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

(1) For a review of the reactivity of enol esters see: (a) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985. For examples of the reactivity of enol esters see: (b) Rothman, E. S.; Hecht, S. S.; Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1972**, *37*, 3551. (c) House, H. O.; Gall, M.; Olmstead, H. D. *Ibid.* **1971**, *36*, 2361. (d) Inokuchi, T.; Takagishi, S.; Akahoshi, F.; Torii, S. *Chem. Lett.* **1987**, *28*, 1553. (e) Noyce, D. S.; Pollack, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 7158. (f) Weissermel, K.; Arpe, H. J. *Chim. Org. Ind.* **1981**, 210. (g) Jeffery, E. A.; Satchell, D. P. N. *J. Chem. Soc.* **1962**, 1906. (h) Baciocchi, E.; Civitarese, G.; Ruzziconi, R. *Tetrahedron Lett.* **1987**, *28*, 5357.

(2) (a) Bach, R. D.; Woodard, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707. (b) Barney, R. P.; Cooper, S. R.; Tulane, V. J.; Delaney, H. *J. Org. Chem.* **1943**, *8*, 153. (c) Micovic, V. M.; Rogic, M. M.; Mihailovic, M. L. *Tetrahedron* **1957**, *1*, 340. (d) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966. (e) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689. (f) Ruppin, C. Thesis, University of Rennes, France, 1988. (g) Ruppin, C.; Dixneuf, P. H.; Lecolier, S. *Tetrahedron Lett.* **1988**, *29*, 6365. (h) Ruppin, C.; Dixneuf, P. H. *Ibid.* **1986**, *27*, 6323. (i) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 2230.

(3) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

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diposition) of the two eventual coligands makes the complexes particularly prone to undergo reductive elimination reactions. In addition, the LRh system (L = PP_3, NP_3) can readily enter into the metal III → I → III oxidation/reduction cycle with no phosphine arm dissociation or apparent destabilization of the resulting complexes.[3] Because of that, the use of tripodal ligands often allows the isolation and characterization of many intermediate species not normally seen in catalysis cycles.[4]

In this paper we describe the reactions of the trigonal-bipyramidal (TBP) monohydrido complexes of rhodium(I) $[(PP_3)RhH]$[3] (**1**) and $[(NP_3)RhH]$[3] (**2**) with 1-alkynes and/or carboxylic acids. A detailed study of the catalytic addition of benzoic acid to propyne has been carried out. This has provided valuable mechanistic information on the catalysis cycle, leading to the selective formation of 2-(benzoyloxy)propene.

Experimental Section

General Data. Tetrahydrofuran (THF) and toluene were purified by distillation over $LiAlH_4$ and sodium 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 3. Alkynes were purchased from commercial suppliers and used without further purification. 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 H_3PO_4 85% 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 on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and 10-ft 100/120 Carbosieve-SII or 6-ft 0.1% SP-1000 80/100 Carbopack C stainless steel columns (Supelco Inc.) or on an Intermat IGC 120DFL gas chromatograph fitted with a flame ionization detector and a 1.5 m × 2 mm i.d. stainless steel column packed with a 10% FFAP on Chromosorb WHMDS (80–100 mesh). Quantification was achieved with a Shimadzu C-R6A Chromatopac or with a Hewlett-Packard integrator coupled with the chromatograph, operating with an automatic correct area normalization method.

Simulation of NMR spectra was achieved by using an updated version of the LAOCN4 program.[5] 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.

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, unless otherwise stated, with ethanol and *n*-pentane before being dried in a stream of nitrogen.

Reactions of 1 and 2 with RCO_2H (R = Me, Ph). To stirred suspensions of **1** (0.31 g, 0.40 mmol) or **2** (0.25 g, 0.32 mmol) in toluene (30 mL) was added a slight excess of either $MeCO_2H$ or $PhCO_2H$. The yellow monohydrides dissolved in a few minutes to give colorless solutions. On addition of $NaBPh_4$ (0.27 g, 0.80 mmol) in ethanol (30 mL), white crystals of $[(PP_3)Rh(H)_2]BPh_4$ (**3**) and $[(NP_3)Rh(H)_2]BPh_4$ (**4**) separated in 90% yield. The compounds were identified by comparison with authentic specimens.[3]

Reactions of 1 and 2 with $HC{\equiv}CCO_2H$. Addition of a slight excess of neat propiolic acid (27 μL, 0.44 mmol) to stirred suspensions of **1** (0.31 g, 0.40 mmol) of **2** (0.30 g, 0.40 mmol) in toluene (30 mL) produced colorless solutions from which **3** and **4** were obtained by addition of $NaBPh_4$ (0.27 g, 0.80 mmol) in ethanol (30 mL), respectively, yields 90%.

