Subsequent refinement of the two uraniums converged to R = 0.2067. The positions of the remaining atoms were obtained in a straightforward fashion from difference maps after several subsequent cycles of refinement. In the final cycles all atoms were refined anisotropically, except for the Cp and Ph rings, which were treated as rigid groups by using the parameters contained in SHELX-76. In the last cycle of refinement, no parameter shifted more than 23% of its standard deviation with R = 0.0555 and R_G = 0.0644. The final difference map showed maximum peaks of 1.41 e/Å^3 at 0.95 Å from uranium. Refinement of the enantiomeric structure gave R = 0.072 and R_G = 0.0792, thus confirming the absolute configuration of the molecule.

Final positional parameters and thermal parameters are listed in Tables II and III, respectively. Bond distances are summarized in Table IV, and bond angles in Table V. Bond angles and distances, but not torsional angles, between the two independent molecules contained in the asymmetric unit are indistinguishable; an ORTEP drawing of one of these is shown in Figure 1.

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Supplementary Material Available: Observed and calculated structure factors for $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ (16 pages). Ordering information is given on any current masthead page.

Interaction of Monohydrido Complexes of Rhodium(I) with 1-Alkynes. Experimental Study on Deceptively Simple Reactions

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The reaction of HC≡CR (R = CO_2Et, Ph, n-C_3H_7, n-C_5H_{11}, $SiMe_3$) with the Rh(I) monohydrides $[(NP_3)RhH]$ (1) and $[(PP_3)RhH]$ (2) in THF is influenced by a number of factors, including stoichiometry, alkyne substituent, and temperature (NP_3 = $N(CH_2CH_2PPh_2)_3$; PP_3 = $P(CH_2CH_2PPh_2)_3$). At room temperature, HC≡CCO_2Et and HC≡CPh react with an equimolar amount of 1, yielding mixtures of the trigonal-bipyramidal complexes $[(NP_3)Rh(C{\equiv}CR)]$ and $[(NP_3)Rh\{(E)\text{-}CH{=}C(H)R\}]$ (R = CO_2Et, Ph). The σ-acetylide compounds form via C(alkyne)–H oxidative addition to rhodium, followed by H_2 elimination. For R = alkyl and $SiMe_3$, no reaction occurs even when a 10-fold excess of 1-alkyne is used. In contrast, by treatment of 1 with an excess of HC≡CCO_2Et, the σ-acetylide complex selectively forms together with ethyl acrylate. At reflux temperature, 1 reacts with a 10-fold excess of 1-alkynes to give σ-acetylide derivatives (R = $SiMe_3$, CO_2Et) or σ-acetylide/σ-alkenyl mixtures (R = alkyl, Ph). A variety of organic products is also formed, including as the major products 1,3,5- and 1,2,4-trisubstituted benzenes, 1,4-butadiynes, and butenynes. The only 1-alkyne that stoichiometrically reacts with 2 in THF at room temperature is HC≡CCO_2Et. As a result, the σ-alkenyl$[(PP_3)Rh\{gem\text{-}C(CO_2Et){=}CH_2\}]$ is obtained. The σ-acetylide complexes $[(PP_3)Rh(C{\equiv}CR)]$ (R = CO_2Et, Ph) are synthesized by reacting 2 with a 10-fold excess of the corresponding 1-alkyne. No reaction is observed for R = alkyl and $SiMe_3$. When performed in refluxing THF, the reactions between 2 and an excess of 1-alkyne lead to the formation of σ-acetylide complexes regardless of the alkyne substituent. Again, the reactions are catalytic and cause extensive conversion of 1-alkynes to a variety of linear and cyclic oligomers. The product distribution is essentially similar to that observed for the NP_3 hydride 1. The stereospecific addition of 1-alkynes to either 1 or 2 is interpreted in terms of a concerted mechanism.

Introduction

The result of a reaction between a terminal alkyne and a transition-metal monohydrido complex is hardly predictable because of the number and variety of the factors that may affect the process. Besides external parameters such as temperature, solvent, and stoichiometry, one has to consider that the course of the reaction much depends also on the polyfunctional nature of both the alkyne and the metal–hydrogen bond. The ability of C–H oxidative addition to the metal center[1] coupled with susceptibility to insert across the M–H bond[2] make terminal alkynes

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attractive reagents to directly synthesize either σ-alkynyl or σ-alkenyl complexes. In turn, the latter compounds may exhibit cis, trans, or geminal structures depending on the hydridic or protonic nature of the hydrogen bound to the metal. The dual mode of reactivity of terminal alkynes is reflected also in the subsequent reaction of the σ-alkynyl and σ-alkenyl compounds with additional alkyne, since such reactions may produce an incredible variety of organometallic complexes[3] and organic products as well, including dimers, linear and cyclic oligomers, mono- and polybutadienes, and polyacetylenes.[4] Finally, an important role in determining the course of the reactions is played by the alkyne substituent, since it may affect both the electron availability of the C–C system[2] and the structure of the primarily inserted product via a bonding interaction with the metal.[5]

In this paper, we present a detailed investigation on the reactions of the trigonal-bipyramidal Rh(I) hydrides [(N-P_3)RhH][6] (**1**) and [(PP_3)RhH][6] (**2**) with 1-alkynes bearing either electron-withdrawing or electron-releasing substituents (NP_3 = $N(CH_2CH_2PPh_2)_3$; PP_3 = $P(CH_2CH_2PPh_2)_3$). Particular attention has been paid to correlate the organometallic and organic products with as many factors as possible potentially influencing the reactions.

Experimental Section

General Data. Tetrahydrofuran (THF) and toluene were purified by distillation over $LiAlH_4$ and sodium/benzophenone under nitrogen just prior to use, respectively. All the other solvents were reagent grade and were used as received. The compounds [(NP_3)RhH] (**1**) and [(PP_3)RhH] (**2**) were prepared as described in ref 6. 1-Alkynes, styrene, 1,3,5-triphenylbenzene, and 1,4-diphenylbutadiyne were purchased from commercial suppliers and used without further purification. Propargylaldehyde,[7a] 1,2,4-triphenylbenzene,[7b] 1,3-diphenylbutenyne,[4j] (*E*)-1,4-diphenylbutenyne,[4x] (*Z*)-1,4-diphenylbutenyne,[7c] 1,3,5-tricarbethoxybenzene,[4e] 1,2,4-tricarbethoxybenzene,[4e] 1,3,5-tri-*n*-pentylbenzene,[4e,f] 1,2,4-tri-*n*-pentylbenzene,[4e,f] and di-*n*-pentylbutenynes[4e,f] were prepared according to the literature methods. Ethyl acrylate was prepared by hydrogenation of ethyl propiolate with the complex [(triphos)RhCl(C_2H_4)] as catalyst.[7d] The ligand PP_3 was purchased from Pressure Chemicals. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 spectrometer. Peak positions are relative to tetramethylsilane as external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR 300 instrument operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Conductivities were measured with a WTW Model LBR/B conductivity bridge. The conductivity data were obtained at sample concentrations of ca. 1×10^{-3} M in nitroethane solutions. GC analyses were performed both on a Perkin-Elmer Sigma 1 system equipped with a 2-m column packed either with OV1 (2.5%) on Chromosorb G AW-DMCS or with FFAP (5%) on Chromosorb G AW-DMCS and on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and with a 10-ft 100/120 Carbosieve-SII or a 6-ft 0.1% SP-1000 80/100 Carbopack C stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method. GC/MS spectra were collected with a Hewlett-Packard Model 5970A chromatograph equipped with a mass detector: an OV-101 capillary column (25 m) was employed. The product composition of the reaction mixture was evaluated by using the total abundance of the mass peak.

Simulation of NMR spectra was achieved by using an updated version of the LAOCN4 program.[8] The initial choices of shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.5 Hz.

