Regio- and Stereoselective Dimerization of Phenylacetylene to (*Z*)-1,4-Diphenylbut-3-en-1-yne by Ruthenium(II) Catalysis. Reaction Mechanism Involving Intermolecular Protonation of σ-Alkynyl by 1-Alkyne

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Received August 9, 1994®

The Ru(II) *cis*-dihydride $[(PP_3)RuH_2]$ (**1**) is a catalyst precursor for the regio- and stereoselective dimerization of HC≡CPh to (*Z*)-PhC≡CCH=C(H)Ph in toluene solution [$PP_3 = P(CH_2CH_2PPh_2)_3$]. The real catalyst of the 1-alkyne coupling reaction is the bis(alkynyl) complex $[(PP_3)Ru(C{\equiv}CPh)_2]$ (**6**), which is formed by treatment of **1** with 4 equiv of HC≡CPh. A study under various experimental conditions, the detection of some intermediates, and the use of isolated complexes in independent reactions, taken altogether, permit mechanistic conclusions which account for both the conversion of **1** to **6** and the catalysis cycle. In particular, the transformation of **1** into **6**, which is accompanied by production of 2 equiv of styrene, is traversed by a number of intermediates among which are Ru(H)(CH=CHPh), Ru(π-CH_2=CHPh), Ru(H)(C≡CPh), and Ru(CH=CHPh)(C≡CPh). It is proposed that key steps in the catalytic cycle of HC≡CPh dimerization are the protonation of a terminal phenylethynyl ligand in **6** by external HC≡CPh and the subsequent C–C bond-forming reaction between *cis* vinylidene and alkynyl groups. X-ray diffraction analyses have been carried out on $[(PP_3)RuH(C{\equiv}CPh)]\cdot C_6H_6$ (**5**·C_6H_6), **6**, and (*E*)-$[(PP_3)RuH\{\eta^1$-$(MeO_2C)C{=}CH(CO_2Me)\}]$·EtOH (**10**·EtOH). Crystal data for **5**·C_6H_6: orthorhombic, *Pbca* with $a = 27.285(7)$ Å, $b = 19.087(6)$ Å, $c = 18.310(9)$ Å, $V = 9536$ Å^3, $Z = 8$, $R = 0.0562$. Crystal data for **6**: monoclinic, $P2_1/a$ with $a = 10.660(2)$ Å, $b = 40.342(9)$ Å, $c = 11.082(4)$ Å, $\beta = 93.27(3)°$, $V = 4758$ Å^3, $Z = 4$, $R = 0.059$. Crystal data for **10**·EtOH: triclinic, $P\bar{1}$ with $a = 11.611(2)$ Å, $b = 22.377(2)$ Å, $c = 9.490(3)$ Å, $\alpha = 93.87(2)°$, $\beta = 109.08(2)°$, $\gamma = 76.26(1)°$, $V = 2263$ Å^3, $Z = 2$, $R = 0.047$.

Introduction

Enynes are organic molecules of both practical and fundamental interest. Practical motivations arise from their use as precursors for the synthesis of natural products as well as building blocks for further structural elaborations.[1] On the other hand, enynes are the simplest oligomerization products of alkynes.[2] Thus, understanding the mechanism of their formation is of key importance for developing selective C–C bond-forming processes involving alkynes.

Until a few years ago, the direct coupling of two 1-alkynes, while attractive since economy of mass is optimized, has failed to be useful for the synthesis of enynes due to the lack of regio- and stereocontrol, and the preference for trimerization. Recently, however, a number of homogeneous catalysts containing either d-block metals[1,3] or lanthanides[4] have been designed which combine efficiency with selectivity. Among the

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® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

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0276-7333/94/2313-4616$04.50/0

group of transition metal catalysts, Ru(II) compounds play a prominent role due to their general capability of inducing high regio- and stereoselectivity.[3a-g]

The literature contains convincing data for a mechanism at ruthenium in which enyne formation occurs *via* C−C coupling between σ-alkynyl and vinylidene ligands, followed by formal σ-bond metathesis between σ-butenynyl and 1-alkyne.[3a-c,h,5-12] The relevant step in all catalytic cycles is, however, the generation of a vinylidene unit at an unsaturated metal center.[13] As a matter of fact, all of the known Ru(II) catalysts for alkyne dimerization contain a free coordination site where the 1-alkyne can tautomerize to vinylidene.

In the present paper, we wish to describe a case of regio- and stereocontrolled catalytic dimerization of HC≡CPh in which the 1-alkyne substrate acts also as a protic acid for the conversion of Ru−C≡CPh to Ru=C=CHPh.

Experimental Section

General Data. Tetrahydrofuran, toluene, and *n*-hexane were purified by distillation over $LiAlH_4$, P_2O_5, and Na, respectively. Lithium phenylacetylide, LiC≡CPh (1.0 M THF solution), and phenylacetylene were purchased from Aldrich; the latter reagent was checked by ^1H NMR spectroscopy and, when necessary, was distilled prior to use. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. All reactions and manipulations were routinely performed under a dry argon or nitrogen atmosphere by using Schlenk tube techniques. The solid complexes were collected on sintered-glass frits and washed with ethanol and petroleum ether (bp 40−70 °C) before being dried in a stream of nitrogen. Literature methods were used for the preparation of $[(PP_3)RuH_2]$ (**1**),[14] $[(PP_3)RuD_2]$ (**1**-d_2),[14] $[(PP_3)Ru(H)Cl]$ (**2**),[14] $[(PP_3)RuH(N_2)]BPh_4$ (**3**),[14] and $[(PP_3)Ru(C{\equiv}CPh)]BPh_4$ (**4**)[3c] [$(PP_3 = P(CH_2CH_2Ph_2)_3$].

Deuterated solvents for NMR measurements (Janssen and Merck) were dried over molecular sieves. Proton NMR spectra were recorded on Varian VXR 300 and Bruker AC 200P instruments operating at 299.94 and 200.13 MHz, respectively. Peak positions are relative to tetramethylsilane as the external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 121.42 and 81.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. $^{13}C\{^1H\}$ NMR spectra and DEPT experiments were performed on the Bruker instrument operating at 50.32 MHz. Peak positions are relative to tetramethylsilane and were calibrated against the solvent resonance. 2D-HETCOR NMR experiments were recorded on the Bruker spectrometer using Bruker's XHCORR pulse program. The 90° ^{13}C pulse was 5.5 μs, the 90° ^1H pulse from the decoupler was 9.3 μs, and the acquisition time was 0.15−0.20 s. The number of incremental spectra was determined according to the concentration of the sample and spectral width used for collection of the FIDs. Zero-filling and a 2D Fourier transformation resulted in a spectrum with resolution of *ca.* 5 and 10 Hz in the proton and carbon dimensions, respectively. Spectra with adequate signal-to-noise ratio were obtained in *ca.* 12 h. 2D-COSY NMR experiments were performed with either Varian or Bruker pulse sequences on the two instruments, respectively. A delay period of 1.0 s was used between acquisitions. The 2D Fourier transformation gave 2D spectra with adequate signal-to-noise ratios after 4−8 h of data collection, depending on sample concentration and spectral width. Proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device using the wide-band phosphorus decoupling sequence GARP. The infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. A Shimadzu GC-14A/GCMS-QP2000 instrument was employed for all GC−MS investigations.

Preparation of DC≡CPh. *n*-Butyllithium (10.0 mL, 13.5 mmol, 1.35 M solution in *n*-hexane) was added dropwise to a stirred solution of phenylacetylene (1.40 g, 13.5 mmol) in THF (10 mL) at 0 °C under nitrogen. After 10 min of stirring at 0 °C, D_2O (1.0 mL, 55.3 mmol) was added dropwise. Distillation under reduced pressure gave DC≡CPh in approximatively quantitative yield. The isotopic purity was higher than 95%, as confirmed by proton NMR spectroscopy.

Synthesis of the Complexes. Preparation of $[(PP_3)RuH(C{\equiv}CPh)]$ (5). Method A. Neat phenylacetylene (0.50 mL, 4.50 mmol) was pipetted into a toluene solution (30 mL) of **1** (0.35 g, 0.45 mmol). Stirring for 1 h at 70 °C produced a light yellow solution. By addition of ethanol (20 mL) and slow evaporation of the solvent under a stream of nitrogen, pale yellow crystals precipitated. GC analysis of the solution before addition of ethanol showed the formation of styrene (ca. 1 equiv). Analysis of the solid product by $^{31}P\{^1H\}$ NMR spectroscopy showed it to contain the hydride alkynyl complex $[(PP_3)RuH(C{\equiv}CPh)]$ (**5**) together with a minor amount (2−5%) of **6** (see below). Recrystallization of the crude material from CH_2Cl_2/EtOH (2:1 v/v) gave pure crystals of **5**. Yield: 85%.

Method B. Compound **5** was selectively obtained, though in lower yield, by reacting $[(PP_3)Ru(H)Cl]$ (**2**) (0.41 g, 0.50 mmol) dissolved in THF (30 mL) with a slight excess of LiC≡CPh (1.0 M THF solution, 0.55 mmol). The resulting solution was stirred for 30 min at room temperature. Addition of ethanol (20 mL) and concentration under nitrogen gave pale yellow crystals of **5**. Yield: 78%. IR: ν(C≡C) 2060 cm^{-1} (s); ν(Ru−H) 1941 cm^{-1} (m); phenyl-reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{50}H_{48}P_4Ru$: C, 68.72, H, 5.54. Found: C, 68.61; H, 5.60. $^{31}P\{^1H\}$ NMR (20 °C, 121.42 MHz, benzene-d_6), AM_2Q system: $\delta(P_A)$ 149.09, $\delta(P_M)$ 58.84, $\delta(P_Q)$ 50.95; $J(P_AP_M)$ 13.1 Hz, $J(P_AP_Q)$ 9.0 Hz, $J(P_MP_Q)$ 14.3 Hz. ^1H NMR (20 °C, 299.94 MHz, benzene-d_6): δ −8.81 [dtd, 1H, $J(HP_Q)$ 78.9 Hz, $J(HP_A)$ 16.7 Hz, $J(HP_M)$ 26.7 Hz, Ru−*H*]. $^{13}C\{^1H\}$ NMR (25 °C, 50.32 MHz, dichloromethane-d_2): δ 117.46 [dq, $J(CP_{trans})$ 22.3 Hz, $J(CP_{cis})$ 2.0 Hz, Ru−*C*≡CPh]; the resonance due to the C_β carbon of the phenylethynyl ligand could not be assigned, as it is masked by the resonances of

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the aromatic carbon atoms. Compound **5** is stable in both the solid state and deareated solutions in which it behaves as a nonelectrolyte.

Preparation of [(PP$_3$)RuD(C≡CPh)] (5-d_1). The isotopomer **5**-d_1 was prepared by substituting DC≡CPh and C_2H_5-OD for HC≡CPh and C_2H_5OH in the above procedure. IR: ν(Ru–D) 1417 cm^{-1}.

Reaction of [(PP$_3$)RuD$_2$] with HC≡CPh. A sample of **1**-d_2 (*ca.* 0.03 mmol) was dissolved in toluene-d_8 (0.7 mL) in a 5 mm NMR tube under nitrogen. After two freeze/pump/thaw cycles at −196 °C, the solution was frozen and pumped on at −196 °C. After phenylacetylene (5 equiv) was added, the tube was sealed and then introduced into a NMR probe preheated at 70 °C. Analysis of the time evolution of the NMR spectra showed that all **1** transformed into **5** after *ca.* 1.5 h and that *ca.* 1 equiv of styrene-d_2 was produced. ^{1}H NMR (70 °C, toluene-d_8, 200.13 MHz), $\delta_{CD=CHD}$: δ_H 5.86 (m, 1H). MS, *m/z*: M^+ = 106 (100), $(M - C_2HD)^+$ = 79 (10), $(M - C_2D_2)^+$ = 78 (10), $(M - C_2HD_2)^+$ = 77 (15), $C_4H_3^+$ = 51 (15).

Preparation of [(PP$_3$)Ru(C≡CPh)$_2$] (6). Method A. A large excess of phenylacetylene (1.11 mL, 10.0 mmol) was pipetted into a toluene solution (50 mL) of **1** (1.17 g, 1.50 mmol). The resulting solution was refluxed for 12 h during which time the color changed from yellow to light yellow. The solution was cooled to room temperature, and *n*-heptane (20 mL) was added. Concentration of the resulting pale yellow solution under a brisk current of nitrogen gave pale cream-colored crystals of [(PP$_3$)Ru(C≡CPh)$_2$] (**6**). Yield: 78%.

Method B. Neat phenylacetylene (0.37 mL, 3.32 mmol) was added to a stirred toluene solution (20 mL) of **5** (0.98 g, 1.12 mmol). The resulting yellow solution was refluxed for 3 h and then cooled to room temperature. Addition of ethanol (20 mL) and concentration of the pale yellow solution gave **6** in *ca.* 90% yield.

Method C. Complex **6** can also be prepared by reacting the phenylacetylide complex [(PP$_3$)Ru(C≡CPh)]BPh$_4$ (**4**) with excess LiC≡CPh (1.0 M THF solution) in THF. Addition of ethanol and slow concentration under nitrogen gave **6** in *ca.* 80% yield. IR: ν(C≡C) 2087, 2073 cm^{-1} (s); phenyl-reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{58}H_{52}P_4Ru$: C, 71.52; H, 5.38. Found: C, 71.39; H, 5.27. ^{31}P{^{1}H} NMR (20 °C, 81.01 MHz, benzene-d_6), AM_2Q system: $\delta(P_A)$ 145.35, $\delta(P_M)$ 52.27, $\delta(P_Q)$ 48.24; $J(P_AP_M)$ 7.1 Hz, $J(P_AP_Q)$ 7.6 Hz, $J(P_MP_Q)$ 21.7 Hz. ^{13}C{^{1}H} NMR (23 °C, 50.32 MHz, dichloromethane-d_2): 126.81 [d, $J(CP_{trans})$ 15.8 Hz, Ru–C≡*C*Ph], 125.15 [d, $J(CP_{trans})$ 14.3 Hz, Ru–C≡*C*Ph], 117.85 [dq, $J(CP_{trans})$ 23.4 Hz, $J(CP_{cis})$ 1.4 Hz, Ru–*C*≡CPh], 114.86 [dq, $J(CP_{trans})$ 21.7 Hz, $J(CP_{cis})$ 2.6 Hz, Ru–*C*≡CPh].

Compund **6** is air stable in both the solid state and solutions of common organic solvents in which it behaves as a nonelectrolyte.