Reactions of 1 and 2 with $PhCO_2H$/HC≡CR Mixtures (R = Ph, *n*-C_3H_7). Room-Temperature Reactions. Benzoic acid (0.053 g, 0.44 mmol) and phenylacetylene (29 μL, 0.44 mmol) or 1-pentyne (44 μL, 0.44 mmol) in toluene (30 mL) were stirred with solid **1** or **2** (0.40 mmol) for 6 h. After usual workup the dihydrides **3** and **4** were obtained in 90% yields.

Reflux-Temperature Reactions. When the above reactions were carried out at reflux temperature for 4 h, the addition of $NaBPh_4$ in ethanol precipitated off-white crystals of the *cis*-(hydride)acetylides $[(PP_3)Rh(H)(C{\equiv}CPh)]BPh_4$ (**5**), $[(PP_3)Rh(H)(C{\equiv}C\text{-}n\text{-}C_3H_7)]BPh_4$ (**6**), $[(NP_3)Rh(H)(C{\equiv}CPh)]BPh_4$ (**7**), and $[(NP_3)Rh(H)(C{\equiv}C\text{-}n\text{-}C_3H_7)]BPh_4$ (**8**) in 75–80% yields. The compounds were identified by comparison with authentic specimens.[9b,10]

Reactions of the Dihydrides 3 and 4 with HC≡CR (R = Ph, *n*-C_3H_7). A 2-fold excess (0.80 mmol) of the appropriate terminal alkyne was added to a suspension of either **3** or **4** (0.40 mmol) in toluene (30 mL) with stirring. On heating the resulting mixtures at reflux temperature for 4 h, the solid complexes completely dissolved. Addition of ethanol (30 mL) precipitated crystals of the *cis*-(hydride)acetylides **5–8** in 75–85% yields. GC-MS analysis of the PP_3 reactions showed the presence of styrene and 1-pentene in the reaction mixtures in amounts corresponding to ca. 25% of the initial alkynes. In contrast, no alkene was produced in the NP_3 reactions, whereas traces of H_2 were detected.

Reaction of $[(PP_3)Rh(C{\equiv}CPh)]$ with $PhCO_2H$. To a stirred solution of the σ-acetylide complex (0.35 g, 0.40 mmol) in toluene (30 mL) was added neat benzoic acid (0.053 g, 0.44 mmol). On gentle heating, the initial pale yellow color disappeared to give an orange solution from which yellow-orange microcrystals of the vinylphosphonium complex $[(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)Rh\{C{=}C(H)Ph\}(O_2CPh)]$ separated after addition of ethanol (30 mL) and slow evaporation of the solvent, yield 75%. Anal. Calcd for $C_{57}H_{53}O_2P_4Rh$: C, 68.68; H, 5.36; P, 12.43; Rh, 10.32. Found: C, 68.20; H, 5.32; P, 12.11; Rh, 10.41.

Reaction of $[(NP_3)Rh(C{\equiv}CPh)]$ with $PhCO_2H$. To a stirred solution of the σ-acetylide complex (0.40 g, 0.47 mmol) in toluene (30 mL) was added a slight excess of neat benzoic acid. On gentle heating, the starting yellow complex dissolved to give a burgundy red solution from which deep red crystals of the vinylidene complex $[(NP_3)Rh\{C{=}C(H)Ph\}]BPh_4$ were obtained by addition of $NaBPh_4$ (0.40 g, 1.17 mmol) in ethanol (30 mL), yield 70%. The vinylidene complex was identified by comparison with an authentic specimen.[9a,11]

Reactions of [(L)RhCl] (L = PP_3, NP_3) with $PhCO_2H$. To stirred suspensions of $[(PP_3)RhCl]$ (0.40 g, 0.50 mmol) or $[(NP_3)RhCl]$ (0.39 g, 0.50 mmol) in THF (30 mL) was added with stirring a slight excess of benzoic acid. The resulting mixtures were gently heated to ca. 40 °C until the starting compounds dissolved to give pale lilac (PP_3) or green (NP_3) solutions. Crystals

(4) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 210. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226.

