Bruce, M. I.; Humphrey, M. G.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *321*, 91.

[28] In the labeled compound **10ad** the $\nu_{^{15}N=N}$ band cannot be unambiguously assigned owing to the presence in the expected region (1500–1550 cm$^{-1}$) of other intense absorptions, and comparison with the IR spectrum of **10aa** shows only the disappearance of a medium intensity band at 1574 cm$^{-1}$ attributed to $\nu_{N=N}$.

**Scheme 3**



ence of diazo–vinylidene was the highly deshielded quintet of carbene carbon resonances $C_\alpha$ near $\delta$ 382 ppm, with $^2J_{CP}$ of 17 Hz, which is split into a quintet of doublets by coupling with $^{15}N$ ($^2J_{C^{15}N}$ = 7 Hz) in the labeled $[Ru(C{\equiv}CPh)\{{=}C{=}C(^{15}N{=}NPh)Ph\}\{P(OEt)_3\}_4]BF_4$ (**10ac**) derivative. The $C_\beta$ vinylic $=C(N{=}NAr)R$ resonances could not be assigned, even in $BF_4^-$ compound **10ac**, probably because they were masked by the phenyl carbon signals. Instead, the $C_\alpha$ and $C_\beta$ of the alkynyl RC≡C ligand appear as quintets at $\delta$ 98.8 and $\delta$ 126.7 ppm (**10**), with $J_{CP}$ of 26 and 3 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectra of the diazo–vinylidene complexes **10** and **11** show a behavior similar to that of the other vinylidenes, showing a sharp singlet up to −70 °C which then broadens and resolves into an $A_2B_2$ multiplet at −90 °C. On this basis, a *trans* geometry with inequivalent P *nuclei* at low temperature can reasonably be proposed for these complexes.

Iodine reacts in diethyl ether with the bis(acetylide) complexes **2** and **3**, affording iodo–vinylidenes **12a** and **13a**, which separate out as $I_3^-$ salts. 2,4-Dinitrobenzenesulfenyl chloride also reacts with $Ru(C{\equiv}CR)_2P_4$, giving the thio–vinylidene derivative $[Ru(PhC{\equiv}C)\{{=}C{=}C(SR_1)Ph\}P_4]^+Cl^-$, **14a**, which is obtained as a solid only with the $P(OEt)_3$ ligand. The spectroscopic properties of these compounds also confirm their formulation as vinylidene–acetylide derivatives, the IR spectra showing the $\nu_{C\equiv C}$ of the alkynyl groups at 2104–2083 cm$^{-1}$ and the $\nu_{C=C}$ of the vinylidene at 1673–1620 cm$^{-1}$, respectively.

In the $^{13}C$ spectra, the characteristic carbene carbon atom resonance appears as a quintet at $\delta$ 336.1 ppm ($^2J_{CP}$ = 17 Hz) for iodo–vinylidene **12a** and at $\delta$ 349.6 ppm for thio–vinylidene **14a**. The $C_\beta$ vinylic carbon atom is also observed at $\delta$ 91.3 (**12a**) and $\delta$ 109.4 ppm (**14a**), as well as the $C_\alpha$ and $C_\beta$ carbon signals of the alkynyl ligand. Finally a *trans* geometry can be proposed in solution for the complexes on the basis of the sharp singlet[29] that appears in the $^{31}P$ spectra between +30 and −80 °C. It is worth noting that diazo–vinylidene[27] and iodo–vinylidene[30] complexes are rare and that the only thio–vinylidene reported[2h] was obtained starting from thio–acetylide complexes, so that $2,4\text{-}(NO_2)_2C_6H_3SCl$ is a new electrophilic reagent for alkynyl derivatives giving thio–vinylidene complexes.

**Reactions of Vinylidene Derivatives.** Whereas methyl– (**7**, **8**), diazo– (**10**, **11**), and iodo– (**12**, **13**) vinylidenes are robust complexes that are quite inert toward ligand substitution, the related H–vinylidenes **4** and **5** quickly react in solution. The results are summarized in Scheme 3.