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Table I. Microanalytical and Selected IR Spectral Data for the Complexes

compd	color	anal.,[a] % C	H	N	Rh	IR, cm^{-1} ν(C≡C)	other
4	yellow	65.12 (65.97)	5.88 (5.77)	1.54 (1.64)	11.96 (12.03)	1510	1640 (ν(C=O)) 1185 (ν(COC))
6	yellow	69.67 (69.85)	5.86 (5.74)	1.59 (1.63)	11.84 (11.97)	1535	
8	orange	68.27 (68.36)	6.20 (6.23)	1.58 (1.70)	12.31 (12.46)	1560	
9	red-orange	68.92 (68.93)	6.52 (6.49)	1.60 (1.64)	11.99 (12.05)	1555	
11	orange	68.94 (69.09)	6.33 (6.27)	1.58 (1.64)	11.86 (12.08)		2095 (ν(C≡C))
12	yellow	64.66 (64.76)	5.49 (5.55)		11.72 (11.80)	1555	1690 (ν(C=O)) 1210 (ν(COC))
13	yellow	65.01 (65.15)	5.66 (5.59)		12.33 (12.40)	1537	1625 (ν(C=O))
18	light yellow	67.71 (67.75)	6.23 (6.15)		11.75 (11.85)		2100 (ν(C≡C))

[a] Calculated values are in parentheses.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a prepurified nitrogen or argon atmosphere by using Schlenk line techniques. The solid compounds were collected on sintered-glass frits and washed with ethanol and *n*-pentane before dried under a stream of nitrogen.

Selected IR absorbances and microanalytical data for all of the new compounds are reported in Table I. Selected NMR data (^{1}H NMR and ^{31}P{^{1}H} NMR) are collected in Table II.

Reactions of [(NP$_3$)RhH] (1) with HC≡CCO$_2$Et. (A) 1:1 Reaction at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **1** (0.76 g, 1 mmol) and ethyl propiolate (102 μL, 1 mmol) in THF (40 mL) and closed by a Suba-Seal septum (Aldrich). The mixture was stirred at room temperature for 24 h. GC analysis of the gas phase revealed the presence of hydrogen. Over a number of different preparations the amount of hydrogen varied from 0.15 to 0.30 mol/mol of **1**. Addition of ethanol (30 mL) and slow evaporation of the solvent gave a crystalline yellow solid, which was chromatographed under nitrogen on a silica gel column with CH$_2$Cl$_2$/*n*-hexane (4:1) as eluent. On addition of ethanol to both yellow fractions the compounds [(NP$_3$)Rh(C≡CCO$_2$Et)][9] (**3**) and [(NP$_3$)Rh{(*E*)-CH=C(H)CO$_2$Et}] (**4**) were isolated in a ca. 9:1 ratio; total yield ca. 88%.

(B) 1:10 Reaction at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **1** (0.76 g, 1 mmol) and ethyl propiolate (1.02 mL, 10 mmol) in THF (40 mL) and closed by a Suba-Seal septum. The mixture was stirred at room temperature for 24 h. GC analysis of the gas phase still revealed the formation of hydrogen in amounts comparable with those found in the above reaction. GC analysis of the solution showed the formation of ethyl acrylate (8–15% of reacted ethyl propiolate). Addition of ethanol (30 mL) and slow evaporation of the solvent gave yellow crystals of **3** in ca. 90% yield.

(C) 1:10 Reaction at Reflux Temperature. A mixture of **1** (0.76 g, 1 mmol) and ethyl propiolate (1.02 mL, 10 mmol) in THF (40 mL) was refluxed for 3 h. After the mixture was cooled to room temperature, ethanol (30 mL) was added and **3** was obtained in ca. 90% yield.

Reactions of 1 with HC≡CPh. By using methods A–C reported for ethyl propiolate, mixtures of [(NP$_3$)Rh(C≡CPh)][9] (**5**) and [(NP$_3$)Rh{(*E*)-CH=C(H)Ph}] (**6**) were invariably isolated in ratios depending on the temperature: 7:3 (room temperature); 8:2 (reflux temperature); total yield 80–84%. The amount of H$_2$ was determined by GC (0.1–0.2 mol/mol of **1**).

Reaction of 1 with HC≡CSiMe$_3$. A mixture of **1** (0.76 g, 1 mmol) and (trimethylsilyl)acetylene (1.44 mL, 10 mmol) in THF (40 mL) was refluxed for 3 h. After the mixture was cooled to room temperature, addition of ethanol (30 mL) and slow concentration gave [(NP$_3$)Rh(C≡CSiMe$_3$)][9] (**7**) in 83% yield.

Reaction of 1 with HC≡CR (R = *n*-C$_3$H$_7$, *n*-C$_5$H$_{11}$). A mixture of **1** (0.76 g, 1 mmol) and the appropriate acetylene (0.99 or 1.32 mL, 10 mmol) in THF (40 mL) was refluxed for 3 h and then allowed to reach room temperature. Addition of ethanol (30 mL) and slow concentration gave ca. 9:1 mixtures of [(NP$_3$)Rh{(*E*)-CH=C(H)-*n*-C$_3$H$_7$}] (**8**) and [(NP$_3$)Rh(C≡C-*n*-C$_3$H$_7$)][9] (**10**) or of [(NP$_3$)Rh{(*E*)-CH=C(H)-*n*-C$_5$H$_{11}$}] (**9**) and [(NP$_3$)Rh(C≡C-*n*-C$_5$H$_{11}$)] (**11**). The compounds were separated by chromatography (silica gel column; CH$_2$Cl$_2$/*n*-hexane (5:2) as eluent).

Reaction of 1 with HC≡CR (R = Ph, *n*-C$_3$H$_7$, *n*-C$_5$H$_{11}$) in Toluene. Compound **1** (0.76 g, 1 mmol) was dissolved in toluene (40 mL), and after addition of the appropriate acetylene (1.12, 0.99, or 1.32 mL, 10 mmol) the mixture was refluxed for 3 h. Pure samples of the σ-acetylides **5**, **10**, and **11** were obtained on addition of ethanol (30 mL) and partial evaporation of the solvent.

Reaction of [(NP$_3$)Rh{(*E*)-CH=C(H)CO$_2$Et}] (4) with HC≡CCO$_2$Et. A stoichiometric amount of ethyl propiolate was added to a THF (15 mL) solution of **4** (0.26 g, 0.3 mmol). The resulting mixture was stirred at room temperature for 24 h. GC tests performed at various steps during the course of the reaction showed the disappearance of ethyl propiolate and the contemporaneous formation of ethyl acrylate. On addition of ethanol (30 mL) compound **3** precipitated in ca. 95% yield.

Reaction of [(NP$_3$)Rh{(*E*)-CH=C(H)Ph}] (6) with HC≡CCO$_2$Et. A stoichiometric amount of ethyl propiolate was added to a THF (15 mL) solution of **6** (0.26 g, 0.3 mmol). The resulting mixture was stirred at room temperature for 24 h. Samples taken at intervals during this period and analyzed by GC methods showed the disappearance of ethyl propiolate and the contemporaneous formation of styrene. On addition of ethanol (30 mL) compound **3** precipitated in almost quantitative yield.

Reaction of 4 or 6 with HSO$_3$CF$_3$ under CO. Neat HSO$_3$CF$_3$ (0.3 mmol) was syringed into a stirred THF (20 mL) solution of **4** (or **6**) (0.3 mmol) under a CO atmosphere. After 10 min the formation of ethyl acrylate (or styrene) was evidenced by GC tests. On addition of NaBPh$_4$ (0.17 g, 0.5 mmol) in ethanol (30 mL) the carbonyl [(NP$_3$)RhCO]BPh$_4$[6] precipitated.

Reaction of [(NP$_3$)Rh(C≡CPh)] (5) with HC≡CCO$_2$Et. A slight excess of ethyl propiolate (41 μL, 0.4 mmol) was added to a stirred THF (15 mL) solution of **5** (0.26 g, 0.3 mmol). After 24 h, ethanol (30 mL) was added and **3** precipitated in almost quantitative yield. The formation of phenylacetylene was evidenced by GC tests.

Reactions of [(PP$_3$)RhH] (2) with HC≡CCO$_2$Et. (A) 1:1 Reaction at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **2** (0.78 g, 1 mmol) and ethyl propiolate (102 μL, 1 mmol) in THF (40 mL) and closed by a Suba-Seal septum. The mixture was stirred at room temperature. After 24 h, GC analysis of the gas phase revealed no trace of hydrogen. Addition of ethanol (30 mL) and slow evaporation of the solvent gave yellow crystals of [(PP$_3$)Rh{*gem*-C(CO$_2$Et)=CH$_2$}] (**12**), yield 92%.