(5) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

(6) (a) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1987**, *326*, C79. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337.

(7) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

(8) To be published.

(9) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics*, in press. Some preliminary results are reported in: (a) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660. (b) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53.

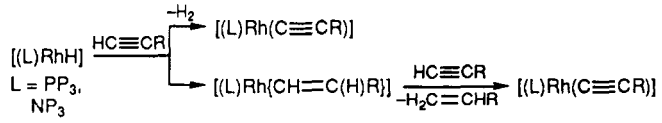
(10) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179.

(11) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241.

(12) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *248*, C13.

(13) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

Scheme I



of $[(PP_3)Rh(H)Cl]BPh_4$ and $[(NP_3)Rh(H)Cl]BPh_4$ were obtained by addition of $NaBPh_4$ (0.25 g, 0.73 mmol) in ethanol (30 mL). The *cis*-(hydride) chlorides were identified by comparison with authentic specimens.[3]

Reaction of [(PP$_3$)RhMe] with PhCO$_2$H. To a stirred suspension of the Rh(I) methyl complex (0.15 g, 0.44 mmol) in toluene (20 mL) was added a slight excess of neat benzoic acid. The resulting mixture was gently heated to reflux temperature. The initial yellow color slowly began to turn purple. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed the complete disappearance of the starting compound (AM_3X spin system)[3] to take place in ca. 6–7 h.

Reaction of 1 with PhCO$_2$H and HC≡Ph. To a stirred suspension of **1** (0.62 g, 0.80 mmol) in toluene (30 mL) were added 2 equiv of $PhCO_2H$ (0.19 g, 1.6 mmol). The yellow monohydride dissolved to give a colorless solution which separated white crystals of $[(PP_3)Rh(H)_2](PhCO_2)$. Neat phenylacetylene (52 μL, 0.80 mmol) was then added to the reaction mixture, which was heated with stirring at reflux temperature for 3 h. By addition of *n*-heptane, yellow–orange crystals of $[(PP_3)Rh(O_2CPh)]$ precipitated, yield 95%. Anal. Calcd for $C_{49}H_{47}O_2P_4Rh$: C, 65.77; H, 5.29; Rh, 11.50. Found: C, 65.20; H, 5.02; Rh, 11.17. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K, 121.42 MHz) AM_3X spin system, $\delta(P_A)$ 152.15, $\delta(P_M)$ 36.68 [$J(P_AP_M)$ = 24.3 Hz, $J(P_ARh)$ = 81.3, $J(P_MRh)$ = 117.4 Hz]. IR: ν(C≡O) 1565 cm^{-1}, additional phenyl vibration at 1595 cm^{-1}.

GC-MS analysis of the solution showed the formation of (benzoyloxy)styrene isomers (*G* 94%, *E* 3%, *Z* 3%).

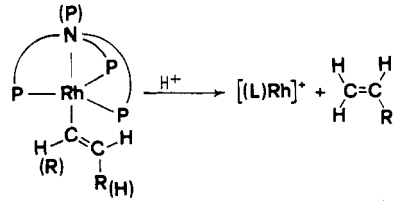
Catalytic Runs. In a 100-mL stainless steel autoclave were successively added 10 mL of toluene, 0.2 mmol of complex (**1** or **2**) and 20 mmol of benzoic acid. Propyne (25 mmol) was introduced while the autoclave was cooled. The reactor was then heated to 100 °C. The reaction was monitored by GLC (10% FFAP on Chromosorb WHMDS). The yield in each enol ester isomer ($PhCO_2C_3H_5$) was calculated according to an area normalization method. After 4 h, the conversion of the acid into propenyl esters was complete. The relative yields were 94% (*G*), 3% (*E*), and 3% (*Z*) for **1** and 92% (*G*), 4% (*E*), and 4% (*Z*) for **2**. After removal of toluene under vacuum, the esters were distilled (80–82 °C/2 mmHg) and identified by comparison with authentic samples.[2f]

In a 100-mL Schlenk tube were introduced 0.2 mmol of either $[(PP_3)Rh(C{\equiv}CPh)]$ (**9**) or $[(NP_3)Rh(C{\equiv}CPh)]$ (**10**), 20 mmol of benzoic acid, 25 mmol of propyne, and toluene (10 mL). After 8 h at 80 °C, the reaction mixture was analyzed by GLC as above, but no formation of esters was observed.