Reactions of 5 and 5-d_1 with HC≡CPh in NMR Tubes. Solid **5** (35 mg, 0.04 mmol) was dissolved in toluene-d_8 degassed under nitrogen (0.8 mL) and then transferred into a 5 mm NMR tube which was then cooled to −78 °C. Four equivalents of HC≡CPh (22 μL, 0.20 mmol) and 5 μL of hexamethyldisiloxane as the ^{1}H internal standard were added *via* syringe, and the tube was flame sealed under nitrogen and checked by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The sample was then heated at 110 °C in a thermostated oil bath and periodically analyzed by NMR spectroscopy. Complete transformation of **5** to **6** occurred in 24 h with no formation of other phosphorus-containing species. Proton NMR spectroscopy showed the formation of 1 equiv of styrene [^{1}H NMR (21 °C, toluene-d_8, 200.13 MHz), $\delta_{(CH_A=CH_BH_C)}$: δ_{H_B} 5.80, δ_{H_C} 5.29, J_{AB} 17.6 Hz, J_{AC} 11.0 Hz, J_{BC} 1.0 Hz; the resonance due to H_A is masked by the aromatic protons of the phenyl groups. MS, *m/z*: M^+ = 104 (100), $(M - C_2H_2)^+$ = 78 (20), $(M - C_2H_3)^+$ = 77 (15), $C_4H_3^+$ = 51 (15)] and of 1 equiv of (*Z*)-1,4-diphenylbut-3-en-1-yne [^{1}H NMR (21 °C, toluene-d_8, 200.13 MHz), $\delta_{CH_A=CH_B}$: 6.61, 5.99, $^3J_{HH}$ 11.9 Hz. ^{13}C{^{1}H} NMR (21 °C, toluene-d_8, 50.32 MHz): δ 138.76 (s, PhC*H*=CH), 131.40 (s, PhCH=*C*H), 96.27 (Ph*C*≡C), 87.15 (s, PhC≡*C*). MS, *m/z*: M^+ = 204 (100)].[3e,15]

The analogous reaction with **5**-d_1 gave 1 equiv of both CH_2=CDPh [^{1}H NMR (21 °C, toluene-d_8, 200.13 MHz), $\delta_{CD=CH_BH_C}$: δ_{H_B} 5.89 (m, 1H), δ_{H_C} 5.40 (m, 1H). MS, *m/z*: M^+ = 105 (100), $(M - C_2HD)^+$ = 78 (15), $(M - C_2H_2D)^+$ = 77 (15), $C_4H_3^+$ = 51 (15)] and (*Z*)-PhC≡CCH=C(H)Ph.

Reaction of 6 with EtOH or (NH$_4$)PF$_6$. Stirring a sample of **6** (0.50 g, 0.51 mmol) in a toluene/EtOH mixture (5:1, v/v) at reflux temperature for 2 h resulted in formation of a bright yellow solution. Addition of NaBPh$_4$ in ethanol (20 mL) precipitated canary yellow crystals which were identified by comparison with an authetic sample as the 1,4-diphenylbutenynyl complex (*E*)-[(PP$_3$)Ru{η^3-PhC$_3$=C(H)Ph}]BPh$_4$ (**7**). Actually, this compound is a 3:1 mixture of two stereoisomers (**7a,b**) differing from each other only in the anchoring mode of the butenynyl ligand.[3c] Yield: 90%.

The reaction of **6** with (NH$_4$)PF$_6$ was performed in THF at room temperature and gave quantitatively **7a,b** after metathetical reaction with NaBPh$_4$.

Preparation of [(PP$_3$)Ru{η^2-CH$_2$=CH(CO$_2$Me)}] (8). Method A. A stirred mixture of **1** (0.78 g, 1.00 mmol) and methyl acrylate (0.18 mL, 2.00 mmol) in THF (35 mL) was heated at reflux temperature for 30 min and then cooled to room temperature. Addition of ethanol (30 mL) and concentration of the resulting solution gave orange crystals of [(PP$_3$)Ru{η^2-CH$_2$=CH(CO$_2$Me)}] (**8**). Yield: 92%. GC analysis of the solution showed the formation of *ca.* 1.0 equiv of methyl propionate.

Method B. A slight excess of methyl propiolate (0.11 mmol, 1.24 mmol) was syringed into a stirred THF solution (25 mL) of **1** (0.78 g, 1.00 mmol) at room temperature. Immediately the solution become light orange, and after 5 min, ethanol (15 mL) was added to the light orange solution. Slow concentration gave crystals of **8**. Yield: 87%. IR: ν(C=O) 1671 cm^{-1} (s); ν(COC) 1144 cm^{-1} (s). Anal. Calcd for $C_{46}H_{48}O_2P_4Ru$: C, 64.41; H, 5.64. Found: C, 64.27; H, 5.55. ^{31}P{^{1}H} NMR, fast exchange spectrum (17 °C, 81.01 MHz, dichloromethane-d_2), AM_3 system: $\delta(P_A)$ 149.47, $\delta(P_M)$ 68.62; $J(P_AP_M)$ 25.0 Hz. ^{31}P NMR, slow exchange spectrum (−83 °C, 81.01 MHz, dichloromethane-d_2), AMNQ system: $\delta(P_A)$ 149.45, $\delta(P_M)$ 73.36, $\delta(P_N)$ 66.06, $\delta(P_Q)$ 67.71; $J(P_AP_M)$ 29.1 Hz, $J(P_AP_N)$ 29.1 Hz, $J(P_AP_Q)$ 14.2 Hz, $J(P_MP_N)$ 254.8 Hz, $J(P_MP_Q)$ 11.4 Hz, $J(P_NP_Q)$ 4.9 Hz. ^{1}H NMR (23 °C, 200.13 MHz, dichloromethane-d_2): δ 3.33 (s, 3H, OC*H*$_3$), 3.08 [m, 1H, $J(H_AH_B)$ 7.5 Hz, $J(H_AH_C)$ 9.7 Hz, $J(H_AP_A)$ 6.3 Hz, $J(H_AP_M)$ 3.2 Hz, C*H*$_A$=CH$_B$H$_C$], 1.56 [m, 1H, $J(H_BH_C)$ 3.7 Hz, $J(H_BP_A) \approx 0$ Hz, $J(H_BP_M)$ 5.3 Hz, CH$_A$=C*H*$_B$*H*$_C$], 1.64 [m, 1H, $J(H_CP_A) \approx 0$ Hz, $J(H_CP_Q) \approx 0$ Hz, $J(H_CP_M)$ 5.2 Hz, CH$_A$=CH$_B$*H*$_C$]. ^{13}C{^{1}H} NMR (20 °C, 50.32 MHz, dichloromethane-d_2): δ 181.19 (s, *C*OOMe), 50.28 [s, O*C*H$_3$], 42.73 [s, *C*H$_2$=CH, assigned by a DEPT experiment], 31.99 [d, J(CP) 14.0 Hz, CH$_2$=*C*H, assigned by a DEPT experiment].

Preparation of [(PP$_3$)Ru{η^2-CH$_2$=CH(CO$_2$Et)}] (9). This compound was obtained as light orange crystals following the synthetic procedures described for **8**, with the use of ethyl acrylate (method A, 0.22 mL, 2.03 mmol) or ethyl propiolate (method B, 0.12 mL, 1.18 mmol) in the place of methyl acrylate and methyl propiolate. The yield was 88% (method A) and 83% (method B). Ethyl propionate (*ca.* 1.0 equiv) was produced in the reaction with ethyl acrylate. IR: ν(C=O) 1673 cm^{-1} (m); ν(COC) 1252 cm^{-1} (s). Anal. Calcd for $C_{47}H_{50}O_2P_4Ru$: C, 64.75; H, 5.78. Found: C, 64.66; H, 5.83. ^{31}P{^{1}H} NMR, fast exchange spectrum (21 °C, 81.01 MHz, dichloromethane-d_2), AM_3 system: $\delta(P_A)$ 149.55, $\delta(P_M)$ 68.84; $J(P_AP_M)$ 24.9 Hz. ^{31}P NMR, slow exchange spectrum (−80 °C, 81.01 MHz, CD_2Cl_2, H_3PO_4 85% reference), AMNQ system: $\delta(P_A)$ 149.12, $\delta(P_M)$ 74.53, $\delta(P_Q)$ 66.49, $\delta(P_N)$ 65.98; $J(P_AP_M)$ 29.3 Hz, $J(P_AP_N)$ 29.3 Hz, $J(P_AP_Q)$ 14.0 Hz, $J(P_MP_N)$ 241.0 Hz, $J(P_MP_Q)$ 10.7 Hz, $J(P_NP_Q)$ 8.8 Hz. ^{1}H NMR (21 °C, 299.45 MHz, benzene-d_6): δ 4.10, 3.91 [ABM_3 system, 2H, $J(H_AH_B)$ 10.9 Hz, $J(H_AH_M)$ 7.1

Hz, $J(H_BH_M)$ 7.1 Hz, $OCH_AH_BCH_3$], 2.98 [m, 1H, $J(H_AH_B)$ 7.7 Hz, $J(H_AH_C)$ 9.8 Hz, $CH_A{=}CH_BH_C$], 1.60 [m, 1H, $J(H_BH_C)$ 3.6 Hz, $CH_A{=}CH_BH_C$], 1.55 [m, 1H, $CH_A{=}CH_BH_C$], 1.09 (t, 3H, J(HH) 7.1 Hz, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (25 °C, 50.32 MHz, dichloromethane-d_2): δ 181.00 (s, CO_2Et), 58.62 (s, OCH_2CH_3), 42.90 [s, $CH_2{=}CH$, assigned by a DEPT experiment], 32.48 [d, J(CP) 15.3 Hz, $CH_2{=}CH$, assigned by a DEPT experiment], 15.07 (s, OCH_2CH_3).

Compounds **8** and **9** are stable in both the solid state and solution in which they behave as nonelectrolytes.

Preparation of (*E*)-[(PP_3)RuH{η^1-$(MeO_2C)C{=}CH(CO_2Me)$}]·C_2H_5OH (10·C_2H_5OH). Dimethyl acetylenedicarboxylate (0.06 mL, 0.49 mmol) was syringed into a THF solution (20 mL) of **1** (0.31 g, 0.40 mmol). After 20 min of stirring, addition of ethanol and slow concentration gave pale yellow crystals of **10**·C_2H_5OH. Yield: 85%. IR: ν(O—H)$_{EtOH}$ 3518 cm^{-1} (w); ν(Ru—H) 2039 cm^{-1} (m); ν(C=O) 1686, 1664 cm^{-1} (s); ν(C=C) 1530 cm^{-1} (w); ν(COC) 1195, 1140 cm^{-1} (s). Anal. Calcd for $C_{50}H_{56}O_5P_4Ru$: C, 62.43; H, 5.87. Found: C, 62.37; H, 5.73 . $^{31}P\{^1H\}$ NMR, fast exchange spectrum (21 °C, 121.4 MHz, dichloromethane-d_2), AM_2Q system: $\delta(P_A)$ 142.72, $\delta(P_M)$ 59.17, $\delta(P_Q)$ 49.76; $J(P_AP_M)$ 15.2 Hz; $J(P_AP_Q)$ 5.9 Hz, $J(P_MP_Q)$ 11.2 Hz. ^{31}P NMR, slow exchange spectrum (−50 °C, 121.4 MHz, dichloromethane-d_2), AMNQ system: $\delta(P_A)$ 142.28, $\delta(P_M)$ 61.15, $\delta(P_N)$ 57.37, $\delta(P_Q)$ 51.34; $J(P_AP_M)$ 16.1 Hz, $J(P_AP_N)$ 16.1 Hz, $J(P_AP_Q)$ 5.6 Hz, $J(P_MP_N)$ 241.0 Hz, $J(P_MP_Q)$ 11.0 Hz, $J(P_NP_Q)$ 11.0 Hz. ^1H NMR (21 °C, 200.13 MHz, dichloromethane-d_2): δ −9.04 [dtd, 1H, $J(HP_Q)$ 80.9 Hz, $J(HP_M)$ 23.9 Hz, $J(HP_A)$ 15.7 Hz, Ru—*H*]; 3.50, 3.03 (s, 3H each, CO_2CH_3); 6.08 [dt, 1H, $J(HP_A)$ 6.2 Hz, $J(HP_M)$ 1.4 Hz, $RuC(CO_2Me){=}CH(CO_2Me)$]. $^{13}C\{^1H\}$ **NMR** (21 °C, 50.32 MHz, dichloromethane-d_2): δ 200.27 [dq, $J(CP_A)$ 54.3 Hz, $J(CP_M) \approx J(CP_Q) \approx$ 11.8 Hz, Ru—*C*], 182.88 [s, RuC—*C*(O)OCH_3; gatedec spectrum, d, ^3J(CH) 14.7 Hz], 163.04 [d, CH—*C*(O)OCH_3, $J(CP_A)$ 7.6 Hz], 126.50 [dt, $J(CP_A)$ 12.1 Hz, $J(CP_M)$ 3.8 Hz; RuC=*CH*; gatedec spectrum, d, ^1J(CH) 164.3 Hz; assigned by a DEPT and 2D-HETCOR NMR experiments], 50.50 [s, OCH_3; gatedec spectrum, d, ^1J(CH) 145.0 Hz; correlated by a 2D-NMR experiment with the ^1H resonance at 3.03 ppm], 49.72 [s, OCH_3; gatedec spectrum, d, ^1J(CH) 144.8 Hz; correlated by a 2D-NMR experiment with the ^1H resonance at 3.50 ppm].

Preparation of (*E*)-[(PP_3)RuD{η^1-$(MeO_2C)C{=}CD(CO_2Me)$}]·C_2H_5OD (10-d_2·C_2H_5OD). The deuterated complex **10**-d_2 was prepared by substituting **1**-d_2 and C_2H_5OD for **1** and C_2H_5OH in the above procedure. IR: ν(Ru—D) 1456 cm^{-1}.

Thermal Rearrangement of 10 to [(PP_3)Ru{η^2-$(MeO_2C)CH{=}CH(CO_2Me)$}] (11). A pale yellow solution of 0.20 g (0.22 mmol) of **10** in THF (20 mL) was gently heated to reflux temperature and then stirred for 1 h. Addition of *n*-hexane (25 mL) to the resulting orange solution and slow concentration under nitrogen gave **11** as pale orange microcrystals. Yield: 90%. IR: ν(C=O) 1667 cm^{-1} (s); ν(COC) 1180 cm^{-1} (m). Anal. Calcd for $C_{48}H_{50}O_4P_4Ru$: C, 62.95; H, 5.50. Found: C, 62.68; H, 5.37. $^{31}P\{^1H\}$ NMR, fast exchange spectrum (21 °C, 81.01 MHz, dichloromethane-d_2), AM_3 system: $\delta(P_A)$ 139.65, $\delta(P_M)$ 64.34; $J(P_AP_M)$ 22.3 Hz. ^{31}P NMR slow exchange spectrum (−90 °C, 81.01 MHz, dichloromethane-d_2), AMNQ system: $\delta(P_A)$ 139.61, $\delta(P_M)$ 59.42, $\delta(P_N)$ 58.42, $\delta(P_Q)$ 74.04; $J(P_AP_M)$ 30.5 Hz, $J(P_AP_N)$ 30.5 Hz, $J(P_AP_Q)$ 1.5 Hz, $J(P_MP_N)$ 79.6 Hz, $J(P_MP_Q)$ < 1 Hz, $J(P_NP_Q)$ < 1 Hz. ^1H NMR (21 °C, 200.13 MHz, dichloromethane-d_2): δ 3.12 [dq, 2H, $J(HP_A)$ 5.2 Hz, $J(HP_M)$ 3.4 Hz, *CH*=*CH*], 2.84 (s, 6H, CO_2CH_3). $^{13}C\{^1H\}$ NMR (21 °C, 50.32 MHz, dichloromethane-d_2): δ 181.28 [s, CO_2CH_3], 50.16 [s, OCH_3], 37.06 [dq, J(CP) 8.7 Hz, J(CP) 2.9 Hz].