(B) 1:10 Reaction at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **2** (0.78 g, 1 mmol) and ethyl propiolate (1.02 mL, 10 mmol) in THF (40 mL) and closed by a Suba-Seal septum. The mixture was stirred at room temperature for 24 h. The ethyl propiolate/ethyl acrylate ratio (by GC analysis) at this stage was ca. 8:1, evidencing the consumption of ca. 2 mmol of ethyl propiolate/mol of **2** and the formation of ca. 1 mmol of ethyl acrylate. Addition of ethanol (30 mL) and slow evaporation of the solvent gave yellow crystals of [(PP$_3$)Rh(C≡CCO$_2$Et)][9] (**14**) in 87% yield.

(C) 1:10 Reaction at Reflux Temperature. A mixture of **2** (0.78 g, 1 mmol) and ethyl propiolate (1.02 mL, 10 mmol) in THF (40 mL) was refluxed for 3 h. Addition of ethanol (30 mL) and

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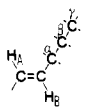
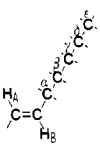
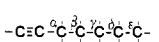
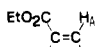
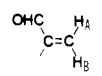
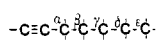
Table II. NMR Spectral Data for the Complexes

compd	^{1}H[a] chem shift[c]	assignt[d]	coupling const[d]		^{31}P{^{1}H}[b] chem shift[e] $\delta(P_{ap})$	$\delta(P_{eq})$	coupling const[d] $J(PP)$	$J(P_{ap}Rh)$	$J(P_{eq}Rh)$
			NP$_3$ Complexes						
	10.22 dpd	H_A	$^3J(H_AH_B)$	15.8		24.28 d			173.6
			$^3J(H_AP)$	9.6					
			$^2J(H_ARh)$	2.1					
4	5.82 dd	H_B	$^3J(H_BRh)$	1.5					
	3.94 q	$CO_2CH_2CH_3$	$^3J(HH)$	7.1					
	1.16 t	$CO_2CH_2CH_3$							
	8.73 dpd	H_A	$^3J(H_AH_B)$	15.8		23.92 d			176.0
			$^3J(H_AP)$	9.5					
			$^2J(H_ARh)$	2.2					
6	6.32 br d	H_B							
	7.80 br m	H_A				22.48 d			177.7
	5.61 dtd	H_B	$^3J(H_AH_B)$	14.7					
			$^3J(H_BH_\alpha)$	6.6					
			$^3J(H_BRh)$	1.3					
8	2.22 pq	H_α	$^3J(H_\alpha H_\beta)$	7.5					
	1.41 psex	H_β	$^3J(H_\gamma H_\beta)$	7.3					
	0.89 t	H_γ							
	7.45 m[f]	H_A				23.68 d			178.1
	5.59 dtd	H_B	$^3J(H_AH_B)$	14.9					
			$^3J(H_BH_\alpha)$	6.5					
			$^3J(H_BRh)$	1.4					
	2.25 pq	H_α	$^3J(H_\alpha H_\beta)$	6.6					
	1.6–1.2 m	H_β, H_γ, H_δ							
9	0.79 t	H_ϵ	$^3J(H_\delta H_\epsilon)$	7.1					
	2.65 tq	H_α	$^5J(H_\alpha P)$	3.1		23.43 d			162.6
			$^3J(H_\alpha H_\beta)$	7.1		23.43 d			162.6
11	1.61 pqu	H_β	$^3J(H_\beta H_\gamma)$	6.9					
	1.44 pqu	H_γ	$^3J(H_\gamma H_\delta)$	8.0					
	1.24 psex	H_δ	$^3J(H_\delta H_\epsilon)$	7.3					
	0.74 t	H_ϵ							
			PP$_3$ Complexes						
	6.42 br d	H_A	$^3J(H_AH_B)$	3.9	144.93 dq	44.97 dd	19.2	87.8	156.6
			$^2J(H_AP_{ap})$	14.4					
	5.36 dd	H_B	$^3J(H_BP_{ap})$	8.2					
12	3.54 q	$CO_2CH_2CH_3$	$^3J(HH)$	7.1					
	0.75 t	$CO_2CH_2CH_3$							
	9.36 s	CHO			149.21 dq	46.81 dd	19.9	87.1	155.1
	6.15 br d	H_A	$^3J(H_AH_B)$	3.8					
			$^4J(H_AP_{ap})$	13.9					
13	5.21 dd	H_B	$^4J(H_BP_{ap})$	7.6					
	2.59 tq	H_α	$^5J(H_\alpha P_{eq})$	3.5	153.91 dq	47.95 dd	21.5	89.9	152.4
			$^3J(H_\alpha H_\beta)$	7.2					
18	1.78–1.19 m	H_β, H_γ, H_δ							
	0.82 t	H_ϵ	$^3J(H_\delta H_\epsilon)$	7.2					

[a] All ^{1}H NMR spectra recorded at 299.945 MHz and 293 K in C_6D_6 solutions, except for **4**, which was recorded in CD_2Cl_2. The resonances due to the hydrogen atoms of the NP_3 and PP_3 ligands are not reported. [b] All the proton-decoupled ^{31}P NMR spectra were recorded at 121.42 MHz and 293 K in C_6D_6 solutions. [c] In ppm from external TMS. Key: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextuplet, m = multiplet, br = broad, p = pseudo. [d] The subscripts A and B denote the vinyl protons. The greek subscripts α, β, γ, δ, and ϵ denote the protons of the *n*-C_3H_7 and *n*-C_5H_{11} substituents. Coupling constants are in Hz. [e] The chemical shifts are in ppm relative to 85% H_3PO_4, with positive values being downfield from the standard. P_{ap} refers to the bridgehead phosphorus atom of the PP_3 ligand, while P_{eq} denotes the equatorial phosphorus atoms of both NP_3 and PP_3. [f] Partially masked by the resonances of the aromatic protons.

slow concentration gave **14** in 90% yield.