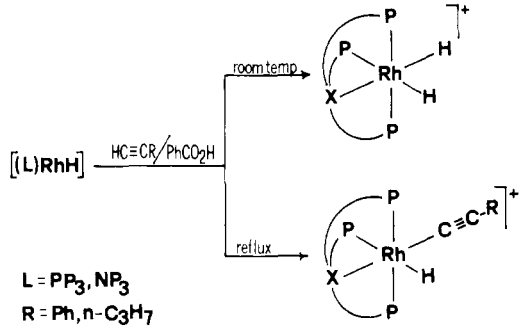
Results and Discussion

Interaction of 1 and 2 with Carboxylic Acids and/or 1-Alkynes. Like most of TBP Rh(I) complexes with PP_3 or NP_3,[3,6] **1** and **2** in THF are readily protonated at the metal by carboxylic acids to give after metathetical reaction with $NaBPh_4$ the known octahedral (OCT) dihydrides $[(L)RH(H)_2]BPh_4$ (L = PP_3, **3**; NP_3, **4**).[3,7] The PP_3 dihydride **3** in solution rearranges to TBP geometry at temperaturs higher than 183 K as a consequence of H–H bonding.[7] The H_2 ligand is rather labile and can be replaced by CO[3] or disubstituted acetylenes such as dimethyl acetylenedicarboxylate[8] (DMAD), yielding σ-carbonyl and η^2-alkyne derivatives, respectively. In contrast, the NP_3 complex **4** is quite stable in solution, in which it maintains the classical dihydride structure regardless of the temperature.[3] However, **4** in toluene can be forced to undergo the reductive elimination of H_2 by treatment with CO or DMAD. As a result, the corresponding substitution products are obtained.[3] Displacement of H_2 by DMAD requires reflux temperature.[8]

Scheme II



Scheme III



The reactions of **1** and **2** with 1-alkynes are much more complicated since they strictly depend on a variety of factors, including the temperature, the stoichiometry, and the alkyne substituent.[9] Scheme I appropriately summarized the possible reaction pathways. In general, the quantitative conversion of the monohydrides into σ-acetylides requires an excess of alkyne and reflux temperature as well. In contrast, the σ-alkenyl complexes, which are often contaminated by the corresponding σ-acetylide because of the competing C–H oxidative addition, are obtained from stoichiometric reactions.

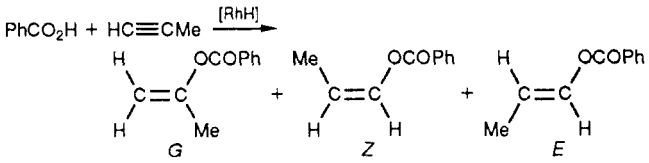
Interestingly, the σ-alkenyl complexes, which may exhibit either *E* (NP_3 compounds) or *G* (PP_3 compounds) stereochemistry, react with protic acids producing alkene and forming the 16-electron fragments $[(L)Rh]^+$ (L = NP_3, PP_3; Scheme II).[9]

Given for granted that **1** and **2** can activate both carboxylic acids and 1-alkynes, we went further on investigating the reactions with mixtures of the two reagents. By treatment of **1** and **2** with equimolar mixtures of benzoic acid and phenylacetylene or 1-pentyne in THF or toluene at room temperature, the OCT dihydrides **3** and **4** are invariably and quantitatively formed. To confirm the prevalence of O–H oxidative addition over C–H oxidative addition at rhodium, **1** and **2** were reacted with propiolic acid, $HC{\equiv}CCO_2H$, which bears both functional groups. Once again, the dihydrides **3** and **4** were obtained.