The isomeric compounds **10** and **11** are stable in both the solid state and solution in which they behave as nonelectrolytes.

Reaction of 11 with HC≡CPh. A mixture of **11** (0.20 g, 0.22 mmol) and HC≡CPh (0.25 mL, 2.25 mmol) in THF was heated at reflux temperature for 2 h. After cooling to room temperature, GC—MS analysis showed the formation of dimethyl maleate. Upon addition of ethanol (20 mL) crystals of **5** precipitated in almost quantitative yield.

***In Situ* Reactions between 5 or 6 and HC≡CCO_2Me.** A sample of **5** (*ca.* 0.03 mmol) was dissolved in toluene-d_8 (0.7 mL) in a 5 mm NMR tube under nitrogen. After two freeze/pump/thaw cycles at −196 °C, the solution was frozen and pumped on at −196 °C. After 4 equiv of HC≡CCO_2Me and 5 μL of hexamethyldisiloxane as the ^1H internal standard were added, the tube was sealed and then introduced into a NMR probe at 20 °C. The reaction between **5** and methyl propiolate occurred above 100 °C. At 110 °C, all HC≡CCO_2Me was consumed in 4 h to give, first, 1 equiv of methyl acrylate [^1H NMR (21 °C, toluene-d_8, 200.13 MHz), $\delta_{CH_A=CH_BH_C}$: δ_{H_A} 6.13, δ_{H_B} 6.44, δ_{H_C} 5.54, J_{AB} 17.4 Hz, J_{AC} 10.3 Hz, J_{BC} 1.8 Hz; δ_{OMe} 3.61 (s, 3H). MS, *m/z*: $(M - H)^+ = 85$ (10), $(M - OMe)^+ = 55$ (100), $C_2H_3^+ = 27$ (70)] and then 1 equiv of (*Z*)-PhC≡CCH=C(H)CO_2Me [^1H NMR (21 °C, toluene-d_8, 200.13 MHz), $\delta_{CH_A=CH_BCO_2Me}$: 5.30 (d, 1H, $^3J_{HH}$ 12.2 Hz, H_B); the resonance due to the other vinyl proton was not observed as it is buried under the aromatic protons; nevertheless, its position was unequivocally confirmed at *ca.* 7.8 ppm by 2D homonuclear correlation spectroscopy; δ_{OMe} 3.56 (s, 3H)]. MS, *m/z*: $M^+ = 186$ (100), $(M - Me)^+ = 171$ (60), $(M - OMe)^+ = 155$ (50), $(M - CO_2Me)^+ = 127$ (45), $(M - HCO_2Me)^+ = 126$ (30), $C_9H_7^+ = 115$ (50), $PhC{\equiv}C^+ = 101$ (20), $C_7H_5^+ = 89$ (35), $Ph^+ = 77$ (40)]. When the reaction was carried out using 2 equiv of HC≡CCO_2Me, methyl acrylate was the largely predominant (*ca.* 0.8 equiv) organic product.

Under analogous conditions and workup, the reaction between **6** and methyl propiolate occurred already at 40 °C to produce selectively (*Z*)-PhC≡CCH=C(H)Ph. At 110 °C, the reaction was complete in 1 h and gave 1 equiv of (*Z*)-PhC≡CCH=C(H)Ph plus traces of dimers and trimers of methyl propiolate (detected only by GC—MS).

Catalytic Reactions. Catalytic experiments were all carried out using 0.1 mmol of the ruthenium catalysts with 10 mmol of HC≡CPh (substrate:catalyst ratio = 100). The metal complexes were introduced into a round bottom flask in a reflux setup already purged of air, and then 20 mL of freshly distilled anhydrous toluene (or THF) was added as solvent. Under N_2, the required volume of substrate was added by syringe. The temperature of the flask was maintained at 110 °C (or at 70 °C in THF) for 6 h by means of a thermostatically controlled oil bath while constantly being stirred. After each experiment, the reaction mixture was quenched by cooling to 0 °C. The organic product compositions were determined by GC—MS. When necessary, multinuclear NMR spectroscopy was used to distinguish the ruthenium complexes present at the end of the catalysis cycle. The results of all catalytic runs are summarized in Table 6. A reaction using **6** as catalyst was carried out in a NMR tube (substrate:catalyst ratio = 10 in order to obtain spectra with an acceptable signal-to-noise ratio) in toluene-d_8 at 110 °C. Analysis of the time evolution of the ^{31}P NMR spectra showed that **6** is both the termination metal complex and the only phosphorus-containing species detectable in the course of the catalytic cycle.

X-ray Diffraction Studies. A summary of crystal and intensity data for the compounds **5**·C_6H_6, **6**, and **10**·C_2H_5OH, is presented in Table 1 (**5**·C_6H_6) and Table 2 (**6** and **10**·C_2H_5OH). Experimental data were recorded at room temperature on an Enraf-Nonius CAD4 diffractometer (**5**·C_6H_6 and **10**·C_2H_5OH) or a Philips-PW1100 diffractometer (**6**) with an upgraded computer control (FEBO system) using graphite-monochromated Mo Kα radiation (**5**·C_6H_6 and **10**·C_2H_5OH) and graphite-monochromated Cu Kα radiation (**6**). A set of 25 carefully centered reflections in the range $6.0° \le \theta \le 7.0°$ (**5**·C_6H_6), $8.0° \le \theta \le 12.0°$ (**6**), and $7.0° \le \theta \le 10.0°$ (**10**·C_2H_5OH), respectively, was used for determining the lattice constants. As a general procedure, the intensities of three standard reflections were measured periodically every 2 h for orientation and intensity control. This procedure did not reveal an appreciable decay

Table 1. Summary of Crystal Data for [(PP$_3$)RuH(C≡CPh)]·C$_6$H$_6$

formula	$C_{56}H_{54}P_4Ru_1$
fw	951.94
cryst size, mm	0.55 × 0.28 × 0.2
temp, K	293(2)
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a, Å	27.285(7)
b, Å	19.087(6)
c, Å	18.310(9)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	9536(6)
Z	8
ϱ(calcd), g cm^{-3}	1.326
radiation; λ, Å	graphite-monochromated Mo Kα; 0.710 69
abs coeff, mm^{-1}	0.500
F(000)	3952
scan type	ω−2θ
θ range, deg	2.52−22.48
scan width, deg	0.8 + 0.35 tan θ
index ranges	$0 \le h \le 29, 0 \le k \le 20, 0 \le l \le 19$
scan speed, deg min^{-1}	5.49
no. of reflns collcd	6848
no. of ind reflns	6215 [*R*(int) = 0.0000]
refinement method	Full-matrix least-squares on F^2
data/restraints/params	6170/0/274
goodness-of-fit on F^2	1.166
final *R* indices [$I > 2\sigma(I)$]	0.0562, *wR*2 = 0.1477
R indices (all data)	*R*1 = 0.1294, *wR*2 = 0.2413
largest diff peak and hole, e Å^3	+0.715 and −0.500

Table 2. Summary of Crystal Data for [(PP$_3$)Ru(C≡CPh)$_2$] (6) and [(PP$_3$)Ru(H){η^1-(MeO$_2$C)C=CH(CO$_2$Me)}] (10·C$_2$H$_5$OH)

	6	**10·C$_2$H$_5$OH**
formula	$C_{58}H_{52}P_4Ru_1$	$C_{50}H_{56}O_5P_4Ru_1$
fw	974.02	961.96
cryst size, mm	0.18 × 0.15 × 0.03	0.50 × 0.30 × 0.27
cryst syst	monoclinic	triclinic
space group	$P2_1/a$ (No 14)	$P\bar{1}$ (No. 2)
a, Å	10.660(2)	11.611(2)
b, Å	40.342(9)	22.377(2)
c, Å	11.082(4)	9.490(3)
α, deg	90	93.87(2)
β, deg	93.27(3)	109.08(2)
γ, deg	90	76.26(1)
V, Å^3	4758.01	2263.41
Z	4	2
ϱ(calcd), g cm^{-3}	1.36	1.41
radiation; λ, Å	graphite-monochromated Cu Kα; 1.5418	graphite-monochromated Mo Kα, 0.710 69
scan type	ω−2θ	ω−2θ
2θ range, deg	5−120	5−50
scan width, deg	1.2 + 0.34 tan θ	0.8 + 0.35 tan θ
scan speed, deg min^{-1}	1.80−3.60	8.24
no. of reflns collcd	7609	8426
no. of unique data, $I > 3\sigma(I)$	2929	6457
no. of refined parameters	185	283
R	0.059	0.047
R_w	0.059	0.052

of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[16] with anomalous dispersion corrections taken from ref 17. An empirical absorption correction was applied using the program DIFABS[18] with transmission factors in the range 0.79−1.80 and the Ψ scan procedure with transmission factors in the range 88.88−99.97. The computational work was performed with a Digital Dec 5000/200 workstation using the programs SIR92,[19] SHELX-76,[20] and SHELX-93.[21] The programs PARST[22] and ORTEP[23] were also used. Final atomic coordinates of all atoms and structure factors are available as supplementary material.

[(PP$_3$)RuH(C≡CPh)]·C$_6$H$_6$ (5·C$_6$H$_6$). Crystals suitable for an X-ray diffraction analysis were grown by slow evaporation from a diluted benzene solution of 5·C$_6$H$_6$ (1:1 v/v). A yellow parallelepiped crystal with dimensions of 0.55 × 0.28 × 0.25 mm was used for the data collection. The structure was solved by direct methods, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least squares calculations, initially with isotropic thermal parameters, and then with anisotropic thermal parameters for Ru and P atoms. The phenyl rings were treated as rigid bodies with D_{6h} symmetry and C−C distances fixed at 1.39 Å. Hydrogen atoms bonded to the carbon atoms were introduced in calculated positions using C−H bond values of 0.97 and 0.93 Å for the sp^3-hybridized carbons and the phenyl rings, respectively. At an advanced stage of the refinement an intensity of 0.7 e/Å^3, near the metal atom, was located in the difference map and successfully refined in the least squares cycles as the hydride ligand, with free positional and isotropic thermal parameters. In the final stage of the refinement a disordered molecule of benzene solvent was found and refined as two rigid groups with a population factor of 0.5 for each one.

[(PP$_3$)Ru(C≡CPh)$_2$] (6). Crystals suitable for an X-ray diffraction analysis were directly obtained from a concentrated sample dissolved in benzene-d_6 in a 5 mm NMR tube. A yellow parallelepiped crystal with dimensions of 0.18 × 0.15 × 0.03 mm was used for the data collection. The structure was solved by direct methods using the program SIR92, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least squares calculations, initially with isotropic thermal parameters, and then, during the least squares refinement, Ru and P were allotted anisotropic thermal parameters. The phenyl rings were treated as rigid bodies with D_{6h} symmetry, C−C distances fixed at 1.395 Å, and calculated hydrogen atom positions (C−H 1.08 Å).

(*E*)-[(PP$_3$)RuH{η^1-(MeO$_2$C)C=CH(CO$_2$Me)}]·C$_2$H$_5$OH (10·C$_2$H$_5$OH). Crystals suitable for an X-ray diffraction analysis were grown by slow evaporation from a diluted CH_2Cl_2/C_2H_5OH solution. A yellow parallelepiped crystal with dimensions 0.50 × 0.30 × 0.27 mm was used for the data collection. The structure was solved by using the heavy atom technique, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least squares calculations, initially with isotropic thermal parameters, and then with anisotropic thermal parameters for Ru, P, O, and all C atoms but phenyl rings. These were treated as rigid bodies with D_{6h} symmetry and C−C distances fixed at 1.39 Å. Hydrogen atoms bonded to the carbon atoms were introduced in calculated positions. At the last stage of the refinement an intensity of 0.66 e/Å^3, near the metal atom, was located in the difference map and successfully refined in the least squares cycles as the hydride ligand, with free positional and isotropic thermal parameters. A solvation molecule of ethanol was found disordered over a center of symmetry. All non-hydrogen atoms of the solvent molecule were treated as carbon atoms.