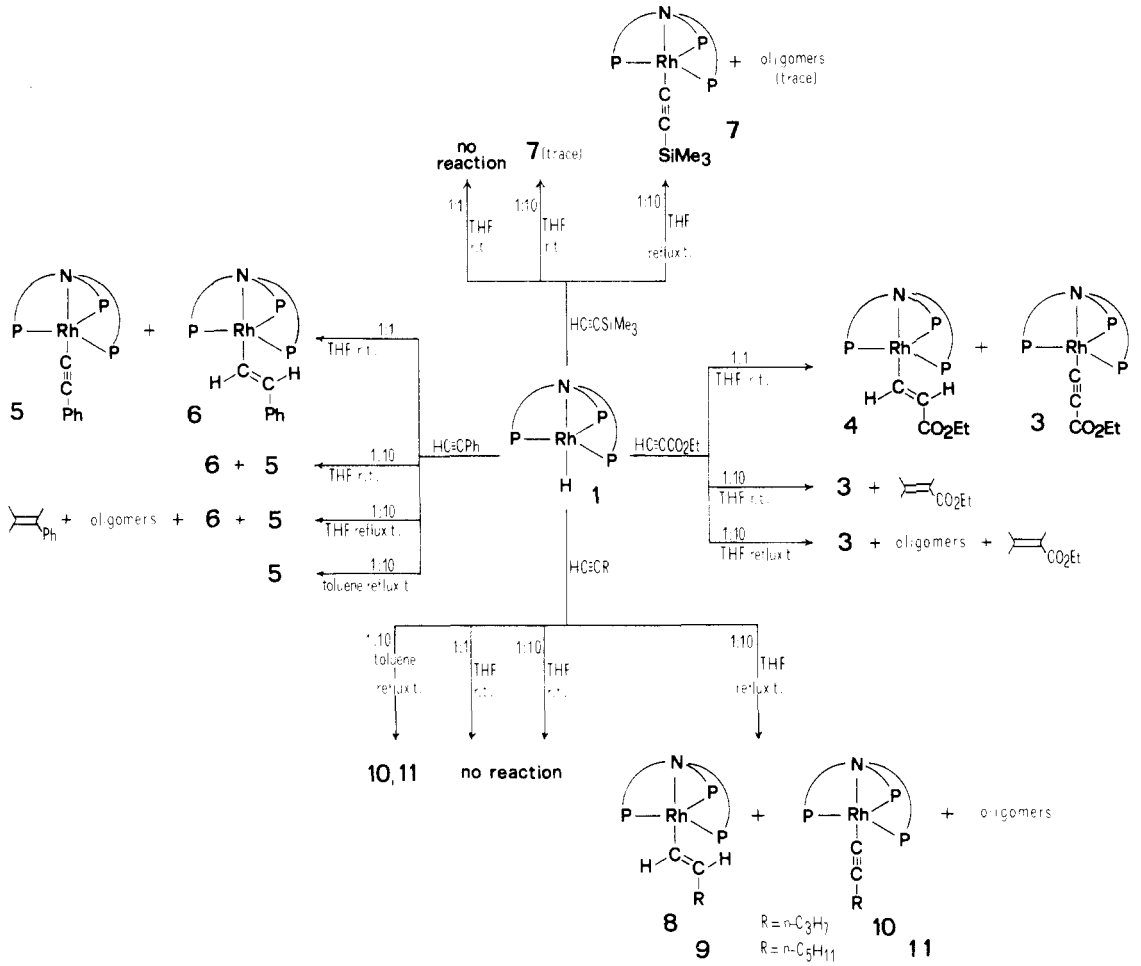
Reactions of 2 with HC≡CCHO. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **2** (0.78 g, 1 mmol) and propargylaldehyde (60 μL, 1 mmol) in THF (40 mL) and closed by a Suba-Seal septum. The mixture was stirred at room temperature for 24 h. Addition of ethanol (30 mL) and slow evaporation of the solvent gave yellow crystals of [(PP_3)Rh{*gem*-C(CHO)=CH_2}] (**13**), yield ca. 50%.

Reaction of 2 with HC≡CPh. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **2** (0.78 g, 1 mmol) and phenylacetylene (1.12 mL, 10 mmol) in THF (40 mL). It was closed by a Suba-Seal cap, and the mixture was stirred at room temperature for 24 h. The formation of 0.3–0.5 mmol of styrene was detected by GC tests. Addition of ethanol (30 mL) and slow evaporation of the solvent gave a crystalline solid constituted of [(PP_3)Rh(C≡CPh)][9] (**15**) and the unreacted starting compound; yield ca. 40% (by ^{31}P{^{1}H} NMR spectroscopy).

Reaction of 2 with HC≡CR (R = Ph, $SiMe_3$, *n*-C_3H_7, *n*-C_5H_{11}) at Reflux Temperature. A mixture of **2** (0.78 g, 1 mmol) and a 10-fold excess of the appropriate acetylene in THF (40 mL) was refluxed for 3 h. After the mixture was cooled to room temperature, addition of ethanol (30 mL) and slow concentration led to the precipitation of the corresponding σ-acetylides **15**, [(PP_3)Rh(C≡CSiMe_3)] (**16**), [(PP_3)Rh(C≡C-*n*-C_3H_7)] (**17**), and [(PP_3)Rh(C≡C-*n*-C_5H_{11})] (**18**) in 82–90% yield.

Oligomerization Runs. In a typical experiment, to a stirred solution of **1** (or **2**) (0.2 mmol) in THF (10 mL) under nitrogen in a 20-mL Schlenk flask, fitted with a reflux condenser and a thermometer, was added by means of a syringe the appropriate acetylene (2 mmol). The mixture was maintained at reflux tem-

Scheme I



perature for 3 h. After the mixture was cooled to room temperature, the composition of the resulting mixture was determined by GC/MS techniques through comparison with retention times and mass spectra of authentic specimens.

Results

Reactions of [(NP$_3$)RhH] (1) with 1-Alkynes at Room Temperature. Stoichiometric Reactions. Stirring equimolar amounts of 1 and ethyl propiolate, HC≡CCO$_2$Et, in THF for 24 h does not produce an appreciable color change. However, no trace of starting hydride is found in the reaction mixture by ^{31}P{^{1}H} NMR spectroscopy. Addition of ethanol precipitates yellow crystals of a 9:1 mixture of the complexes [(NP$_3$)Rh(C≡CCO$_2$Et)] (**3**) and [(NP$_3$)Rh{(*E*)-CH=C(H)CO$_2$Et}] (**4**), which can be separated from each other by chromatography (Scheme I). In the course of the reaction dihydrogen is evolved. However, it is not possible to determine precisely the amount of evolved hydrogen, most likely because of the long reaction time. In particular, GC analysis of the gas phase over a number of different preparations showed the formation of H$_2$ in amounts ranging from 0.15 to 0.30 mol/mol of **1**.

The trigonal-bipyramidal (TBP) σ-acetylide complex **3** was identified by comparison with an authentic specimen prepared by treatment of the cis hydride acetylide [(NP$_3$)Rh(H)(C≡CCO$_2$Et)]BPh$_4$ with NaBH$_4$.[9] The novel σ-alkenyl complex **4** has been properly characterized by IR and NMR techniques. The compound is air-stable in the solid state but slowly decomposes in solution unless air is excluded. It behaves as a nonelectrolyte in nitroethane solution. Strong IR absorptions at 1640 and 1185 cm^{-1} are readily assigned to ν(C=O) and ν(C—O—C) of the carbethoxy substituent, respectively.[2a-d] A medium-intensity band at 1510 cm^{-1} is attributed to ν(C=C) of an alkenyl ligand.[2] The ^{31}P{^{1}H} NMR spectrum in benzene consists of a single resonance (A_3X spin system; J(PRh) = 173.6 Hz), which exhibits only a slight temperature dependence of the chemical shift from 24.28 ppm at 293 K to 25.70 ppm at 173 K. The magnetic equivalence of the three terminal phosphorus nuclei is typical of TBP metal complexes of NP$_3$.[6] Precious information on the stereochemistry of the metal–alkenyl moiety, and, therefore, on the type of insertion of ethyl propiolate across the Rh–H bond, is provided by the ^{1}H NMR spectrum (CD$_2$Cl$_2$, 293 K). This contains two multiplets (1 H each) centered at 10.22 and 5.82 ppm, which are correlated to each other as shown by a chemical shift correlated 2D NMR (COSY) experiment. The lower field resonance has been properly computed as the A part of an ABM_3X spin system by using the following parameters: $J(H_AH_B)$ = 15.8 Hz, $J(H_AP)$ = 9.6 Hz, and $J(H_ARh)$ = 2.1 Hz (Figure 1). The higher field signal appears as a doublet of doublets and exhibits $J(H_BRh)$ = 1.5 Hz. The J(HH) value of 15.8 Hz is consistent with an *E* structure of the complex (cis insertion).[2b-d,f,h] The resonances of the ethoxy hydrogens fall in the proper range for such species (3.94 ppm, q, OCH_2CH_3; 1.16 ppm, t, OCH_2CH_3; J(HH) = 7.1 Hz) and do not show coupling to any other magnetically active nucleus of the complex molecule.

On the basis of all of these data, compound **4** is assigned a structure in which the metal is coordinated by the four donor atoms of NP$_3$ and by an alkenyl ligand in a TBP environment. The alkenyl ligand is located trans to the

Table III. Oligomerization of 1-Alkynes by [(NP$_3$)RhH]^a

R	conversn, %	product distribn,^{b} %						
		1-alkyne	1-alkene	1,3,5-benzene	1,2,4-benzene	butenynes	butadiyne	other^c
CO_2Et	90 (2)	10 (2)	2 (1)	40 (2)	48 (2)			
Ph	81 (2)	19 (2)	2 (1)	3 (1)	7 (1)	33 (2)	30 (2)	6 (1)
C_5H_{11}	75 (2)	25 (2)		22 (2)	31 (2)	8 (1)		14 (2)
$SiMe_3$	2 (1)	98 (2)				trace	trace	

^{a} Conditions: catalyst, 0.2 mmol; 1-alkyne, 2 mmol; THF, 10 mL; time, 3 h; temperature, 67 °C. ^{b} Numbers in parentheses are estimated standard deviations. ^{c} Butadienes, linear trimers, and tetramers.