Acetylide–vinylidene complexes **4** and **5** react in solutions of $CH_2Cl_2$, ethanol, *etc.* to give enynyl derivatives $[Ru\{\eta^3\text{-}RC_3CHR\}P_4]^+$ [11c] which can be isolated and characterized. The reaction occurs slowly enough to be measured by following the disappearance of the $^{31}P$ signal of the vinylidene complexes. Kinetic measurements[31] of the reaction of **5a** (eq 3) show that the

$$\underset{(\mathbf{5a})}{[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]^+} \rightarrow \underset{(\mathbf{15})}{[Ru\{\eta^3\text{-}PhC_3C(H)Ph\}\{P(OEt)_3\}_4]^+} \quad (3)$$

reaction rate is first-order in vinylidene (**5a**) and that it is inhibited by the presence of free acetylene PhC≡CH in the reaction mixture, thus ruling out an intramolecular mechanism. The plot of the reciprocal of $k_{obs}$ for the reaction of disappearance of vinylidene **5a** (Table 5) versus [PhC≡CH] gives a good straight line, as shown in Figure 2.

Chemical studies also showed (Scheme 3) that the vinylidene ligand is so labile in **4** and **5** that it is readily replaced by $P(OMe)_3$, *p*-tolNC and *p*-tolCN ligands. Furthermore, the mixed-enynyl complex $[Ru\{\eta^3\text{-}PhC_3C(H)^tBu\}\{P(OEt)_3\}_4]BF_4$ (**16**) was isolated in pure form and almost quantitative yield by reacting $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ with an excess of $^tBuC{\equiv}CH$.

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(29) In contrast with the other vinylidene complexes, only slight broadening of the signal was observed in the temperature range between −70 and −100 °C and no $A_2B_2$ multiplet appeared, even at the lowest temperature attained.

(30) Bruce, M. I.; Koutsantonis, G. A.; Liddell, M. J.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *320*, 217.

(31) Preliminary measurements show that the kinetic behavior of all vinylidene complexes **4** and **5** is strictly similar to that of **5a**, only values for $k_{obs}$ being different.

**Table 5. Observed Rate Constants for Reaction of Vinylidene 5a To Give Enynyl Complex 15 at 15 °C in $CDCl_3$**

| [PhC≡CH], mol/L | $k_{obs}$, $s^{-1}$ |
|---|---|
| $0.00 \times 10^{-2}$ | $1.29 \times 10^{-3}$ |
| $4.89 \times 10^{-2}$ | $4.92 \times 10^{-4}$ |
| $6.98 \times 10^{-2}$ | $2.96 \times 10^{-4}$ |
| $1.00 \times 10^{-1}$ | $2.18 \times 10^{-4}$ |
| $1.52 \times 10^{-1}$ | $1.49 \times 10^{-4}$ |
| $2.05 \times 10^{-1}$ | $1.33 \times 10^{-4}$ |
| $3.05 \times 10^{-1}$ | $9.50 \times 10^{-5}$ |