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Scheme 1

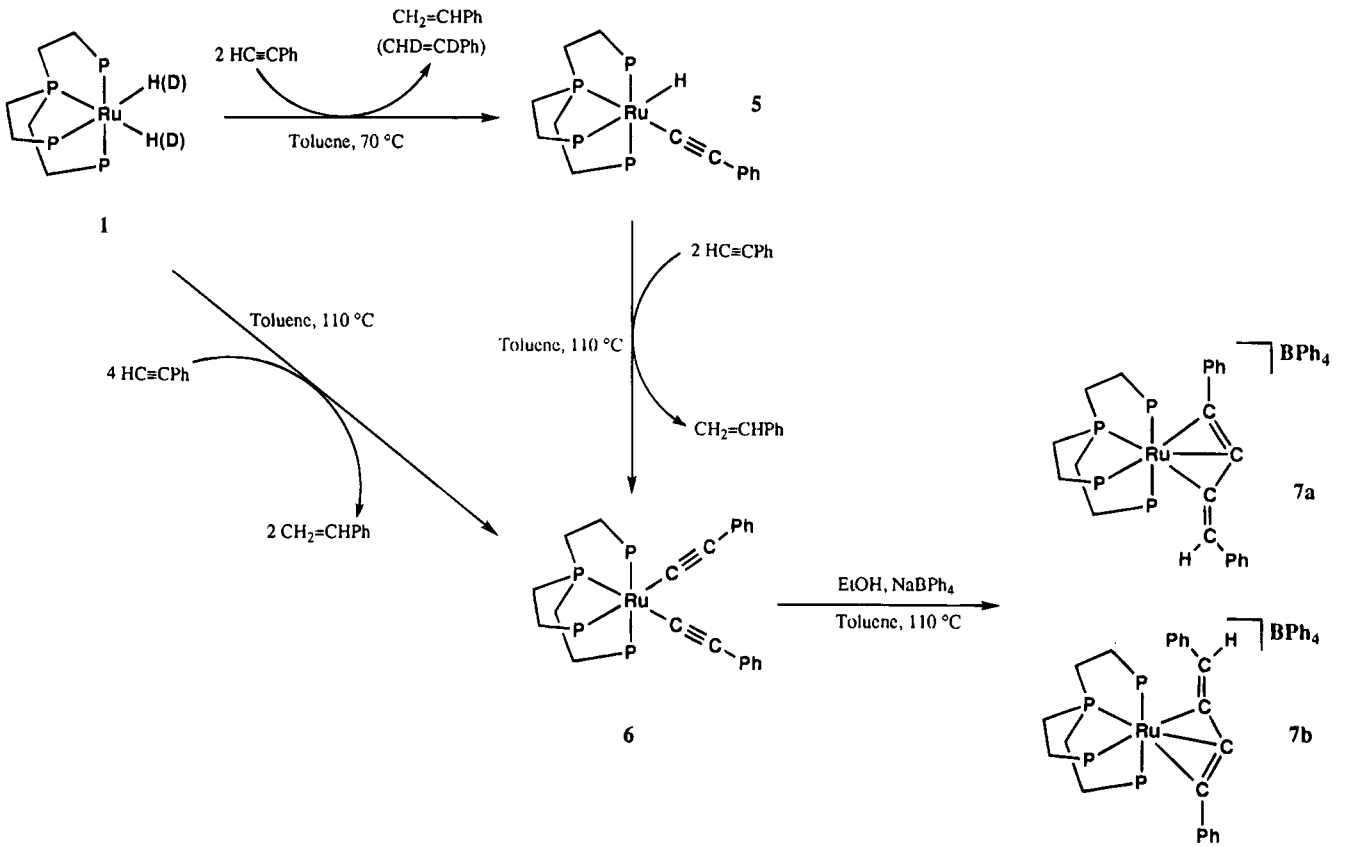


Table 3. $^{31}P\{^1H\}$ NMR Spectral Data for the Complexes

compd	solvent[a]	temp (K)	pattern[b]	chem shift (ppnm)[c] $\delta(P_A)$	$\delta(P_M)$	$\delta(P_N)$	$\delta(P_Q)$	coupling const (Hz) J_{AM}	J_{AN}	J_{AQ}	J_{MN}	J_{MQ}	J_{NQ}
5	A	293	AM_2Q	149.09	58.84		50.95	13.1		9.0		14.3	
6	A	293	AM_2Q	145.35	52.27		48.24	7.1		7.6		21.7	
8	B	290	AM_3	149.47	68.62			25.0					
		190	AMNQ	149.45	73.36	66.06	67.71	29.1	29.1	14.2	254.8	11.4	4.9
9	B	294	AM_3	149.55	68.84			24.9					
		193	AMNQ	149.12	74.53	65.98	66.49	29.3	29.3	14.0	241.0	10.7	8.8
10	B	294	AM_2Q	142.72	59.17		49.76	15.2		5.9		11.2	
		223	AMNQ	142.28	61.15	57.37	51.34	16.1	16.1	5.6	241.0	11.0	11.0
11	B	294	AM_3	139.65	64.34			22.3					
		183	AMNQ	143.61	59.42	58.42	74.04	30.5	30.5	1.5	79.6	≤1	≤1

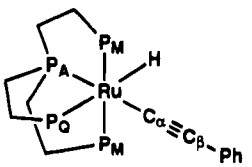
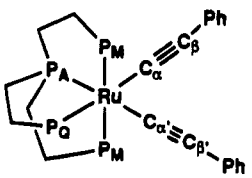
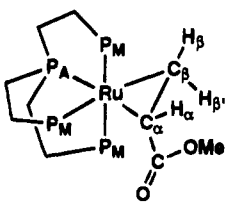
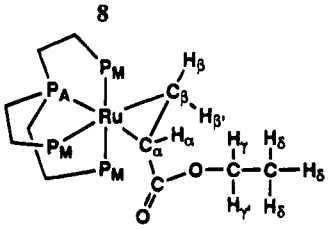
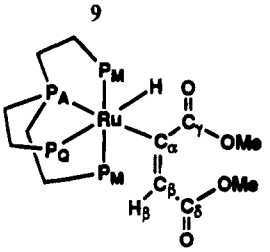
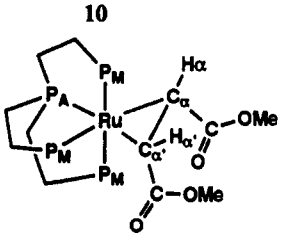
[a] A, benzene-d_6; B, dichloromethane-d_2. [b] P_A denotes the bridgehead phosphorus atom of PP_3, whereas P_M, P_N, and P_Q refer to the terminal phosphorus donors. [c] The chemical shifts (δ's) are relative to 85% H_3PO_4; downfield values are assumed as positive.

Results

The preparations and the principal reactions of the compounds described in this paper are summarized in Schemes 1, 3, and 4. Selected IR and NMR spectral data are reported in the Experimental Section and in Tables 3 ($^{31}P\{^1H\}$ NMR) and 4 (^1H and $^{13}C\{^1H\}$ NMR). $^1H\{^{31}P\}$, ^{13}C-DEPT, $^{13}C-^1H$ 2D-HETCOR, and $^1H-^1H$ 2D-COSY NMR spectra allowed the total and unequivocal assignment of all ^1H and ^{13}C resonances for all compounds as labeled in Table 4.

Reactivity of [(PP$_3$)RuH$_2$] with HC≡CPh. (A) At 70 °C. Independently of the reaction time, stirring **1** in toluene with a 10-fold excess of phenylacetylene at 70 °C results in the formation of a light yellow solution from which crystals of the *cis* alkynyl hydride [(PP_3)-RuH(C≡CPh)] (**5**) separate by addition of ethanol. No appreciable reaction occurs below this temperature. The complete conversion of **1** to **5** is accompanied by stoichiometric production of styrene (^1H NMR, GC–MS) due to incorporation of the terminal hydride ligands of the starting organometallic complex into the alkyne reagent. As a matter of fact, treatment of [(PP_3)RuD_2] (**1**-d_2) in THF-d_8 with HC≡CPh (1 h, 70 °C) leads to selective formation of styrene-d_2, with no deuterium incorporation into the ruthenium product **5**. The IR spectrum of the latter compound contains a medium intensity bands at 1941 cm^{-1} and a more intense absorption at 2060 cm^{-1}, which are assigned to ν(Ru–H) and ν(C≡C), respectively. In keeping with this assignment, the lower energy vibration is not present in the IR spectrum of the isotopomer [(PP_3)RuD(C≡CPh)] (**5**-d_1), which, in fact, shows a medium intensity absorption at 1417 cm^{-1} due to the ν(Ru–D) bond ($k_{H/D}$ = 1.37). The presence of a terminal hydride ligand is confirmed by the ^1H NMR spectrum which contains a well-resolved multiplet (dtd pattern) at −8.81 ppm. The $^{31}P\{^1H\}$ NMR spectrum consists of a temperature-invariant AM_2Q spin system. This pattern is typical of octahedral

Table 4. Selected ^1H and $^{13}C\{^1H\}$ NMR Spectral Data for the Complexes[a]

complex	^1H NMR assign	^1H NMR δ (multiplicity)[b]	^1H NMR J[c]	$^{13}C\{^1H\}$ NMR assign	$^{13}C\{^1H\}$ NMR δ (multiplicity)[b]	$^{13}C\{^1H\}$ NMR J[c]
	Ru−H[d]	−8.81 (dtd)	$^2J(HP_Q)$ 78.9 $^2J(HP_A)$ 16.7 $^2J(HP_M)$ 26.7	C_α	117.46 (dq)	$^2J(CP_A)$ 22.3 $^2J(CP_Q)$ 2.0 $^2J(CP_M)$ 2.0
				C_β	*e*	
5						
				$C_\alpha C_{\alpha'}$	117.85 (dq)	$^2J(CP_{trans})$ 23.4 $^2J(CP_{cis})$ 1.4
					114.86 (dq)	$^2J(CP_{trans})$ 21.7 $^2J(CP_{cis})$ 2.6
				$C_\beta C_{\beta'}$	126.81 (d) 125.15 (d)	$^3J(CP_{trans})$ 15.8 $^3J(CP_{trans})$ 14.3
6						
	OCH_3	3.33 (s)		CO_2Me	181.19 (s)	
	H_α[f]	3.08 (m)	$^3J(H_\alpha H_\beta)$ 7.5 $^3J(H_\alpha H_{\beta'})$ 9.7 $^3J(H_\alpha P_A)$ 6.3 $^3J(H_\alpha P_M)$ 3.2	OCH_3	50.28 (s)	
				C_β[g]	42.73 (s)	
				C_α[g]	31.99 (d)	$^2J(CP_A)$ 14.0
	H_β[f]	1.64 (m)	$^2J(H_\beta H_{\beta'})$ 3.7 $^3J(H_\beta P_M)$ 5.2			
	$H_{\beta'}$[f]	1.56 (m)	$^3J(H_{\beta'} P_M)$ 7.5			
8						
	$H_\gamma H_{\gamma'}$[d]	4.10 (dq)	$^2J(H_\gamma H_{\gamma'})$ 10.9 $^3J(H_\gamma H_\delta)$ 7.2	CO_2Et	181.00 (s)	
		3.91 (dq)	$^3J(H_{\gamma'} H_\delta)$ 7.0	OCH_2CH_3	58.82 (s)	
				C_β[g]	42.90 (s)	
	H_α[f]	2.98 (m)	$^3J(H_\alpha H_\beta)$ 7.7 $^3J(H_\alpha H_{\beta'})$ 9.8	C_α[g]	32.48 (d)	$^2J(CP_A)$ 15.3
				OCH_2CH_3	15.07 (s)	
	H_β[f]	1.60 (m)	$^2J(H_\beta H_{\beta'})$ 3.6			
	$H_{\beta'}$[f]	1.55 (m)				
	H_δ	1.09 (t)				
9						
	Ru−H	−9.04 (dtd)	$^2J(HP_Q)$ 80.9 $^2J(HP_A)$ 15.7 $^2J(HP_M)$ 23.9	C_α	200.27 (dq)	$^2J(CP_A)$ 54.3 $^2J(CP_Q)$ 11.8 $^2J(CP_M)$ 11.8
	OCH_3	3.03 (s)		C_γ[h]	182.88 (s)	
	OCH_3	3.50 (s)		C_δ	163.04 (d)	$^2J(CP_A)$ 7.6
	H_β	6.08 (dt)	$^4J(HP_A)$ 6.2 $^2J(HP_M)$ 1.4	C_β[i]	126.50 (dt)	$^3J(CP_A)$ 12.1 $^2J(CP_M)$ 3.8
				OCH_3[j]	50.50 (s)	$^2J(CP_Q)$ 3.8
				OCH_3[k]	49.72 (s)	
10						
	OCH_3[l]	2.84 (s)		CO_2Me	181.28 (s)	
	$H_\alpha H_{\alpha'}$[f,m]	3.12 (dq)	$^3J(HP_A)$ 5.2 $^3J(HP_M)$ 3.4 $^3J(HP_N)$ 3.4 $^3J(HP_Q)$ 3.4	OCH_3	50.16 (s)	
				$C_\alpha C_{\alpha'}$[g]	37.06 (dq)	$^2J(CP)$ 8.7 $^2J(CP)$ 2.9
11						

[a] All spectra were recorded at room temperature in CD_2Cl_2 solutions unless otherwise stated. The resonances due to the hydrogen and carbon atoms of the PP_3 ligand and the phenyl group on the phenylethynyl ligand are not reported. [b] Chemical shifts are given in ppm and are relative to either residual ^1H resonances in the deuterated solvents (^1H NMR) or the deuterated solvent resonances ($^{13}C\{^1H\}$ NMR). Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [c] Coupling constants (J) are in hertz. [d] The ^1H NMR spectrum was recorded in benzene-d_6. [e] Masked by the aromatic carbons of the PP_3 and phenylethynyl ligands. [f] The coupling constants were determined from selective and broad-band $^1H\{^{31}P\}$ NMR spectra. [g] Assigned by a DEPT-135 experiment. [h] Gatedec experiment: $^3J(C_\gamma H_\beta)$ 14.7 Hz. [i] Gatedec experiment: $^1J(C_\beta H_\beta)$ 164.3 Hz. [j] Gatedec experiment: $^1J(CH)$ 145.0 Hz. [k] Gatedec experiment: $^1J(CH)$ 144.8 Hz. [l] Slow exchange spectrum (173 K): δ OMe 3.42 (s), 2.25 (s). [m] Slow exchange spectrum (173 K); δ_{H_α}, $\delta_{H_{\alpha'}}$ 3.06 (b) 2.76 (b).

metal complexes of PP_3 with a mirror plane defined by the metal, the terminal phosphorus P_Q, and the bridgehead phosphorus P_A.[3c,h,14,24] The latter nucleus resonates at lowest field relative to the other phosphorus

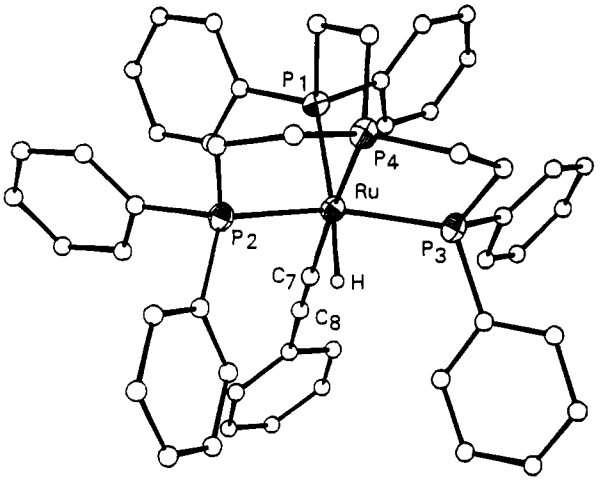


Figure 1. ORTEP drawing of [(PP_3)RuH(C≡CPh)] (**5**·C_6H_6). Except for the terminal hydride ligand, all of the hydrogen atoms are omitted for clarity. Thermal ellipsoids (30% probability) are shown only for the ruthenium and phosphorus atoms.

atoms, as expected for a phosphine common to three five-membered metallorings.[24,25] A proton-coupled ^{31}P NMR spectrum unequivocally locates the hydride ligand *trans* to the terminal phosphorus atom P_Q, which, in fact, appears at highest field as compared to the other phosphorus nuclei. Accordingly, the phenylethynyl ligand is located *trans* to the bridging phosphorus P_A (δC_α 117.46, J_{CP_A} = 22.3 Hz, $J_{CP_Q} = J_{CP_M}$ = 2.0 Hz). It is therefore reasonable to conclude that **5** exists in solution as neutral molecules in which the metal center is coordinated by the four phosphorus donors of PP_3 and by mutually *cis* hydride and σ-phenylethynyl ligands. An identical structure is adopted by **5** in the solid state, as shown by an X-ray analysis after the compound was recrystallized from C_6H_6/EtOH (1:1 v/v) to give **5**·C_6H_6.