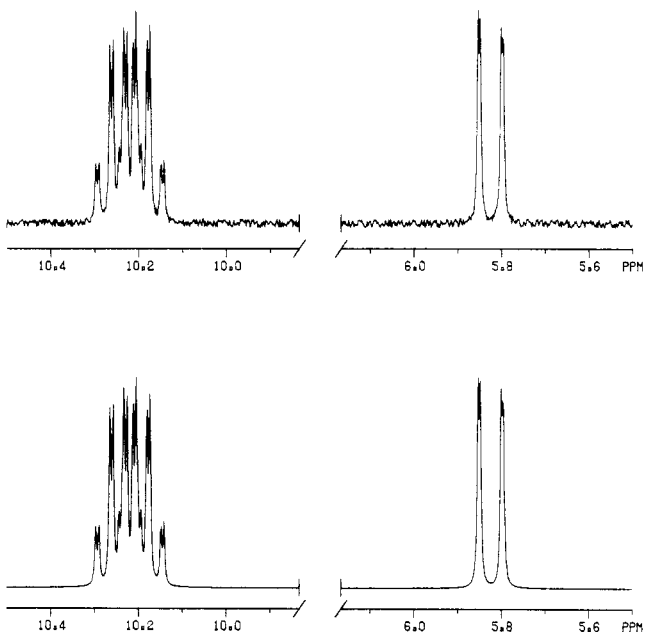


Figure 1. Experimental (top) and computed (bottom) ^{1}H NMR resonances due to the vinyl hydrogens in **4** (300 MHz, CD_2Cl_2, 293 K, TMS reference).

bridgehead nitrogen and exhibits *E* stereochemistry.

In accord with the σ-alkenyl formulation, compound **4** dissolved in THF decomposes in the GC injector (250 °C), producing ethyl acrylate. Ethyl acrylate is quantitatively liberated also by protonation of **4** with strong protic acids. The resulting unsaturated fragment [(NP$_3$)Rh]$^+$ can be trapped by reaction with CO to give the carbonyl [(NP$_3$)RhCO]$^+$.[6]

Phenylacetylene, HC≡CPh, reacts with **1** in a manner essentially identical with that shown by HC≡CCO$_2$Et, the only difference being the relative amounts of the products: the σ-acetylide [(NP$_3$)Rh(C≡CPh)][9] (**5**) and the σ-alkenyl [(NP$_3$)Rh{(*E*)-CH=C(H)Ph}] (**6**) now form in a 7:3 ratio (Scheme I). The evolution of H_2 was determined by GC tests. In view of the IR and NMR data reported in Tables I and II and of the data for the related complex **4**, **6** is assigned a TBP (*E*) structure.

Compound **1** does not react at all with 1-alkynes bearing electron-releasing substituents such as *n*-C_3H_5, *n*-C_5H_{11}, and $SiMe_3$.

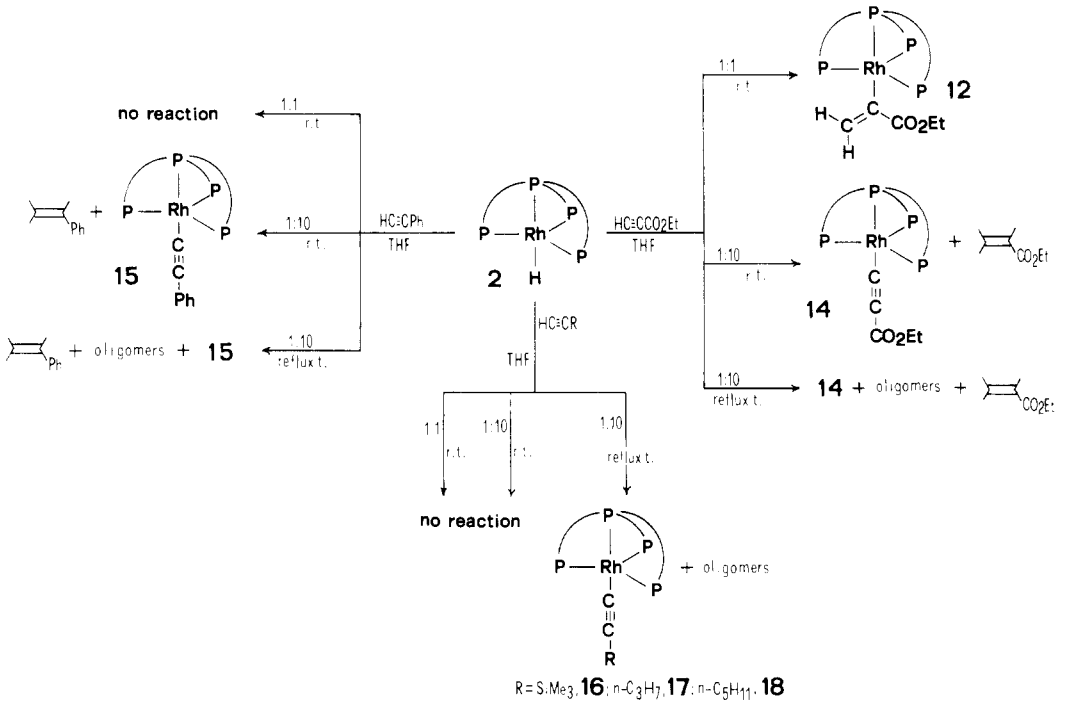
Reactions with a 10-fold Excess of 1-Alkynes. Increasing the amount of 1-alkynes up to 10 times does not significantly affect the course of the reactions except for HC≡CCO$_2$Et. In this case, in fact, the reaction quantitatively yields the σ-acetylide **3**. Ethyl acrylate is found in the reaction mixture as the only organic product except for the starting acetylene. Since ethyl acrylate and **3** are also obtained by reacting the σ-alkenyl **4** with a stoichiometric amount of HC≡CCO$_2$Et, we conclude that the excess of 1-alkyne is just necessary to bring about the σ-alkenyl → σ-acetylide conversion. Traces (<2%) of a σ-acetylide complex were determined in the reaction mixture of **1** and (trimethylsilyl)acetylene, HC≡CSiMe$_3$ (see below).

Reactions of 1 with a 10-fold Excess of 1-Alkynes at Reflux Temperature. Quite different results have been found for the reactions of **1** in THF with an excess of 1-alkynes at reflux temperature. The reactions are reported for a 10-fold excess of 1-alkynes and 3 h. Addition of ethanol to the reaction mixtures with HC≡CCO$_2$Et or HC≡CSiMe$_3$ invariably precipitates the corresponding σ-acetylides **3** and [(NP$_3$)Rh(C≡CSiMe$_3$)] (**7**) as the only metal-containing products.[9] In contrast, mixtures of σ-acetylide and σ-alkenyl complexes are obtained from the reactions with HC≡CPh, HC≡C-*n*-C_3H_7, and HC≡C-*n*-C_5H_{11}. Interestingly, the product composition of the reactions with the alkyl-substituted acetylenes is the reverse of that with phenylacetylene; i.e., the formation of the σ-alkenyl complexes prevails over that of the σ-acetylides for R = *n*-C_3H_7, *n*-C_5H_{11}. Provided the spectroscopic criteria used for determining the structure of the preceding σ-alkenyl compounds **4** and **6** are correct, [(NP$_3$)Rh{(*E*)-CH=C(H)-*n*-C_3H_7}] (**8**) and [(NP$_3$)Rh{(*E*)-CH=C(H)-*n*-C_5H_{11}}] (**9**) are assigned trigonal-bipyramidal *E* structures (Tables I and II).