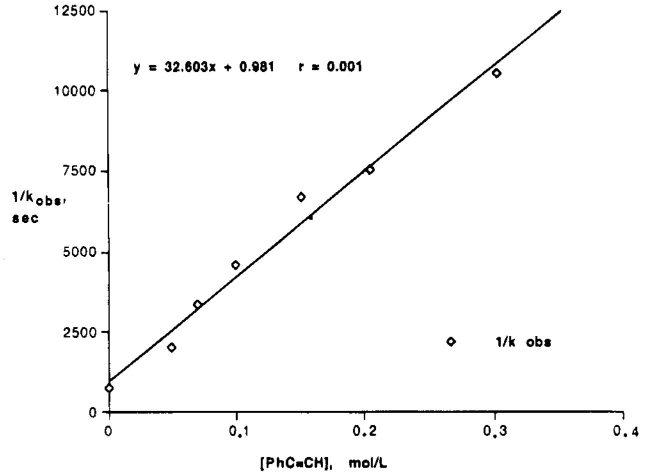
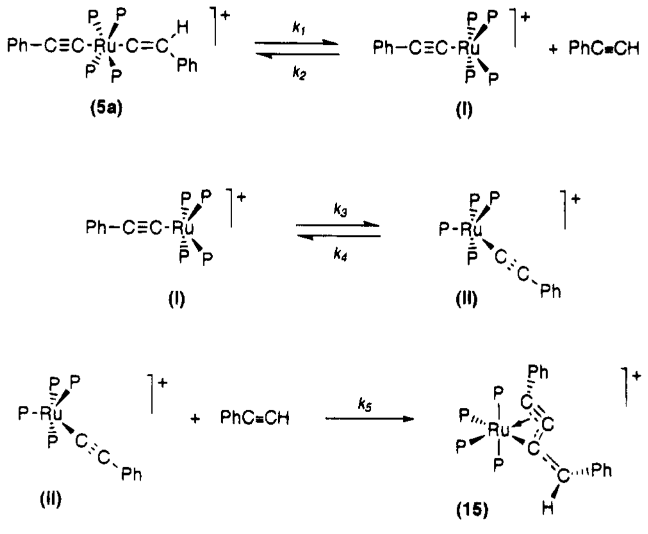


**Figure 2.** Plot of [PhC≡CH] vs $1/k_{obs}$, the reciprocal of the observed rate constant obtained at 15 °C in $CDCl_3$ for the reaction $[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]^+ \rightarrow [Ru\{\eta^3\text{-}PhC_3C(H)Ph\}\{P(OEt)_3\}_4]^+$.

**Scheme 4**[a]



[a] Legend: P = $P(OEt)_3$.

These results suggest the mechanism of Scheme 4 for the reaction of formation of enynyl complexes from alkynyl–vinylidene derivatives. Steady-state treatment gives the following expression for the rate:

$$-d[\mathbf{5a}]/dt = [\mathbf{5a}]k_1k_3k_5/\{k_2k_4 + k_3k_5 + k_2k_5[PhC{\equiv}CH]\}$$

which leads to $k_{obs} = k_1k_3k_5/\{k_2k_4 + k_3k_5 + k_2k_5[PhC{\equiv}CH]\}$ for the observed rate constant. This equation gives $1/k_{obs}$ = constant + $k_2[PhC{\equiv}CH]/k_1k_3$ as experimentally observed, in a plot of $1/k_{obs}$ versus [PhC≡CH] (Figure 2), in agreement with the proposed mechanism.

The dissociation of the vinylidene ligand (Scheme 4) to give free alkyne and the pentacoordinate intermediate **I** may first involve a $\eta^2$-PhC≡CH complex of the type $[Ru(C{\equiv}CPh)(\eta^2\text{-}PhC{\equiv}CH)P_4]^+$ (**I***) in equilibrium with **5a** through a 1,2 H-shift on PhC≡CH (**5a** ⇌ **I***). The dissociation of the alkyne ligand from this $\eta^2$-complex (**I***) may give the pentacoordinate **I**. However, no spectroscopic (IR and NMR) evidence of the formation of a $\eta^2$-RC≡CH complex was detected from our acetylide–vinylidene compounds **4** and **5**, and, although examples of $\eta^2$-RC≡CH complexes are known[32] and in two cases the rearrangement[33] to a vinylidene derivative is reported,[2f,m] the dissociation of **5a** into **I** and RC≡CH may also take place without any $\eta^2$-alkyne intermediate. In the same way, the reaction of intermediate **II** with PhC≡CH to give enynyl **15** may involve a series of other intermediate compounds such as the *cis*-$\eta^2$-RC≡CH complex, which rearranges to *cis*-$[Ru(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}P_4]^+$ and gives the final product **15** through a C–C coupling reaction.