A quite different result was found for the reactions of **1** and **2** in toluene with benzoic acid/1-alkyne mixtures at reflux temperature. In fact, the OCT *cis*-(hydride)-acetylides $[(L)Rh(H)(C{\equiv}CR)]BPh_4$ (L = PP_3, R = Ph, **5**; R = *n*-C_3H_7, **6**; L = NP_3, R = Ph, **7**; R = *n*-C_3H_7, **8**) were produced in good yields.[9b,10] For L = PP_3, partial hydrogenation of 1-alkynes to the corresponding alkenes was observed (Scheme III).

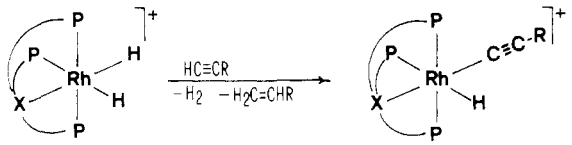
The *cis*-(hydride)acetylides were the only isolable metal-containing products also when **1** and **2** were reacted with a 10-fold excess of benzoic acid/1-alkyne mixture. After 4 h in refluxing toluene, only traces of 1-alkyne and benzoic acid (<4%) were detected in the reaction mixture by GC-MS, thereby indicating the occurrence of a catalytic reaction consuming the two reagents. Accordingly, we decided to carry out a detailed study on the reactions of **1** and **2** with benzoic acid/propyne under catalytic conditions ($PhCO_2H$, 20 mmol; HC≡CMe, 25 mmol; **1** or **2**,

Scheme IV



[RhH] = **1**: (*G*) 94%, (*E*) 3%, (*Z*) 3%
[RhH] = **2**: (*G*) 92%, (*E*) 4%, (*Z*) 4%

Scheme V



X = P, N
R = Ph, n-C_3H_7

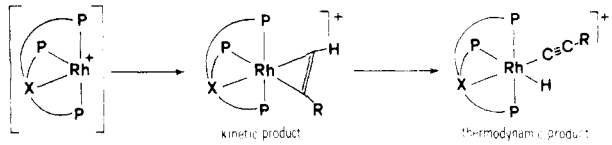
0.2 mmol; toluene, 10 mL; 4 h, 100 °C). After 4 h, a complete conversion of benzoic acid/propyne into *G*-, *Z*-, and *E*-(benzoyloxy)propenes was observed. The product distribution is reported in Scheme IV.

Interaction of the Rhodium(III) Dihydrides [(L)Rh(H)$_2$]BPh$_4$ with 1-Alkynes (L = PP$_3$, NP$_3$). Having found that carboxylic acids prevail over 1-alkynes in the reaction with **1** or **2** we looked at the reactions of the dihydride products **3** and **4** with 1-alkynes. In accord with the results presented in the previous section, the dihydrides do not react with HC≡CPh or HC≡C-*n*-C_3H_7 in THF at room temperature, whereas a fast reaction takes place in toluene at reflux temperature yielding the *cis*-(hydride)acetylide derivatives **5**–**8** (Scheme V). Once again, for L = PP$_3$, partial hydrogenation of alkyne to alkene was observed.

Several attempts were made to detect the eventual evolution of H_2 from the NP$_3$ reactions. In a couple of runs, traces of H_2 were found by GC. Actually, we believe that the alkyne forces the reductive elimination of H_2 from **4** as it occurs in the reaction with CO.[3] However, the present reaction conditions are too drastic to permit a reliable quantitative analysis of H_2 either in the gas phase or in solution. In this context, it is worth reporting that the Rh(III) *cis*-(hydride)acetylides **5**–**8** can be straightforwardly prepared by reacting the [(L)Rh]$^+$ fragments prepared in situ with either HC≡CPh or HC≡C-*n*-C_3H_7 (vide infra).[9b,10]