Interestingly, the product composition of the reaction between **1** and HC≡CPh in THF does not change much on increasing the temperature (**5**:**7** ratio of 4). In contrast, when the reaction is carried out in refluxing toluene, only the σ-acetylide **5** is obtained. In a similar way, the reactions between **1** and HC≡C-*n*-C_3H_7 and HC≡C-*n*-C_5H_{11} in refluxing toluene quantitatively give the σ-acetylides [(NP$_3$)Rh(C≡C-*n*-C_3H_7)][9] (**10**) and [(NP$_3$)Rh(C≡C-*n*-C_5H_{11})] (**11**). Compound **11** is a novel Rh(I) σ-acetlyide complex that shares with the known derivative **10** most of the chemical and physical properties (Tables I and II).

Whatever the alkyne substituent may be except for $SiMe_3$, the reactions between **1** and a 10-fold excess of HC≡CR in THF at reflux temperature consume a large part of the organic reagents. In order to elucidate the fate of the 1-alkynes, the reaction mixtures have been carefully analyzed. The organic product composition was determined by GC/MS techniques through comparison with authentic specimens either prepared by us or purchased from commercial suppliers. The product distribution after 3 h is reported in Table III. The most active and selective reagent proves to be ethyl propiolate, which is almost totally converted to an equivalent mixture of the two cyclic oligomers 1,3,5- and 1,2,4-tricarbethoxybenzenes. A similar product distribution is found for the reaction with HC≡C-*n*-C_5H_{11} (the analogous reaction with HC≡C-*n*-C_3H_7 has not been studied because of the evident analogy between the two reagents). However, the yield is lower and an appreciable amount of di-*n*-pentylbutenynes is produced. In contrast, a quite different product distribution is observed for the reaction with HC≡CPh. Dimerization to 1,4-diphenylbutadiyne and diphenylbutenynes prevails over cyclotrimerization. Also, the reaction is much less selective than that with HC≡CCO$_2$Et since other products

Scheme II



are formed in appreciable yields, including diphenylbutadienes and higher linear oligomers. Finally, only traces of butadiyne and butenynes are found for the reaction with $HC{\equiv}CSiMe_3$ (<2% conversion).

Reaction of [(PP_3)RhH] (2) with 1-Alkynes at Room Temperature. Stoichiometric Reactions. No reaction is observed when **2** is stirred in THF with a stoichiometric amount of $HC{\equiv}CR$ for 24 h (R = Ph, *n*-C_3H_7, *n*-C_5H_{11}, $SiMe_3$) except for R = CO_2Et (Scheme II). In this case, the σ-alkenyl complex [(PP_3)Rh{*gem*-$C(CO_2Et){=}CH_2$}] (**12**) is almost quantitatively obtained. Compound **12** is stable in the solid state and in deareated solutions of common organic solvents, in which it behaves as a nonelectrolyte. The presence of a σ-bonded alkenyl ligand is readily inferred by IR absorptions at 1690 (s), 1555 (w), and 1210 (s) cm^{-1} that are assigned to ν(C=O), ν(C=C), and ν(C—O—C) of a carbethoxyvinyl ligand, respectively.[2] The $^{31}P\{^1H\}$ NMR spectrum (benzene, 293 K), which consists of an AM_3X spin system ($\delta(P_A)$ 144.93 ppm, $\delta(P_M)$ 44.97 ppm; $J(P_AP_M)$ = 19.2 Hz, $J(P_ARh)$ = 87.8 Hz, $J(P_MRh)$ = 156.6 Hz), is typical of TBP Rh(I) complexes of PP_3.[6] The stereochemistry of the metal–alkenyl moiety has been established by ^1H NMR spectroscopy (C_6D_6, 293 K). Unlike the related NP_3 derivative **4**, compound **12** exhibits geminal (*gem*) stereochemistry.[2a-d] In fact, the two vinyl hydrogens, which constitute the AB portion of an ABMX spin system, are coupled by 3.9 Hz only. The parameters used to simulate this portion of the spectrum are as follows: $\delta(H_A)$ 6.42 ppm, $\delta(H_B)$ 5.36 ppm; $J(H_AH_B)$ = 3.9 Hz, $J(H_AP_{ap})$ = 14.4 Hz, $J(H_BP_{ap})$ = 8.2 Hz, $J(H_ARh)$ = $J(H_BRh) \cong$ 1.5 Hz. The ethoxy protons of the CO_2Et substituent constitute an A_3M_2 pattern with $J(HH)$ = 7.1 Hz. The two resonances are significantly shifted to higher field ($\delta(H_M)$ 3.54 ppm, $\delta(H_A)$ 0.74 ppm) as compared to the analogous signals in the spectrum of the (*E*)-CH=C(H)-CO_2Et complex **4**.

On the basis of all of these data, a TBP structure may be assigned to **12** where rhodium is coordinated by the four phosphorus atoms of PP_3 and by a carbethoxyvinyl ligand. The two vinyl hydrogens appear to be disposed in a *gem* manner.

In order to confirm the role of the substituent in determining the course of the reactions with 1-alkynes, we have reacted **2** with propargylaldehyde, HC≡CCHO, under the same reaction conditions. As a result, the TBP σ-alkenyl [(PP_3)Rh{*gem*-$C(CHO){=}CH_2$}] (**13**) is obtained in 50% yield (the low yield is due to spontaneous polymerization of propargylaldehyde). Accordingly, we conclude that electron-withdrawing substituents favor the insertion of 1-alkynes across the (PP_3)Rh–H bond.

Reactions with a 10-fold Excess of 1-Alkynes. No reaction is observed when **2** is treated with a 10-fold excess of $HC{\equiv}CR$ (R = $SiMe_3$, *n*-C_3H_7, *n*-C_5H_{11}) in THF solution, but with $HC{\equiv}CCO_2Et$ and HC≡CPh a reaction occurs. As a result, the known σ-acetylides [(PP_3)Rh($C{\equiv}CCO_2Et$)] (**14**) and [(PP_3)Rh(C≡CPh)] (**15**) are precipitated by addition of ethanol.[9] Compound **14** forms quantitatively together with an equimolar quantity of ethyl acrylate. In contrast, only 40% of the starting compound is converted to the σ-phenylacetylide **15**. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and no phosphorus-containing species other than **2** and **15** could be detected at any stage. GC analysis and proton NMR spectra of reaction mixtures in THF-d_8 indicate that the formation of **15** is accompanied by the appearance of an equivalent amount of styrene.

Reactions of 2 with a 10-fold Excess of 1-Alkynes at Reflux Temperature. When performed in refluxing THF, the reactions between **2** and 10-fold excess of $HC{\equiv}CR$ lead to the formation of TBP σ-acetylide complexes regardless of the alkyne substituent. After 3 h, the following complexes can be isolated in good yield as the only metal-containing products: **14**, **15**, [(PP_3)Rh($C{\equiv}CSiMe_3$)] (**16**), [(PP_3)Rh(C≡C-*n*-C_3H_7)] (**17**), and [(PP_3)Rh(C≡C-*n*-C_5H_{11})] (**18**).[9] Again, the reactions cause extensive conversion of the excess 1-alkynes to a variety of linear and cyclic oligomers. The product distribution is reported in Table IV. The results are quite similar to those found for the analogous reactions of 1-alkynes with the NP_3 derivative **1**.