Our chemical and kinetic results do not allow us to clarify the nature of these debated intermediates.[34] However, they do exclude an intramolecular mechanism and are consistent with a pathway, similar to that found in *cis–trans* octahedral isomerization,[35] which involves a pentacoordinate acetylide intermediate. This should be present in the two isomers **I** and **II**, which can be assumed to have square-pyramidal geometries (or geometries distorted toward trigonal bipyramidal) with the acetylide ligand in the apical and in the equatorial position, respectively, in the two isomers, as proposed in Scheme 4.

Enynyl complexes have been reported for the Fe,[2g,36] Ru,[2i,11b,25c,37] Os[38] families and for W,[32b] their study stimulated by the fact that these $\eta^3$-ligands may be key intermediates in alkyne dimerization/oligomerization processes catalyzed by transition-metal complexes. The alkynyl–vinylidene coupling reaction had been proposed for the formation of enynyl compounds and $[Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}(P\text{–}P)_2]^+$ (P–P = $Me_2PCH_2CH_2PMe_2$) complexes[2g,36] have recently been reported to give enynyls as well as $[W\{{=}C{=}C(Me)^tBu\}(\eta^2\text{-}HC{\equiv}C^tBu)(CO)\text{-}Cp^*]^+$ after deprotonation.[32b] Our complexes **4** and **5** represent new examples of such a reaction that also allows kinetic information to be obtained.

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(32) (a) Caldarelli, J. L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10097. (b) McMullen, A. K.; Selegue, J. P.; Wang, J. *Organometallics* **1991**, *10*, 3421. (c) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700. (d) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079.

(33) For the rearrangement of 1-alkynes in vinylidenes see ref 21 and the following: Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. Albiez, T.; Bernhardt, W.; von Schnering, C.; Roland, E.; Bantel, H.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 141.

(34) It may be noted that a mechanism also involving $\eta^2$-PhC≡CH complexes as additional intermediates in equilibrium with vinylidene tautomers, after a steady-state treatment, gives an expression for the rate that shows linear dependence of $1/k_{obs}$ on [PhC≡CH], as for the simpler proposed mechanism.

(35) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions*; Wiley-Interscience: New York, 1967. Wright, G.; Glyde, R. W.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 220.

(36) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3151.

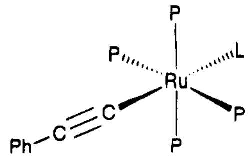
(37) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453.

(38) Gotzig, J.; Otto, H.; Werner, H. J. *J. Organomet. Chem.* **1985**, *287*, 247.

Results of the $\mathrm{P(OMe)_3}$ and $\mathrm{P(OEt)_3}$ derivatives can also explain the behavior of $\mathrm{Ru(C{\equiv}CR)_2\{PPh(OEt)_2\}_4}$ complexes **3**, which do not allow vinylidene cations $\mathrm{[Ru(C{\equiv}CR)\{{=}C{=}C(H)R\}P_4]^+}$ to be isolated by protonation, only $\eta^3$-enynyl derivatives **6**. In this case, too, protonation probably affords a $\mathrm{{=}C{=}C(H)R}$ complex that rearranges very quickly to the final product, preventing isolation of the vinylidene intermediate.

The vinylidene ligand in complexes **4** and **5** can be easily deprotonated with bases such as $\mathrm{NEt_3}$ or LiOH to give bis(acetylide) compounds (**1** and **2**) in almost quantitative yields (Scheme 3). Complexes **1** and **2** can also be obtained by treating vinylidenes **4** and **5** with $\mathrm{NaBH_4}$ which in this case does not reduce the $\mathrm{{=}C{=}C(H)R}$ group[39] to vinyl $\mathrm{{-}CH{=}C(H)R}$ but acts as a base, affording the acetylide derivatives. Furthermore, the $\mathrm{{=}C{=}C(H)R}$ ligand in these derivatives (**4** and **5**) is shown to be a good leaving group[40] and can easily be substituted by several ligands operating at low temperature (−20 °C) to prevent rearrangement to enynyl derivatives. As a result, the new mono(acetylide) $\mathrm{[Ru(C{\equiv}CPh)\{P(OMe)_3\}\{P(OEt)_3\}_4]^+}$ (**17**) and $\mathrm{[Ru(C{\equiv}CPh)(}p\mathrm{\text{-}tolNC)\{P(OEt)_3\}_4]^+}$ (**18**) derivatives can be prepared and characterized. Both complexes show *trans* geometry (**II**) in solution, as indicated by the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra, appearing as an $\mathrm{AB_4}$ multiplet for **17** and as a sharp singlet for the isocyanide complex **18**, in agreement with structure (**II**).