An ORTEP drawing of the molecule is shown in Figure 1, and a list of selected bond lenghts and angles is reported in Table 5. The crystal structure consists of discrete mononuclear [(PP_3)RuH(C≡CPh)] molecules with benzene solvent molecules interspersed in the lattice. The coordination geometry around the ruthenium center is a distorted octahedron. Distortions from the idealized geometry are invariably encountered in metal complexes with tripodal tetradentate ligands and are generally caused by the steric restrictions imposed by this type of ligand.[3a,24,26]

The largest deviation from the octahedral geometry in **5** is represented by the P_2–Ru–P_3 angle [152.58(8)°] which is significantly reduced with respect to the ideal value of 180°. The Ru–P distances [2.228(2)–2.335(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for [(PP_3)RuH(C≡CPh)]·C_6H_6 (5**·C_6H_6) and [(PP_3)Ru(C≡CPh)$_2$] (6)**

	5	6		5	6
Ru–P_1	2.335(2)	2.347(4)	P_1–Ru–P_2	98.67(8)	96.9(1)
Ru–P_2	2.298(2)	2.336(4)	P_1–Ru–P_3	104.67(8)	99.8(1)
Ru–P_3	2.298(2)	2.342(4)	P_1–Ru–P_4	84.72(9)	85.1(1)
Ru–P_4	2.228(2)	2.242(4)	P_2–Ru–P_3	152.58(8)	158.3(2)
Ru–H	1.57(8)		P_2–Ru–P_4	84.29(8)	83.9(1)
Ru–C_7	2.078(8)	2.05(1)	P_3–Ru–P_4	83.70(8)	83.8(1)
Ru–C_9		2.08(1)	P_1–Ru–H	173(3)	
C_7–C_8	1.16(1)	1.21(2)	P_2–Ru–H	75(3)	
C_9–C_{10}		1.19(2)	P_3–Ru–H	81(3)	
C_8–$C_{1,7}$	1.47(1)	1.45(2)	P_4–Ru–H	92(3)	
C_{10}–$C_{1,8}$		1.48(2)	C_7–Ru–H	87(3)	
P_1–C_1	1.846(8)	1.87(1)	C_7–Ru–P_1	96.8(2)	172.1(4)
P_3–C_5	1.845(9)	1.86(1)	C_7–Ru–P_2	97.6(2)	79.5(4)
P_4–C_4	1.827(8)	1.87(1)	C_7–Ru–P_3	93.9(2)	82.2(4)
P_2–C_3	1.834(8)	1.86(1)	C_7–Ru–P_4	177.4(2)	87.5(4)
P_4–C_2	1.828(8)	1.84(1)	C_7–Ru–C_9		90.7(5)
P_4–C_6	1.823(8)	1.82(1)	C_9–Ru–P_1		96.8(4)
			C_9–Ru–P_2		97.1(4)
			C_9–Ru–P_3		94.5(4)
			C_9–Ru–P_4		177.7(4)
			Ru–C_7–C_8	177.3(7)	173(1)
			Ru–C_9–C_{10}		176(1)
			C_7–C_8–$C_{1,7}$	178.1(9)	177(1)
			C_9–C_{10}–$C_{1,8}$		177(1)

Å], though inequivalent, fall within the range of values reported in the literature.[27,28] In particular, the largest separation is between Ru and the terminal phosphorus, P_1, *trans* to the hydride which, in fact, is known to exert a strong *trans* influence.[29] The Ru–H bond distance, 1.57(8) Å, correlates with analogous separations in several Ru(II) hydrido complexes;[28,30] see for example the series of arylruthenium complexes [RuH(Ar)(pp_3)] [Ar = aryl; pp_3 = $P(CH_2CH_2CH_2PMe_2)_3$] which exhibit Ru–H distances ranging from 1.42(2) Å (Ar = *m*-xylyl) to 1.65(3) Å (Ar = phenyl).[31]

The Ru–C separation, 2.078(8) Å, is shorter than is expected for a Ru–C(*sp*) single bond (2.127 Å).[32] This difference [$|Ru-C_{found} - Ru-C_{calcd}|$ = 0.049(8) Å] is statistically significant and may reflect a scarce dπ(metal) → π^*(alkynyl) back-donation.[33] The high-energy IR stretching of the C–C triple bond [ν(C≡C) 2060 cm^{-1}] is consistent with this conclusion as is the C_7–C_8 bond length [1.16(1) Å] which does not significantly differ from the analogous separation in either disubstituted organic alkynes (*ca.* 1.20 Å)[34] or organometallic alkynyls (1.14–1.24 Å).[5a,24,28,35,36] The five-atom sequence P_4–

(24) (a) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (c) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179. (d) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1991**, *30*, 1001. (e) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (f) Bianchini, C.; Linn, K.; Masi, D.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Inorg. Chem.* **1993**, *32*, 2366. (g) Osman, R.; Pattison, D. I.; Perutz, R. N.; Bianchini, C.; Peruzzini, M. *J. Chem. Soc., Chem. Commun.* **1994**, 513.

(25) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241.

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(30) Bianchini, C.; Innocenti, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Gazz. Chim. Ital.* **1992**, *122*, 461 and references therein.

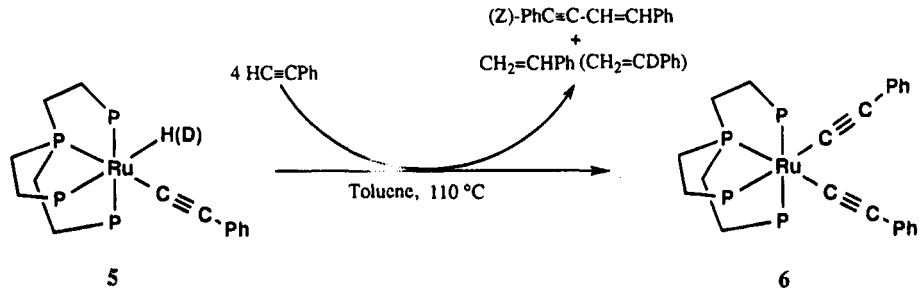
(31) (a) Antberg, M.; Dahlenburg, L.; Frosin, K.-M.; Höck, N. *Chem. Ber.* **1988**, *121*, 859. (b) Dahlenburg, L.; Frosin, K.-M. *Chem. Ber.* **1988**, *121*, 865.

(32) (a) Sun, Y.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1992**, *423*, C43. (b) Chakravarty, A. R.; Cotton, F. A. *Inorg. Chim. Acta* **1986**, *113*, 19.

(33) On the problem of dπ(metal)–π^*(alkynyl) back-bonding, see for example: (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, M. F. *Organometallics* **1990**, *9*, 360. (b) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1987**, *3049*. (c) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.

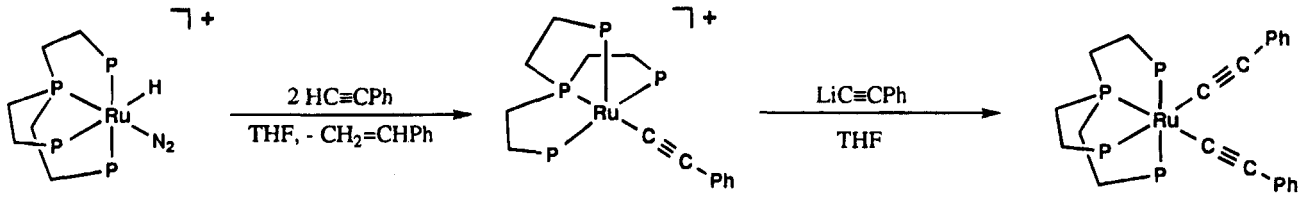
(34) (a) March, J. W. *Advanced Organic Chemistry*; Wiley: New York, 1985. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 108.

Scheme 2



5 6

Scheme 3



3 4 6

Ru—C_7—C_8—$C_{1,7}$ is virtually linear with angles 177.4(2)° (P_4—Ru—C_7), 177.3(7)° (Ru—C_7—C_8), and 178.1(9)° (C_7—C_8—$C_{1,7}$).

(B) At 110 °C. Increasing the temperature from 70 to 110 °C of the reaction between **1** and a 10-fold excess of HC≡CPh results in quantitative conversion of the starting organometallic complex to the bis(alkynyl) complex [(PP_3)Ru(C≡CPh)$_2$] (**6**) and formation of 2 equiv of styrene and of some (*Z*)-PhC≡CCH=C(H)Ph (*vide infra*). For reaction times shorter than 12 h or at lower temperature (80–100 °C), mixtures of **6** and **5** are invariably obtained, while the concentration of **6** increases with time and temperature. In accord with this finding, treatment of isolated **5** with an excess of phenylacetylene in refluxing toluene gives **6** and produces 1 equiv of sytrene plus some (*Z*)-PhC≡CCH=C(H)Ph. Analysis of the time evolution of NMR spectra of the reaction between **5** (or **5**-d_1) and a 4-fold excess of HC≡CPh in toluene-d_8 in a sealed tube at 110 °C (Scheme 2) provides the following evidence: (i) All HC≡CPh is consumed in 24 h to give equivalent amounts of styrene and (*Z*)-PhC≡CCH=C(H)Ph. (ii) The formation of styrene precedes the formation of the butenyne. (iii) Deuterium from **5**-d_1 is selectively incorporated into styrene. (iv) No other phosphorus-containing species is observable by ^{31}P NMR during the transformation of **5** into **6** and during the total consumption of the 1-alkyne. (v) Compound **6** is stable in toluene at 110 °C for several days. (vi) Further phenylacetylene syringed into the NMR tube (opened and resealed) after complete transformation of **5** into **6** is slowly consumed to give (*Z*)-PhC≡CCH=C(H)Ph. Only traces of (*E*)-PhC≡CCH=C(H)Ph are formed.[37]

Like the alkynyl hydride precursor, the bis(alkynyl) complex **6** is stereochemically rigid on the NMR time scale (AM_2Q pattern in the temperature range from +30 to −85 °C). The presence of two inequivalent σ-phenylethynyl ligands is shown by both IR [ν(C≡C) at 2087 and 2073 cm^{-1}] and multinuclear NMR spectroscopy, particularly by the $^{13}C\{^1H\}$ NMR spectrum which contains two multiplets in the region of C_α quaternary carbon atoms of σ-alkynyl ligands.[3h,10a] Both these resonances disappear in the DEPT spectrum and exhibit chemical shifts and coupling constants in good correlation with those reported for a variety of σ-alkynyl metal complexes. As expected, complexation to ruthenium(II) causes the terminal sp carbons of the alkynyl ligands to experience a strong downfield shift as compared to the free alkyne [$\Delta\delta = \delta_{RuC\equiv CPh_{av}} - \delta_{HC\equiv CPh} = (116.4 - 78.5)$ ppm = 37.9 ppm].

On the basis of all these spectroscopic data as well as the independent synthesis of **6** illustrated in Scheme 3, a structure is assigned to the latter compound in which the ruthenium center is octahedrally coordinated by PP_3 and by two mutually *cis* σ-phenylethynyl ligands. Indeed, this structure is adopted by **6** in the solid state, as shown by a single crystal X-ray analysis. Selected bond distances and angles are given in Table 5; an ORTEP view of the molecule is shown in Figure 2 along with the labeling scheme. To the best of our knowledge, **6** is the first *cis*-dialkynylruthenium complex authenticated by an X-ray structural determination.[38,39]

The structure consists of discrete molecules of [(PP_3)Ru(C≡CPh)$_2$] with no clathrated solvent molecules in the lattice.

The overall structure of **6** is essentially analogous to that of the alkynyl hydride precursor, the only difference being a phenylethynyl group in the place of hydride. Interestingly, the P_1—Ru bond length [2.347(4) Å] si quite similar to the analogous distance in **5**·C_6H_6 [2.335(2) Å], thus suggesting that the hydride and phenylethynyl ligands exert a comparable *trans* influence. The Ru—C separations of 2.05(1) and 2.08(1) Å along with ν(C≡C) at 2087 and 2073 cm^{-1} indicate a possible weak

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(37) ^1H NMR (21 °C, toluene-d_8, 299.94 MHz): $\delta_{CH_A-CH_B}$ 7.12, 6.53 (d, $^3J_{HH}$ 16.5 Hz). $^{13}C\{^1H\}$ NMR (21 °C, toluene-d_8, 75.43 MHz): δ 142.64 (s, PhCH=CH); 109.16 (s, PhCH=CH); 92.80, 90.71 (s, PhC≡C).

Table 6. Dimerization of HC≡CPh Catalyzed by (PP_3)Ru Complexes

catalyst	products (%)				
	(*Z*)-1,4-Diphenylbut-3-en-1-yne	(*E*)-1,4-Diphenylbut-3-en-1-yne	styrene	phenylacetylene	other
$[(PP_3)RuH_2]$[a]	29(1)	traces	1(0.5)	70(2)	
$[(PP_3)RuH(C{\equiv}CPh)]$[a]	58(2)	1(0.5)	2(0.5)	37(1)	2[c]
$[(PP_3)Ru(C{\equiv}CPh)_2]$[a]	78(2)	2(0.5)		20(1)	1[c]
$[(PP_3)Ru(\eta^3\text{-}PhC_3CHPh)]^+$ [b]	84(2)	5(1)		11(1)	
$[(PP_3)Ru(C{\equiv}CPh)]^+$ [b]	83(2)	5(1)		12(1)	
$[(PP_3)Ru(C{\equiv}CPh)_2]/NH_4PF_6$	84(2)	5(1)		11(1)	

[a] Catalyst, 0.1 mmol; substrate/catalyst ratio = 100; toluene, 20 mL; T = 100 °C; reaction time, 6 h. [b] See ref 3a,c. [c] 1,3,5-Triphenylbenzene and 1,2,4-triphenylbenzene in a *ca.* 2:1 ratio.

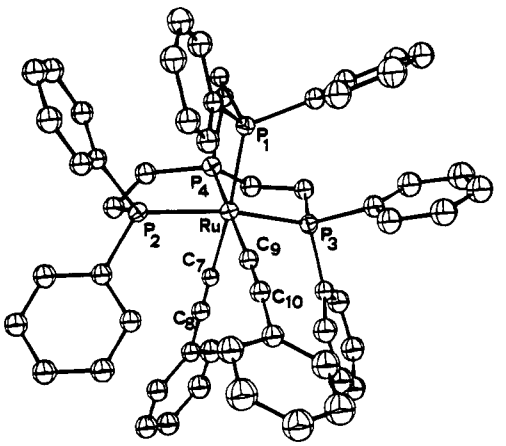

Figure 2. ORTEP drawing (30% thermal ellipsoids probability) of $[(PP_3)Ru(C{\equiv}CPh)_2]$ (**6**). All of the hydrogen atoms are omitted for clarity.