Discussion

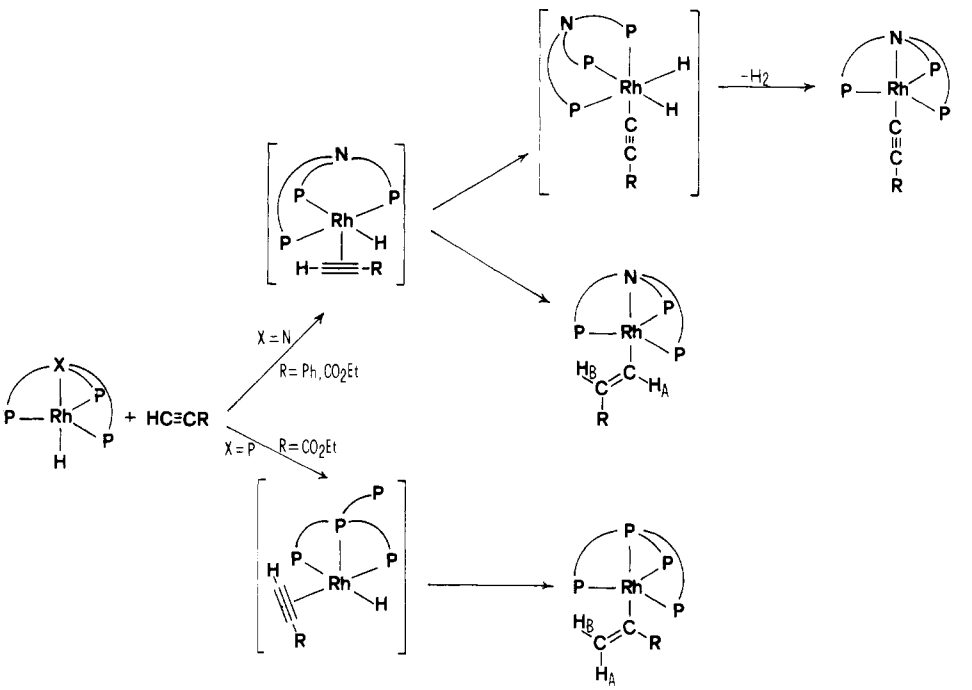
NP_3 Complexes. The insertion of ethyl propiolate and phenylacetylene across the Rh–H bond of **1** occurs in a cis

Table IV. Oligomerization of 1-Alkynes by [(PP_3)RhH][a]

R	conversn, %	product distribn,[b] %						
		1-alkyne	1-alkene	1,3,5-benzene	1,2,4-benzene	butenynes	butadiyne	other[c]
CO_2Et	92 (2)	8 (1)	2 (1)	38 (2)	50 (2)			2 (1)
Ph	70 (2)	30 (2)	1 (1)	3 (1)	6 (2)	39 (2)	17 (2)	4 (1)
C_5H_{11}	69 (2)	31 (2)		16 (2)	24 (2)	8 (1)		21 (2)
$SiMe_3$	1 (1)	99 (2)				trace	trace	

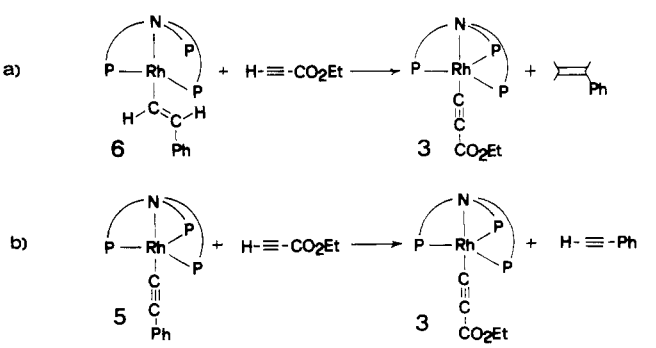
[a] Conditions: catalyst, 0.2 mmol; 1-alkyne, 2 mmol; THF, 10 mL; time, 3 h; temperature, 67 °C. [b] Numbers in parentheses are estimated standard deviations. [c] Butadienes, linear trimers, and tetramers.

Scheme III



manner to give (*E*)-alkenyl complexes. Even in the absence of supporting structure proofs, a cis insertion could be inferred from the nature of the reactants and the mild conditions under which reactions occur.[10] In turn, the reaction conditions and the stereospecific formation of *E* products are indicative of a concerted mechanism rather than an ionic or a free radical type.[2a,j,r,10] A concerted mechanism is strongly supported also by the contemporaneous, predominant formation of H_2 and σ-acetylide complexes via C(alkyne)–H oxidative addition to rhodium. In actuality, it is well-known that 18-electron TBP metal complexes of NP_3 or PP_3 have a dual nature. Electrophiles can attack the metal to give Rh(III) octahedral adducts,[6] while nucleophiles can insert across the metal–fifth coligand bond to give TBP insertion products.[6,11] The latter pathway needs the creation of a vacant site at a certain stage of the reaction. Such a vacant site can be provided by the decoordination of either the amine group (NP_3 complexes)[11] or a terminal phosphorus donor (PP_3 complexes).[6] Accordingly, a reasonable mechanism that accounts for both 1-alkyne insertion and C–H oxidative addition is the one shown in Scheme III. This implies a cis hydride π-alkyne transition complex, which can undergo either hydride migration from rhodium to alkyne or insertion of the metal across the C–H bond. Which of the two competing pathways prevails is a matter that may depend on several factors. Certainly, the electron-withdrawing character of the alkyne substituent seems to play an important role, as we find that C–H oxidative addition (σ-acetylide formation) prevails more over insertion (σ-alkenyl formation) for R = CO_2Et than for R = Ph.

Scheme IV



The key role of the alkyne substituent both in promoting and in driving the course of the reactions is further evidenced by the 1:10 runs. For R = Ph, σ-alkenyl and σ-acetylide complexes are still obtained, in the same ratio as for the 1:1 reaction, thus confirming that the formation of both products intramolecularly proceeds through a common intermediate species (Scheme III). In contrast, only a σ-acetylide complex and ethyl acrylate form for R = CO_2Et. Interestingly, we have found that the σ-phenylvinyl complex **6** reacts in THF with HC≡CCO_2Et at room temperature, yielding the corresponding σ-(ethoxycarbonyl)acetylide derivative **3** and styrene (Scheme IVa).

(10) (a) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (b) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975/76**, *1*, 285.
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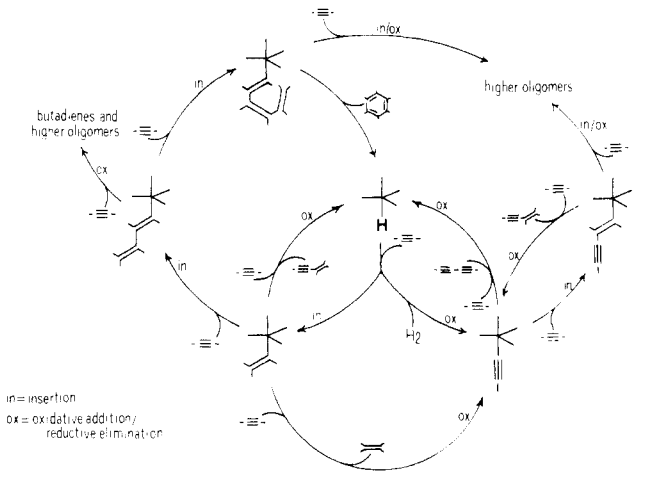
Scheme V



In accord with the previous conclusions, this reaction likely proceeds through the oxidative addition of the ethyl propiolate C–H bond at rhodium, followed by reductive elimination of styrene. Within this context, it is worth mentioning that the σ-phenylacetylide **5** reacts with a slight excess of ethyl propiolate, yielding **3** and phenylacetylene, whereas the reverse reaction does not occur. Again, this metathesis reaction is interpreted in terms of oxidative addition of the C–H bond from ethyl propiolate at rhodium, followed by reductive elimination of the less "acidic" 1-alkyne molecule, i.e. phenylacetylene (Scheme IVb).

Another factor that greatly affects the reactions between **1** and 1-alkynes is the temperature. In fact, 1-alkynes bearing electron-releasing substituents such as n-C_3H_7 and n-C_5H_{11} react with **1** in THF only at reflux temperature to give mixtures of σ-alkenyl and σ-acetylide compounds. The prevailing formation of insertion products (ca. 90%) is consistent with the much lesser "acidity" of the C–H bond in alkyl-substituted acetylenes. On the other hand, increasing the temperature from 67 °C (THF) to 111 °C (toluene) permits the conversion of the σ-alkylvinyl products to the corresponding σ-acetylides.

The reactions of **1** with HC≡CSiMe$_3$ deserve a separate comment. As is clearly shown in Schemes I and II, no reaction occurs between the two reactants at room temperature even when a large excess of alkyne is used. In contrast, a fast reaction occurs in refluxing THF. As a result the σ-acetylide **7** is quantitatively obtained with only traces of oligomerization products. Accordingly, we conclude that, for a reason which is not yet understood (steric hindrance?), the formation of the σ-acetylide selectively proceeds through H_2 elimination.