*p*-Toluonitrile also substitutes the acetylide ligand in **5a** giving the bis(nitrile) complex $\mathrm{[Ru(}p\mathrm{\text{-}tolCN)_2\{P(OEt)_3\}_4](BPh_4)_2}$ (**19**) which shows an $\mathrm{A_2B_2}$ multiplet in the $^{31}\mathrm{P}$ spectra, in agreement with a *cis* geometry. Finally, the lability of the $\mathrm{{=}C{=}C(H)R}$ ligand in **4** and **5** prompted us to attempt the preparation of halogen−acetylide complexes $\mathrm{RuX(C{\equiv}CR)P_4}$ (X = Cl, Br) by substitution reaction with $\mathrm{Cl^-}$ or $\mathrm{Br^-}$. The reaction proceeded easily with substitution of the vinylidene ligand and formation of a new species with only one $\nu_{\mathrm{C{\equiv}C}}$ band at 2035−2040 cm$^{-1}$ reasonably attributed to the $\mathrm{RuX(C{\equiv}CR)P_4}$ complex. However, these compounds were found to be rather instable; every attempt to isolate them failed, and the only products isolable from the reaction mixture were the already known bis(acetylide) $\mathrm{Ru(C{\equiv}CR)_2P_4}$ derivatives.



(**II**)

P = $\mathrm{P(OEt)_3}$

L = $\mathrm{P(OMe)_3}$, *p*-tolNC

## Conclusions

A series of bis(alkynyl) derivatives $\mathrm{Ru(C{\equiv}CR)_2P_4}$ can easily be prepared using monodentate phosphite as an ancillary ligand. Reactions with electrophilic reagents of these acetylides allow new alkynyl−vinylidene $\mathrm{[Ru(C{\equiv}CR)\{{=}C{=}C(R_1)R\}P_4]^+}$ ($\mathrm{R_1}$ = H, Me, PhN=N, *p*-tolyl-N=N, I, 2,4-$\mathrm{(NO_2)_2C_6H_3S}$; R = Ph, *p*-tol, $^t$Bu) derivatives to be obtained. The simple H−vinylidene $\mathrm{[Ru(C{\equiv}CR)\{{=}C{=}C(H)R\}P_4]^+}$ compounds show some novel properties, including easy replacement of the vinylidene ligand and rearrangement of the complexes in solution to give enynyl $\mathrm{[Ru(}\eta^3\mathrm{\text{-}RC_3CHR)P_4]^+}$ derivatives according to a proposed mechanism.

**Acknowledgment.** The financial support of MURST and CNR (Progetto Finalizzato Chimica Fine II), Rome, is gratefully acknowledged. We thank Daniela Baldan for her valuable technical assistance.

**Supporting Information Available:** Details of the structural determination are available for the complex $\mathrm{[Ru(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OEt_3\}_4]CF_3SO_3}$ including listings of atomic coordinates for hydrogen, anisotropic and isotropic displacement parameters, and complete listings of bond distances and angles (13 pages). Ordering information is given on any current masthead page.

OM9409377

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[39] Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.

[40] One example of substitution of the vinylidene ligand on protonation with the $\mathrm{NH_4PF_6}$ salt of the $\mathrm{Ru(C{\equiv}CR)_2(dppe)_2}$ complex has been shown: Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859.