$d\pi$(metal) → π^*(alkynyl) transfer.[33] Consistently, the C_7-C_8 and C_9-C_{10} separations [1.21(2) and 1.19(2) Å, respectively] are typical of C−C triple bonds.[5a,24c,28,35,38]

Of the two five-atom arrays $P_4-Ru-C_9-C_{10}-C_{1,8}$ and $P_1-Ru-C_7-C_8-C_{1,7}$ only the former is virtually linear [P_4-Ru-C_9 = 177.7(4)°; $Ru-C_9-C_{10}$ = 176(1)°; $C_9-C_{10}-C_{1,8}$ = 177(1)°], while the latter slightly deviates from linearity [P_1-Ru-C_7 = 172.1(4)°; $Ru-C_7-C_8$ = 173(1)°; $C_7-C_8-C_{1,7}$ = 177(1)°]. A possible reason for this observation is that the face of the complex opposite to the terminal phosphorus P_1 is more sterically crowded by the phenyl substituents on the *trans* phosphines than the face opposite the bridging phosphine.[40]

Finally, the interatomic contact between the two ruthenium bonded C(sp) carbons [$d_{C_7-C_8}$ = 2.94(2) Å] excludes any interaction between the two alkynyl ligands.

Besides being thermally stable, **6** is also air-stable in the solid state, whereas it slowly decomposes in solutions exposed to air. Interestingly, compound **6** reacts with protic acids, even very weak ones such as NH_4^+ (pK_a 9) or EtOH (pK_a 18), converting to a *ca.* 3:1 mixture of the known butenynyl complexes (*E*)-[$(PP_3)Ru\{\eta^3$-$PhC_3C(H)Ph\}]BPh_4$ (**7a,b**).[3c] These differ from each other only in the anchoring mode of the η^3-butenynyl ligands, as shown in Scheme. 1.

Regio- and Stereoselective Dimerization Reactions of Phenylacetylene to (*Z*)-1,4-Diphenylbut-3-en1-yne. From the observation that toluene solutions of **6** at 110 °C consume HC≡CPh, one may readily infer that the bis(alkynyl) complex is a catalyst or catalyst precursor for the oligomerization of 1-alkynes. Catalytic experiments do confirm this hypothesis. The results obtained are shown in Table 6, which summarizes also the activities exhibited by the precursors **1** and **5**, the η^3-butenynyl complexes **7a,b**,[3c] the σ-alkynyl complex $[(PP_3)Ru(C{\equiv}CPh)]BPh_4$,[3c] and a 1:1 mixture of **6** and NH_4PF_6.

Reaction of **6** with an excess of phenylacetylene (100:1) in refluxing toluene for 6 h results in conversion (*ca.* 80%) of the alkyne to (*Z*)-1,4-diphenylbut-3-en-1-yne (95%) and (*E*)-1,4-diphenylbut-3-en-1-yne (5%). In the catalytic reaction, phenylacetylene is thus regio- and stereoselectively dimerized. No trace of the 1,3-disubstituted regioisomer was detected by either NMR or GC−MS. After the reaction was quenched and the solvent was removed under reduced pressure, ^{31}P NMR spectroscopy showed the solid residue to contain **6** as the only phosphorus-containing product. The reaction was also followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in a sealed tube at a constant temperature of 110 °C in toluene-d_8. A higher catalyst to substrate ratio (1:10) was used in order to obtain proton spectra with a reasonable signal-to-noise ratio. The spectra, recorded every 30 min, showed that **6** is both the termination metal complex and the only phosphorus-containing species observable on the NMR time scale in the course of the catalytic reaction. This suggests the participation of the bis(alkynyl) complex in the rate-determining step of phenylacetylene dimerization.

The Ru catalyst is very robust; a number of subsequent reactions can be performed using the same catalyst with no appreciable decay of activity.

As is evident from a perusal of Table 6, compound **6** is more efficient than **5** which, in turn, is more efficient than **1**. Conversely, all of these systems show identical, excellent selectivity in the *Z* stereoisomer. The experi-

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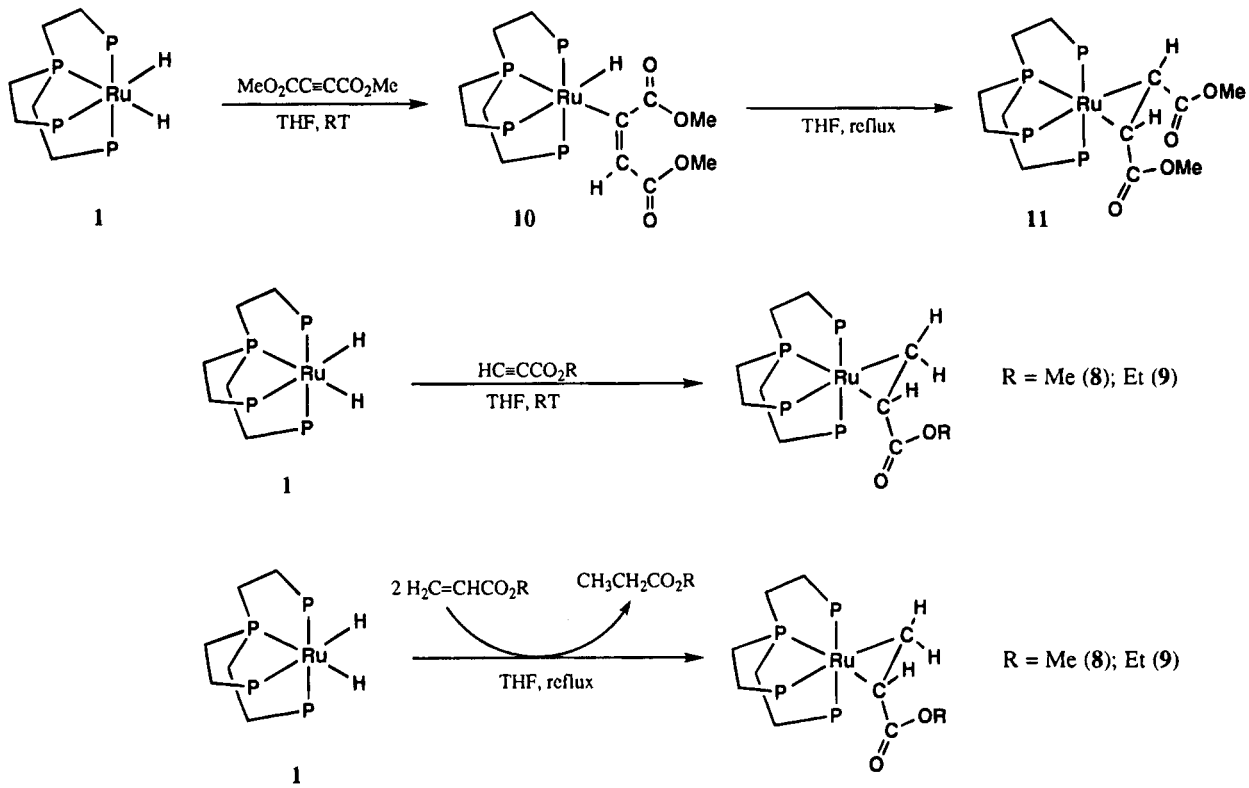
Scheme 4



mental observation that **1** is precursor to **5** and **5** is precursor to **6** (see Schemes 1 and 2) accounts for the trend in activity and selectivity summarized in Table 6. In other words, the minor efficiency of the dihydride and alkynyl hydride complexes can be ascribed to induction periods necessary for converting both compounds to **6**, which is the termination metal product of all catalytic runs.

The isomeric Ru(II) η^3-butenynyl complexes (*E*)-$[(PP_3)Ru\{\eta^3\text{-}PhC_3C(H)Ph\}]^+$ and their σ-alkynyl precursor $[(PP_3)Ru(C{\equiv}CPh)]^+$ are slightly more efficient than the neutral bis(alkynyl) complex **6** (84 *vs* 78%), while exhibiting a comparable selectivity.[3a,c] It is worth noticing, however, that the catalytic reactions with these cationic complexes were performed in refluxing THF due to their poor solubity in toluene. In keeping with the facile protonation of the bis(alkynyl) **6** to the cationic η^3-butenynyl complexes, a catalytic run performed in THF using a 1:1 mixture of **6** and NH_4PF_6 as catalyst system, gave results identical with those from the mixture catalyzed by isolated **7a,b**.

Model Reactions. In an attempt to gather as much information as possible about the mechanism of formation of **5** from **1** and of **6** from **5** as well as the catalysis cycle of phenylacetylene dimerization, the following independent reactions have been performed.

Reaction of $[(PP_3)RuH_2]$ with $HC{\equiv}CCO_2R$ (R = Me, Et). The η^2-alkene complexes $[(PP_3)Ru\{\eta^2\text{-}CH_2{=}CH(CO_2Me)\}]$ (**8**) and $[(PP_3)Ru\{\eta^2\text{-}CH_2{=}CH(CO_2Et)\}]$ (**9**) are obtained as yellow orange crystals by reacting **1** at room temperature in THF with a slight excess of either methyl propiolate or ethyl propiolate. Identical products are obtained when **1** is reacted in refluxing THF with a double proportion of methyl or ethyl acrylate. In this case, however, 1 equiv of alkene is hydrogenated to the corresponding alkane (methyl or ethyl propionate).

The IR spectra of **8** and **9** contain ν(C=O) and ν(C—O—C) bands which are readily attributable to uncoordinated ester groups (1673/1671 cm^{-1} and 1144/1252 cm^{-1}, respectively). The $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 show **8** and **9** to be fluxional on the NMR time scale. In both compounds, the fluxionality apparently involves only the phosphorus donors and not the alkene ligands which, in fact, show no temperature variation of the chemical shifts of their hydrogen and carbon nuclei. With the help of homo- and heteronuclear selective decoupling experiments, it has been possible to locate unambiguously the substituted carbon of acrylate *trans* to the bridgehead phosphorus. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **9** are presented in Figure 3.

In the fast exchange regime (>20 °C), the spectrum consists of an AM_3 spin system which shows the three terminal PPh_2 groups to be magnetically equivalent. Thus, due to a rapid site-exchange process involving all terminal phosphorus atoms, the signal of the bridgehead phosphorus atom appears as a narrow quartet in the high-field region of the spectrum (δ 149.55 ppm, J_{PP} = 24.9 Hz), while a doublet at 68.64 ppm features the three terminal PPh_2 groups. On decreasing the temperature to −80 °C, at which temperature the molecule is stereochemically rigid, the low-field resonance progressively transforms into a triplet of doublets indicating that the terminal P atoms have become magnetically inequivalent. This process involves neither coalescence of the low-field resonance nor a change of its chemical shift. In contrast, the high-field doublet broadens as the temperature is decreased, merges into the baseline at *ca.* −40 °C, and then decoalesces to give a set of three resonances. In the slow exchange regime at −80 °C,

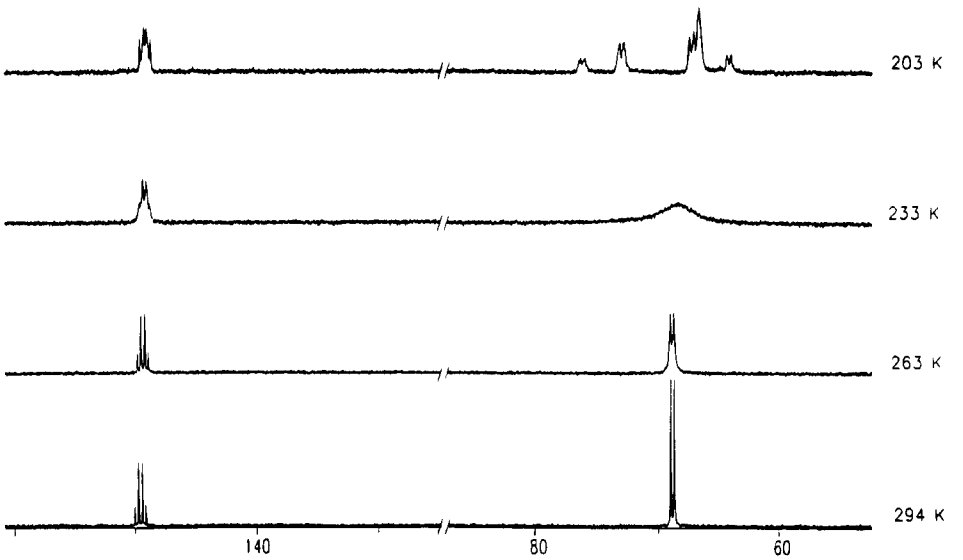


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[(PP_3)Ru\{\eta^2\text{-}CH_2{=}CH(CO_2Et)\}]$ (**9**) (CD_2Cl_2, 81.15 MHz, H_3PO_4 reference).

these signals are well-resolved and unequivocally constitute the MNQ part of an AMNQ pattern. The terminal phosphorus P_Q (δ 66.49), which is located *trans* to the CH_2 group of the ethyl acrylate ligand (*vide infra*), appears as a triplet of doublets, while the P_M and P_n nuclei give rise to a strongly perturbed second-order system with resonances centered at 74.53 and 65.98 ppm and coupled by 241.0 Hz, as is expected for inequivalent phosphorus atoms *trans* to each other.[29a,41,42] Inequivalence of the axial phosphorus nuclei in octahedral metal complexes of both PP_3 and related tripodal tetradentate ligands bearing identical substituents on the phosphorus atoms is observed whenever there is no mirror plane in the complex molecule.[43] This may occur as a consequence of restricted rotation of bulky substituents on either the phosphorus donors or the coligands. In the case at hand, we believe that only the orientation of the ester group with respect to the plane defined by the bridging phosphine and the two olefin carbons can differentiate P_M and P_N in the slow exchange regime. In the fast exchange regime, rapid rotation of the alkene makes the three terminal phosphorus atoms equivalent. Alternative mechanisms involving dissociation of a phosphine arm can be ruled out in light of the retention of all J_{PP} along the entire dynamic process.

A final comment regards the nature of the metal–alkene bond in **8** and **9**. The mode of formation of these compounds would imply interaction of the Ru(0) fragment [(PP_3)Ru] with a molecule of alkyl acrylate (*vide infra*). The maintainment of the formal d^8 metal configuration in the resulting alkene complexes thus depends on the extent of the $d\pi$(metal) → π^*(alkene) transfer. In **8** and **9**, the metal–alkene bonding seems to be midway between ruthenacyclopropane and π-olefin structures.[44] In fact, while the fluxionality of the

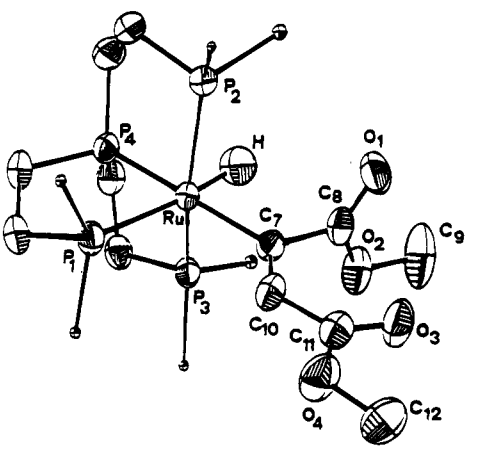


Figure 4. ORTEP drawing (30% thermal elliposoids probability) of $[(PP_3)RuH\{\eta^1\text{-}C(CO_2Me){=}CH(CO_2Me)\}]$ (**10**·C_2H_5OH) showing only the *ipso* carbons of the phenyl rings of PP_3. Except for the terminal hydride ligand, all of the hydrogen atoms are omitted for clarity.

complexes indicates a scarce π-back-bonding contribution, both the magnetic shielding of the alkene C_α and C_β nuclei in the $^{13}C\{^1H\}$ NMR spectra (Table 4)[44] and the ^{31}P chemical shifts (Table 3),[3a,c,14] typical of Ru(II) compounds, point to a significant amount of metal-to-olefin π-bonding.