PP$_3$ Complexes. The substitution of phosphorus for nitrogen in the framework of the tripodal ligand significantly affects the reactivity of the resulting monohydrido complex toward 1-alkynes, since the system appears less prone either to form σ-alkenyl compounds or to oxidatively add to the alkyne C–H bond. At room temperature, only ethyl propiolate reacts with **2**, yielding a σ-alkenyl product with *gem* stereochemistry. As for the analogous reaction of **1**, the reaction conditions and the stereospecific addition are consistent with a concerted mechanism involving a four-centered transition complex, the only difference being that the dissociation of a terminal phosphorus is now a much more likely process than the decoordination of the bridgehead phosphorus.[6] In this respect, it is possible that the different types of alkyne addition to the metal, *gem* vs *E*, may well be a consequence of the different geometries of the transition complex. In actuality, the PP$_3$ transition complex appears more open at the metal so as to permit a closer proximity of the substituted carbon to the Rh–H bond (Scheme III).

Increasing the amount of 1-alkynes results in no reaction with HC≡C-n-C_3H_7, HC≡C-n-C_5H_{11}, and HC≡CSiMe$_3$, whereas the quantitative and partial (40%) formations of σ-acetylides occur for HC≡CCO$_2$Et and HC≡CPh, respectively. In both cases, the corresponding alkene is liberated, thus indicating that C–H oxidative addition to rhodium, followed by reductive elimination of hydride and σ-alkenyl ligands, prevails over H–H elimination. This finding is not new for the (PP$_3$)Rh^{III} system, which is known to readily eliminate hydride and σ-organyl ligands in a cis disposition whereas it tolerates two cis hydride ligands.[12,13]

The hydride **2** reacts with 1-alkynes in THF at reflux temperature regardless of the substituent, yielding σ-acetylides and a mixture of organic products whose distribution is quite similar to that observed for **1**.

Catalytic Oligomerization of 1-Alkynes. Surveying Tables III and IV and Schemes I and II, one may readily infer that the main effect of increasing the reaction temperature is to minimize the role played by the tripodal ligand. In fact, quite similar product distributions are observed for **1** and **2**.

For R = CO$_2$Et, n-C_5H_{11}, the product distribution is consistent with the σ-alkenyl species as the most active species in the catalysis cycles. In particular, the selectivity for cyclotrimerization vs enyne formation indicates that insertion of alkyne across the Rh–C(alkenyl) bond prevails over C–H oxidative addition. In contrast, the major formation of enyne and butadiyne vs cyclotrimerization in the reaction with HC≡CPh suggests that also the σ-acetylide termination product can take an active part in the catalytic conversion of phenylacetylene. As a matter of fact, the direct reactions of the NP$_3$ and PP$_3$ σ-(ethoxycarbonyl)acetylides with a 10-fold excess of HC≡CCO$_2$Et in refluxing THF for 3 h do not afford an appreciable oligomerization of the alkyne. In contrast, the reactions of the σ-phenylacetylides **5** and **15** with an excess of phenylacetylene, under the same reaction conditions, essentially produce 1,4-diphenylbutadiyne (15%), diphenylbutenynes (28%), and cyclic trimers (2%) (total conversion 50%).

In light of the experimental evidence herein presented, a possible mechanism based on insertion and addition/elimination steps that can account for the conversion of 1-alkynes to organic products is shown in Scheme V. Although appreciable amounts of higher oligomers have been produced in the course of some reactions, the catalysis cycle shown in Scheme V has been purposefully restricted to dimerization and cyclotrimerization, the following, eventual oligomerization to higher cyclic or linear oligomers proceeding in an identical way. In addition, it is worth mentioning that butenynes are thermally unstable, decomposing to higher oligomers.[12j] Therefore, it is not possible to exclude a priori the thermal decomposition of butenynes to account for the formation of such higher oligomers.

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Registry No. **1**, 85233-91-6; **2**, 109786-30-3; **3**, 120384-51-2;

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4, 124224-71-1; **5**, 114580-95-9; **6**, 124224-70-0; **7**, 122068-43-3; **8**, 125591-75-5; **9**, 125591-76-6; **10**, 122068-42-2; **11**, 125610-25-5; **12**, 125591-77-7; **13**, 125591-78-8; **14**, 122092-50-6; **15**, 122092-46-0; **16**, 122092-47-1; **17**, 122092-45-9; **18**, 125591-79-9; CH_2=$CHCO_2Et$, 140-88-5; $PhCH$=CH_2, 100-42-5; $[(NP_3)RhCO]BPh_4$, 89530-44-9; HC≡CCO_2Et, 623-47-2; HC≡CPh, 536-74-3; HC≡$CSiMe_3$, 1066-54-2; HC≡C(*n*-C_3H_7), 627-19-0; HC≡C(*n*-C_5H_{11}), 628-71-7; HC≡CCHO, 624-67-9.

Activation of 1-Alkynes at Tripodal (Polyphosphine)rhodium Systems. Regioselective Synthesis of Enol Esters from 1-Alkynes and Carboxylic Acids Catalyzed by Rhodium(I) Monohydrides

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Regioselective formation of 2-(benzoyloxy)propene results from the addition of benzoic acid to propyne in the presence of the trigonal-bipyramidal Rh(I) monohydrides $[(PPh_3)RhH]$ (**1**) and $[(NP_3)RhH]$ (**2**, PP_3 = $P(CH_2CH_2PPh_2)_3$, NP_3 = $N(CH_2CH_2PPh_2)_3$). The reactions are catalytic under relatively mild conditions (catalyst to substrate ratio 1:100, toluene, 100 °C). A detailed experimental study on the reactions of **1** and **2** with carboxylic acids, 1-alkynes, or carboxylic acid/1-alkyne mixtures has allowed us to draw a catalysis cycle involving the 16-electron fragments $[(L)Rh]^+$ as catalysts (L = PP_3, NP_3). The catalytic behavior of the precursors **1** and **2** has been compared and contrasted with those of the isostructural and isoelectronic derivatives $[(L)Rh(C{\equiv}CPh)]$, $[(L)RhCl]$, and $[(PP_3)RhMe]$. The novel vinylphosphonium complex $[(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)Rh\{C{=}C(H)Ph\}(O_2CPh)]$ has been synthesized and fully characterized by IR and ^1H and $^{31}P\{^1H\}$ NMR techniques.

Introduction

The participation of enol esters as starting compounds in a wide range of stoichiometric and catalytic organic reactions[1] makes the large-scale preparation of these fine chemicals the object of intense research.[1a,2] Conceptually, the most straightforward way to look at the synthesis of enol esters is to think of the 1:1 condensation of 1-alkynes and carboxylic acids. Such a process necessarily requires the activation of the C–C triple bond by means of a catalyst, which may be either an electrophile or a transition-metal complex (eq 1).[2]

$$RCO_2H + HC{\equiv}CR' \xrightarrow{cat.} \underset{G}{RC(O)OC(R')=CH_2} + \underset{E,\,Z}{RC(O)OC(H)=C(H)R'} \quad (1)$$

Besides catalyzing reaction 1, metal complexes have the potential of driving the reactions to the selective formation of the *G*, *E*, or *Z* isomers through a fine tuning of the components of the complex framework. This is an important point since enol esters are largely employed as polymer precursors, particularly for the polymerization of the C–C double bond.[1f]

A number of catalyst systems, essentially ruthenium complexes, have been so far reported to effectively assist reaction 1.[2e-i] In most instances, the reactions led to mixtures of the three stereoisomers. Recently, some of us developed a quite efficient ruthenium system, namely, $RuCl_2(PR_3)(p\text{-cymene})$, that brings about the selective synthesis of the *G* isomer.[2f,g] However, the mechanism of the catalysis cycle has not been completely elucidated as yet. Therefore we decided to study reaction 1 using as catalyst precursors, rhodium complexes containing the tripodal polyphosphines $P(CH_2CH_2PPh_2)_3$ (PP_3) and $N(CH_2CH_2PPh_2)_3$ (NP_3). The choice of PP_3 and NP_3 as ancillary ligands was suggested by their geometry, which is such that as many as two free coordination sites only are available at the metal.[3] The forced proximity (cis

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