Reaction of $[(PP_3)RuH_2]$ with $MeO_2CC{\equiv}CCO_2Me$. Reaction of **1** in THF with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ (DMAD) at room temperature results in stereoselective *cis* insertion of the disubstituted alkyne into the Ru–H bond *trans* to the bridging phosphorus. The structure of the resulting vinyl hydride complex (*E*)-$[(PP_3)RuH\{\eta^1\text{-}(MeO_2C)C{=}C(H)CO_2Me\}]$ (**10**) has been determined by an X-ray analysis after the compound was recrystallized from CH_2Cl_2/EtOH to give **10**·C_2H_5-OH.

An ORTEP drawing of the complex is shown in Figure 4, while a list of selected bond distances and angles is presented in Table 7. Like in the alkynyl hydride and

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Table 7. Selected Bond Distances (Å) and Angles (deg) for [(PP$_3$)RuH{η^1-(MeO$_2$C)C≡CH(CO$_2$Me)}]·C$_2$H$_5$OH (10·C$_2$H$_5$OH)

Ru–P$_1$	2.376(1)	P$_1$–Ru–P$_2$	101.07(6)
Ru–P$_2$	2.299(1)	P$_1$–Ru–P$_3$	103.49(6)
Ru–P$_3$	2.324(1)	P$_1$–Ru–P$_4$	83.30(5)
Ru–P$_4$	2.252(1)	P$_2$–Ru–P$_3$	149.85(7)
Ru–H	1.48(5)	P$_2$–Ru–P$_4$	83.90(6)
Ru–C$_7$	2.140(5)	P$_3$–Ru–P$_4$	81.89(6)
C$_7$–C$_{10}$	1.349(8)	P$_1$–Ru–H	173(1)
C$_7$–C$_8$	1.476(6)	P$_2$–Ru–H	77(2)
C$_{10}$–C$_{11}$	1.455(7)	P$_3$–Ru–H	77(2)
C$_8$–O$_1$	1.204(6)	P$_4$–Ru–H	90(2)
C$_{11}$–O$_3$	1.202(5)	C$_7$–Ru–H	88(2)
C$_8$–O$_2$	1.351(6)	C$_7$–Ru–P$_1$	98.5(1)
C$_{11}$–O$_4$	1.348(7)	C$_7$–Ru–P$_2$	97.1(1)
O$_1$–C$_9$	1.448(6)	C$_7$–Ru–P$_3$	96.3(1)
O$_4$–C$_2$	1.443(8)	C$_7$–Ru–P$_4$	177.7(1)
P$_1$–C$_1$	1.847(5)	Ru–C$_7$–C$_8$	113.0(3)
P$_3$–C$_5$	1.849(5)	Ru–C$_7$–C$_{10}$	130.2(3)
P$_4$–C$_4$	1.830(5)	C$_7$–C$_8$–O$_1$	111.9(4)
P$_2$–C$_3$	1.857(5)	C$_7$–C$_8$–O$_2$	124.9(5)
P$_4$–C$_2$	1.846(4)	O$_1$–C$_8$–O$_2$	122.9(5)
P$_4$–C$_6$	1.821(5)	C$_8$–O$_1$–C$_9$	116.4(4)
		C$_7$–C$_{10}$–C$_{11}$	124.8(4)
		C$_8$–C$_7$–C$_{10}$	116.8(4)
		C$_{10}$–C$_{11}$–O$_3$	127.2(5)
		C$_{10}$–C$_{11}$–O$_4$	110.9(4)
		O$_3$–C$_{11}$–O$_4$	122.0(5)
		C$_{11}$–O$_4$–C$_{12}$	116.6(4)

bis(alkynyl) derivatives **5** and **6**, the coordination geometry around the metal center can be described as a distorted octahedron. The main distortion from the idealized geometry is again due to the angle P$_2$–Ru–P$_3$ which closes up to 149.85(7)°.

The Ru–P bond distances [2.252(2)–2.376(1) Å] are similar to the analogous separations in **5** and **6** as well as in other (PP$_3$)Ru complexes.[3a,45] As discussed above for **5**, the lengthening of the Ru–P$_1$ distance [2.376(1) Å] is consistent with the presence of a *trans* hydride ligand. The Ru–H separation in **10**·C$_2$H$_5$OH [1.48(5) Å] is comparable with the Ru–H bond distances found in [RuH(H$_2$BH$_2$)(PMe$_3$)$_3$][46] [1.49(4) Å] and [RuHCl(Ph$_2$PCH$_2$PPh$_2$)$_2$][47] [1.49(8) Å].

In the alkenyl ligand, which bears two *cis* methyl carboxylate substituents, the C$_7$–C$_{10}$ distance [1.349(8) Å] is typical of C–C double bonds in dimethyl carboxylate vinyl complexes[48] of which there are some Ru derivatives.[49] The Ru–C$_7$ distance [2.140(5) Å] compares well with the value reported for the alkenyl complex [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)Cl}Cl(PMe$_2$Ph)$_2$] [2.16(2) Å][50] but is significantly longer than those of the majority of ruthenium vinyl complexes [2.034(5)–2.082(6) Å].[28]

The equatorial plane of the coordination polyhedron containing the metal atom is essentially coplanar with the atoms C$_7$, C$_8$, C$_{10}$, C$_{11}$, O$_3$, and O$_4$ but virtually perpendicular to the plane containing the other ester group (torsional angles Ru–C$_7$–C$_8$–O$_1$ and Ru–C$_7$–C$_8$–O$_2$ of −88.7(4) and +86.2(5)°, respectively).

The different orientation of the methyl carboxylate substituents with respect to the plane defined by P$_4$, P$_3$, Ru, and H is of particular interest, as it allows rationalization of the stereochemical nonrigidity of **10** in solution where, in the temperature range from −80 to +60 °C, the Ru center apparently retains the coordination geometry determined in the solid state (*vide infra*). In fact, the ^{31}P{^{1}H} NMR spectrum of **10** at room temperature shows an AM$_2$Q pattern analogous to that of the rigd alkynyl hydride **5** and thus consistent with the solid-state octahedral geometry. As the temperature is decreased, the M$_2$ portion of the spectrum broadens, coalesces at *ca.* −30 °C, and then at −50 °C resolves into a second-order MN system (overall AMNQ pattern). At this temperature the spectrum is thus fully comparable with that of the η^2-alkene complexes **8** and **9** in the slow motion regime where the *trans* P$_M$ and P$_N$ nuclei are made inequivalent by slowing down the rotation of the unique ester substituent. In a similar way, the *trans* P$_M$ and P$_N$ phosphorus atoms in **10** appear magnetically equivalent as long as the alkenyl fragment rotates faster than the nuclear spin transition, whereas they become inequivalent as such motion is slowed down or eventually frozen.

In the temperature range investigated, the ^{1}H and ^{13}C NMR spectra of **10** are fully consistent with the solid state structure (Table 4) and do not exhibit features that require a detailed account. It may, however, be worthwhile commenting on the coupling constant between the H and C$_\alpha$ nuclei of the σ-alkenyl ligand as well as the chemical shifts of the alkenyl C$_\alpha$ and C$_\beta$ carbons. The observed $^3J_{C_\alpha H}$ value of 14.7 Hz is for *trans* H and C atoms and thus witnesses the reliability of the Herberich and Barlage criterion for determining the stereochemistry of insertion of alkynes into M–H bonds.[51–53]

Complex **10** is highly thermally stable in solution and does not undergo the reductive elimination of dimethyl maleate up to 60 °C. Evidently, a second electron-withdrawing substituent on the alkyne (see the reaction between **1** and methyl acrylate) strengthens the Ru–C bond of the insertion product (**10**) in such a way that only at a higher temperature (*ca.* 70 °C) does **10** convert in solution to its η^2-dimethyl maleate isomer [(PP$_3$)Ru{η^2-*cis*-(MeO$_2$C)CH=CH(CO$_2$Me)}] (**11**).

The chemico-physical properties of **11** are quite comparable with those of the η^2-acrylate congeners **8** and **9**. Thus a detailed description of the IR and NMR spectral data of **11** is not in order, while it may be interesting to mention a few relevant chemical features.

Upon reductive elimination of the H and C(CO$_2$Me)=CH(CO$_2$Me) groups occurring as a thermal step, the *cis* stereochemistry of the vinyl ligand in **10** is maintained in the resulting η^2-alkene complex which, in fact, contains dimethyl maleate and not dimethyl fumarate. Indeed, the formation of the *cis* alkene ligand is unambiguously demonstrated by NMR spectra as well as the reaction between **11** and HC≡CPh in refluxing THF that yields **5** and free dimethyl maleate (Scheme 5).

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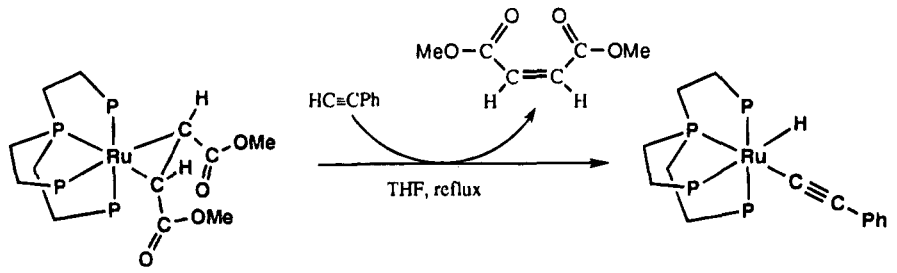
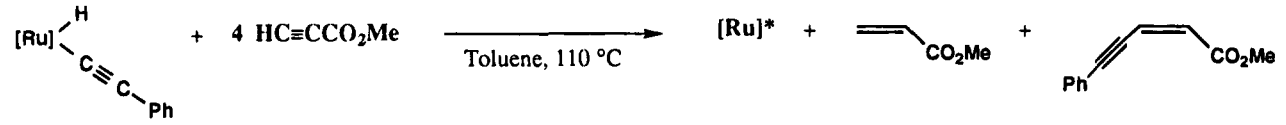
(53) Vessey, J. D.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1993**, 51.

Scheme 5

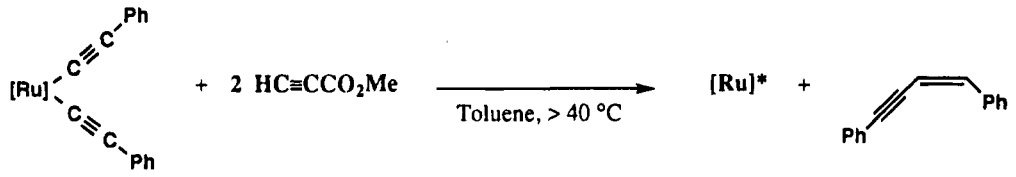


11 5

Scheme 6



5



6

[Ru] = $(PP_3)Ru$

[Ru]* = "$(PP_3)Ru(C{\equiv}CCO_2Me)_2$"

Currently undefined structure

Compound **11** is stereochemically nonrigid in solution down to −85 °C with a dynamic process analogous to that of the η^2-acrylate congeners. Like in the latter compounds, the magnetic inequivalence of the *trans* P nuclei in the slow exchange regime is originated by the lack of a mirror plane in the octahedral structure of **11**.

Reactions of $[(PP_3)RuH(C{\equiv}CPh)]$ and $[(PP_3)Ru(C{\equiv}CPh)_2]$ with $HC{\equiv}CCO_2Me$. In Situ Experiments. The reactions of the alkynyl hydride **5** and of the bis(alkynyl) **6** with 4 equiv of methyl propiolate have been carried out in sealed NMR tubes in toluene-d_8 and have been followed by ^1H NMR spectroscopy (Scheme 6).

Compound **5** reacts with $HC{\equiv}CCO_2Me$ at 110 °C and consumes all the 1-alkyne in *ca.* 4 h to give 1 equiv of both methyl acrylate and the mixed butenyne (*Z*)-$PhC{\equiv}CCH{=}C(H)CO_2Me$. Notably, the formation of the acrylate precedes that of the butenyne. The two organic products were also identified by GC–MS. Purposefully, no attempt has been made to characterize the ruthenium products, as we were essentially interested in the interaction between the Ru(H)(C≡CPh) moiety and added 1-alkyne.

The reaction between **6** and methyl propiolate occurs already at 40 °C and consumes 2 equiv of 1-alkyne in 3 h. Formed in its place is 1 equiv of (*Z*)-$PhC{\equiv}CCH{=}C(H)Ph$. At 110 °C, the reaction is complete in 1 h and produces 1 equiv of the 1,4-diphenylbut-3-en-1-yne plus traces of oligomers of methyl propiolate (*essentially dimers and trimers*).[54]

Discussion

Formation of the Bis(alkynyl) Complex $[(PP_3)Ru(C{\equiv}CPh)_2]$. The reaction that converts the dihydride **1** to the bis(phenylethynyl) complex **6** has close precedents in the transformations of $[FeH_2(dmpe)_2]$ and $[OsH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ into *trans*-$[Fe(C{\equiv}CPh)_2(dmpe)_2]$[10a,55] and $[Os(C{\equiv}CPh)_2(PMe_3)_4]$,[56] respectively [dmpe = 1,2-bis(dimethylphosphino)ethane]. A bis(phenylethynyl) complex of the formula $[Ru(C{\equiv}CPh)_2(Cyttp)]$ was also suggested to play an intermediate role in the reaction between $[RuH_4(Cyttp)]$ and $HC{\equiv}CPh$ to give $[Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)]$ [Cyttp = C_6-

(54) The trace amount of such oligomers has prevented their identification. However, since this point is not relevant to the chemistry presented in this paper, we have not carried out large-scale reactions.

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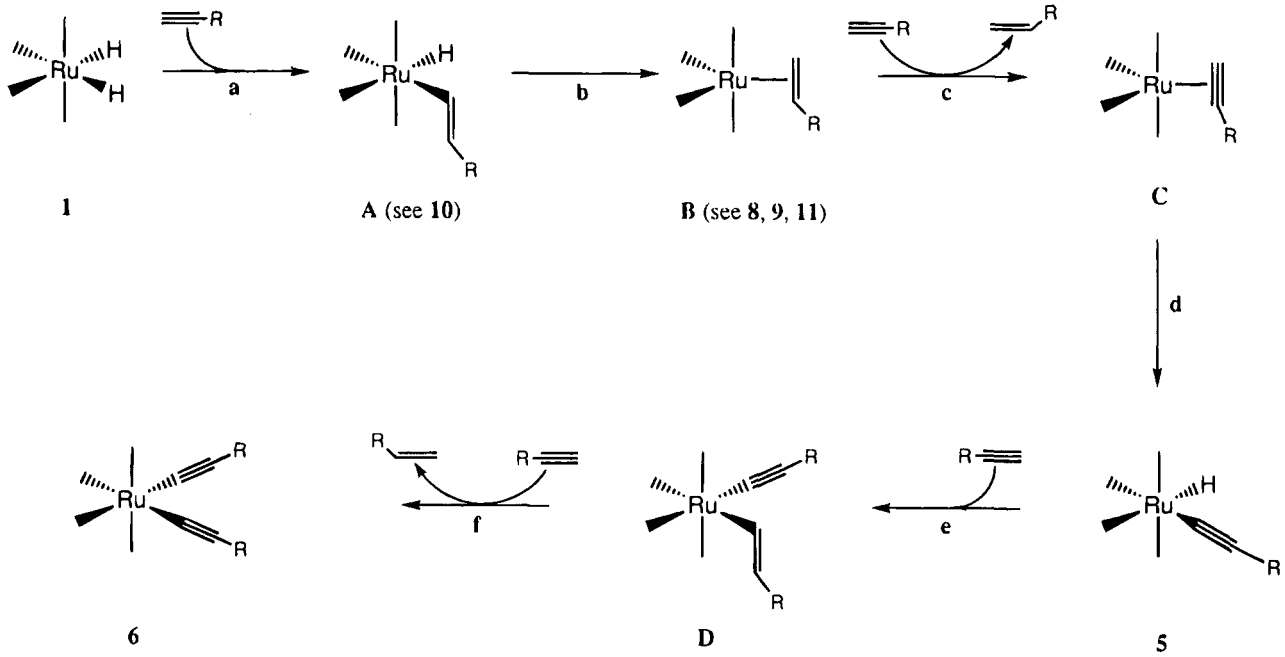
Scheme 7



$H_5P\{CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2\}_2]$.[5c] In no case, however, was the mechanism of these reactions studied in detail, though Field *et al.* reported that 2 equiv of styrene was formed in the reaction of the iron complex with HC≡CPh.[10a]

In light of the experimental evidence accumulated during this work, it is now possible to look at the conversion of **1** to **6** as a sequence of well-defined steps (Scheme 7).

The first step is the insertion of HC≡CPh into a Ru—H bond of **1** (step a).[57] Labeling experiments (formation of *cis*-CHD=CDPh) as well as a number of precedents, including the formation of (*E*)-[(PP_3)Ru(CH=CHPh)]BPh_4 from the reaction of [(PP_3)RuH(N_2)]BPh_4 with HC≡CPh,[3c] are consistent with a *cis* insertion of the 1-alkyne.[58] The mechanism of insertion most likely involves decoordination of the terminal phosphorus *trans* to H to create a free site at ruthenium for the incoming HC≡CPh molecule. Once the 1-alkyne has inserted, the pendent phosphine arm can return to saturate the metal. This unfastening/fastening motion is well-known along several reactivity patterns of PP_3 metal complexes, particularly in insertion reactions.[24a,58b] No evidence has ever been provided for the alternative decoordination of the bridgehead phosphorus.

A limiting temperature of 70 °C is required to promote a reaction between **1** and HC≡CPh in toluene. At this temperature the *cis* styryl hydride product **A** is not stable and rapidly undergoes the reductive elimination of styrene (step b) (see the reaction of **1** with $HC{\equiv}CCO_2R$; R = Me, Et). The alkene is subsequently displaced by phenylacetylene which is in fact a much better ligand (step c) (see the reaction between **11** and HC≡CPh).[59] The first equivalent of styrene is thus formed through the sacrifice of the two hydride ligands of **1** (see labeling experiment with **1**-d_2).

At this point, the reaction mixture contains a d^8 ML_4 fragment which is appropriate for the oxidative cleavage of sp C—H bonds (step e). As a result, the alkynyl hydride **5** is formed. The precursor of such an oxidative addition step is most likely a π-alkyne intermediate **C** (step d) analogous to that which traverses the formation of [(PP_3)MH(C≡CPh)]BPh_4 from the reactions of the 16-electron fragments $[(PP_3)M]^+$ (M = Co, Rh) with 1-alkynes.[24c,e]

The *cis* alkynyl hydride **5** is stable in toluene solution at the temperature of its formation from **1** (70 °C), whereas it rather rapidly converts to the bis(alkynyl) **6** at 110 °C in the presence of excess HC≡CPh. Along this transformation a second equivalent of styrene is liberated in the reaction mixture. The result of the reaction between isolated **5** and 2 equiv of $HC{\equiv}CCO_2$-Me sheds some light on the mechanism of formation of this second equivalent of styrene (Scheme 6). Indeed, only insertion of $HC{\equiv}CCO_2Me$ into the Ru—H bond of **5**, followed by sp C—H bond cleavage/sp^2 C—H bond formation (formal σ-bond metathesis between Ru—vinyl and 1-alkyne) accounts for the selective formation of methyl acrylate. The *cis* styryl phenylethynyl species **D** (step e in Scheme 7) is thus a probable intermediate along the conversion of **5** to **6** while its formation obviously requires the occurrence of a phosphine arm-off mechanism.[60]

The reaction conditions, particularly the temperature at which each single step of the overall mechanism occurs, as well as the increasing number of electron-

(57) For general aspects of hydrometalation of alkynes see: (a) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886. (b) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. (c) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146.

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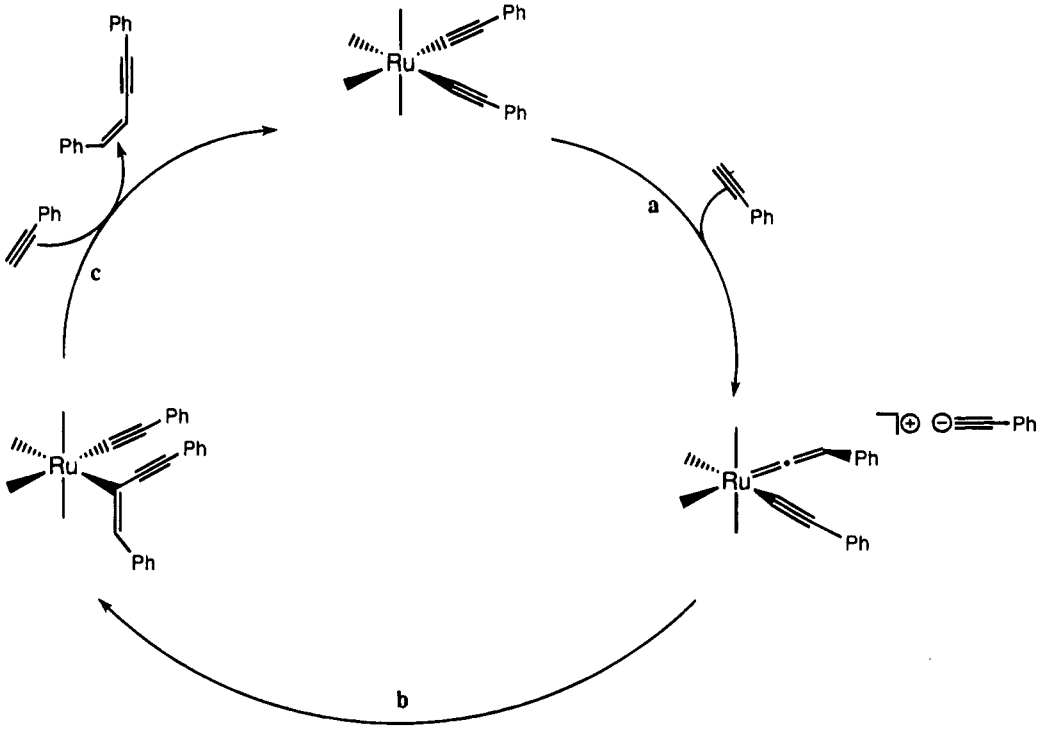
Scheme 8



withdrawing substituents on the alkyne which are needed to stabilize a Ru *cis* vinyl hydride, unequivocally indicate that the insertion of HC≡CPh into the Ru—H bond in **5** is the process with the highest activation energy. Also, from the type of organometallic and organic compounds produced, one may conclude that in Ru(II) complexes with phosphine coligands, both the insertion of 1-alkynes into Ru—H bonds and the reductive elimination of H and σ-organyl groups are favored over insertion into Ru—C bonds or reductive C—C bond formation.

Catalytic Cycle of Phenylacetylene Dimerization to (*Z*)-1,4-Diphenylbut-3-en-1-yne. Incorporation of all the above experimental evidence leads to the mechanism shown in Scheme 8 for the Ru(II)-catalyzed dimerization of HC≡CPh. In the scheme, the skeleton of the tripodal ligand and the phosphorus donors are omitted for clarity.

The most intriguing point of the proposed mechanism is the intermolecular protonation by external HC≡CPh of a σ-alkynyl is **6** (step a) to give a vinylidene intermediate. Indeed, since **6** is readily protonated by EtOH (pK_a 18) at the alkynyl C_β atom, a similar reaction may reasonably occur with HC≡CPh (pK_a 18.5).[61] Though new for (σ-alkynyl)metal complexes, the capability of 1-alkynes to act as protic acids toward nucleophilic ligands, such as terminal hydrides, is well-known.[62] Once an alkynyl group in **6** has been protonated, the consequent coupling reaction between the vinylidene and σ-alkynyl ligands to give η^3-butenynyl is a downhill process that has many precedents in the literature, particularly for Ru compounds.[3a-f] In the present case, however, the conjugate base (PhC≡C$^-$) is itself a good ligand and thus can saturate the free coordination site generated following the C—C bond formation reaction. In the absence of a conjugate base with good ligating properties, the coordination vacancy is saturated by the triple bond of the butenynyl ligand. Further to this point, we have shown that, when **6** is protonated by NH_4PF_6, η^3-butenynyl complexes **7** are obtained.

From the σ-alkynyl η^1-butenynyl intermediate, the enyne is then liberated by interaction with a second molecule of HC≡CPh *via* formal σ-bond metathesis between Ru—vinyl and 1-alkyne, as occurs in the reaction of **5** with HC≡CCO_2Me to give methyl acrylate (Scheme 6). Along with production of (*Z*)-PhC≡CCH=C(H)Ph, this process regenerates the catalyst **6** (step c).

Alternative mechanisms involving 1-alkyne insertion across Ru—C are ruled out by the independent reaction between **6** and HC≡CCO_2Me which leads to selective formation of the homocoupled enyne. The absence of the cross-coupled product (*Z*)-1-phenyl-4-(carbomethoxy)-but-3-en-1-yne excludes also a mechanism involving decoordination of a phosphine arm during the incorporation of phenylacetylene by **6**. In fact, were phosphine decoordination a feasible path, either the cross-coupled butenyne or a random distribution of homo- and cross-coupled products would have been obtained. On the other hand, unlike catalysts with f or early d elements,[4] no evidence has been provided so far for the occurrence of 1-alkyne insertion into Ru—C(alkynyl) bonds in the catalytic synthesis of enynes.

The mechanism proposed in Scheme 8, based on C—C bond coupling between σ-alkynyl and vinylidene, also accounts for the regioselectivity of the catalytic reaction. In contrast, the stereocontrol seems to be a characteristic of PP_3 metal complexes in which the repulsive

(60) Arm-off mechanisms are well documented in transition-metal polyphosphine chemistry. See, for example: (a) Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664. (b) Thaler, E. G.; Caulton, K. G. *Organometallics* **1990**, *9*, 1871. See also refs 24a and 58b.

(61) Hopkinson, A. C. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; Vol. 24, Chapter 4.

(62) Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1750.

interaction between the six phenyl rings on the tripodal phosphine and the substituents on the vinylic moiety, forces 1,4-substituted butenynyl ligands to adopt an *E* structure.[3a,ch]

A significant contribution of the bulky tripodal ligand PP_3 to the stereochemical control of phenylacetylene dimerization is consistent with the result of the reactions catalyzed by the cationic η^3-butenynyl complexes **7a,b** and their σ-alkynyl precursor $[(PP_3)Ru(C{\equiv}CPh)]^+$ as well.[3a,c] In fact, these catalytic runs, while proceeding *via* a different mechanism, display identical selectivity in the (*Z*)-butenyne (Table 6).

Conclusions

A Ru(II) bis(alkynyl) complex has been found to catalyze the regio- and stereoselective dimerization of phenylacetylene to (*Z*)-diphenylbut-3-en-1-yne. Several observations are consistent with a catalytic cycle involving protonation of a σ-phenylethynyl ligand by external HC≡CPh, followed by C—C bond formation between *cis* σ-alkynyl and vinylidene groups.

A study under various experimental conditions, the detection of some intermediates, and the use of model and crossover experiments, taken altogether, show that the ruthenium bis(alkynyl) catalyst is formed from a dehydride precursor. The reaction sequence that converts the dihydride to the bis(alkynyl) complex consumes 4 equiv of HC≡CPh and comprises a number of reaction steps: insertion of 1-alkyne into a Ru—H bond, reductive coupling of hydride and σ-vinyl groups, displacement of the resulting alkene by 1-alkyne, hydroruthenation of 1-alkyne, and σ-bond metathesis between (sp)C—H and Ru—C(sp^2) moieties. While most of these elemental reaction steps have precedents in organometallic chemistry, the present system is unique in that they all occur at the same metal—ligand fragment. This allows one to draw several mechanistic conclusions. Among these, the most relevant is the observation that, under the experimental conditions, the reductive coupling of *cis* σ-organyl ligands is an unaccessible reaction at Ru(II). The only C—C bond-forming reaction that has been observed is the one involving σ-alkynyl and vinylidene groups which, in fact, may be viewed as a migratory insertion of the latter group into a ruthenium—alkynyl bond.[63]

Finally, it is worth highlighting the multifunctional role exerted by the phenylacetylene substrate in the precatalysis and catalysis systems: hydride scavenger, hydride producer, σ-bond metathesis reagent, and protic acid.

Acknowledgment. Thanks are due to EC for financial support (program CHRX-CT930147).

Supplementary Material Available: Tables of final positional parameters for all atoms of **5**·C_6H_6, **6**, and **10**·C_2H_5OH and anisotropic displacement parameters for **5**·C_6H_6 (11 pages). Ordering information is given on any current masthead page.

OM940633K

(63) Selnau, H.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.