Interaction of the σ-Acetylides [(L)Rh(C≡CR)] with Carboxylic Acids. In an attempt to elucidate the mechanism of the present catalytic addition of carboxylic acids to 1-alkynes, the eventual participation of the Rh(I) σ-acetylides [(L)Rh(C≡CR)][9,10] (L = PPh$_3$, NP$_3$) in the catalysis cycle was properly considered by us. In fact, the σ-acetylides are the termination products of the reactions between **1** or **2** and excess of 1-alkynes (see Scheme I).[9] In particular, it was important to verify whether and, possibly, how the σ-acetylides react with carboxylic acids. The reactions are exemplified with [(PP$_3$)Rh(C≡CPh)] (**9**) and [(NP$_3$)Rh(C≡CPh)] (**10**). Both compounds react with benzoic acid in THF or toluene undergoing the protonation of the acetylide β-carbon. As a result, the vinylphosphonium complex [(Ph$_2$PCH$_2$CH$_2$)$_2$P(CH$_2$CH$_2$PPh$_2$)Rh{C=C(H)Ph}(O$_2$CPh)] (**11**) and the vinylidene [(NP$_3$)Rh{C=C(H)Ph}]BPh$_4$ (**12**) were obtained, respectively. The vinylidene complex was identified by comparison with an authentic specimen prepared as reported in the literature.[9a,11] In contrast, **11** is a novel

Scheme VI



product, although the formation of vinylphosphonium complexes on protonation of Rh(I) σ-acetylides has been already observed.[11] Compound **11** is collected as yellow, air-stable crystals that slowly decompose in solution unless air is excluded. A medium-intensity band at 1575 cm^{-1} is assigned to ν(C=C) of a vinyl ligand. The presence of a benzoate ligand η^1-bonded to rhodium is inferred by two IR absorptions at 1610 and 1350 cm^{-1}, which are readily assigned to ν(C=O) and ν(C=O···Rh), respectively.[11,12] Precious information on the structure of **11** is provided by $^{31}P\{^1H\}$ spectroscopy. The experimental and computed spectra are reported in Figure 1 together with a labeled sketch of the proposed structure. The spectrum (acetone, 293 K) exhibits a quasi-first-order AMQRX spin system. The lowest field signal, which consists of a doublet of pseudotriplets of doublets, is readily assigned to the bridgehead phosphorus atom of the PP$_3$ ligand.[11] Its multiplicity arises from coupling to rhodium [$J(P_ARh)$ = 118.8 Hz] and to the two terminal phosphorus atoms P_M and P_Q. The quasi-coincidence of the coupling constants to the equatorial phosphorus atoms [$J(P_AP_M)$ = 10.4 Hz, $J(P_AP_Q)$ = 11.5 Hz] is responsible for the observed pseudotriplets' multiplicity. In turn, each component of the two triplets is doubled by an additional small long-range coupling to the P_R phosphonium atom [$J(P_AP_R)$ = 5.2 Hz]. The unusual high-field position of this signal[3] can be explained by considering that following the formation of a P–C linkage, the bridgehead phosphorus atom moves from a highly deshielding five-membered metallorings to a shielding six-membered ring.[14] A similar argument is invoked to account for the high-field position of the P_R resonance with respect to those of metal-bonded terminal PPh$_2$ groups. The phosphonium P_R signal, centered at 19.55 ppm, appears as a well-resolved doublet of pseudoquartets. The coupling connection responsible for the halving of the multiplet is due to one of the two terminal PPh$_2$ phosphorus atoms. In keeping with previous considerations on related vinylphosphonium salts derived from PP$_3$,[11] we conclude that the coupling interaction P_R–P_M is stronger than the P_R–P_Q one because P_M lies trans to the vinylphosphonium ligand [$J(P_RP_M)$ = 29.0 Hz, $J(P_RP_Q)$ = 5.7 Hz]. In turn, the pseudoquartet structure is due to a fortuitous coincidence of the coupling constants to rhodium and to the apical phosphorus P_A [$J(P_RRh) = J(P_RP_A)$ = 5.3 Hz]. Finally, the two middle-field resonances are assigned to the remaining PPh$_2$ groups, which exhibit chemical shifts in the proper range for equatorial phosphorus atoms of five-coordinate PP$_3$ rhodium complexes.[3] In fact, the formation of the present vinylphosphonium moiety is not expected to alter significatively the magnetic properties of the P_M and P_Q atoms, each of which continues to be engaged in a deshielding five-membered metallorings. The two multiplets show the expected 16-line pattern for canonical AMQRX spin systems, and their assignments can be safely done on the basis of the values of the coupling constants to the phosphonium P_R atom.

The proton NMR spectrum recorded in deuterioacetone at room temperature is fully consistent with the vinylphosphonium structure shown in Figure 1. In fact, the

(14) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

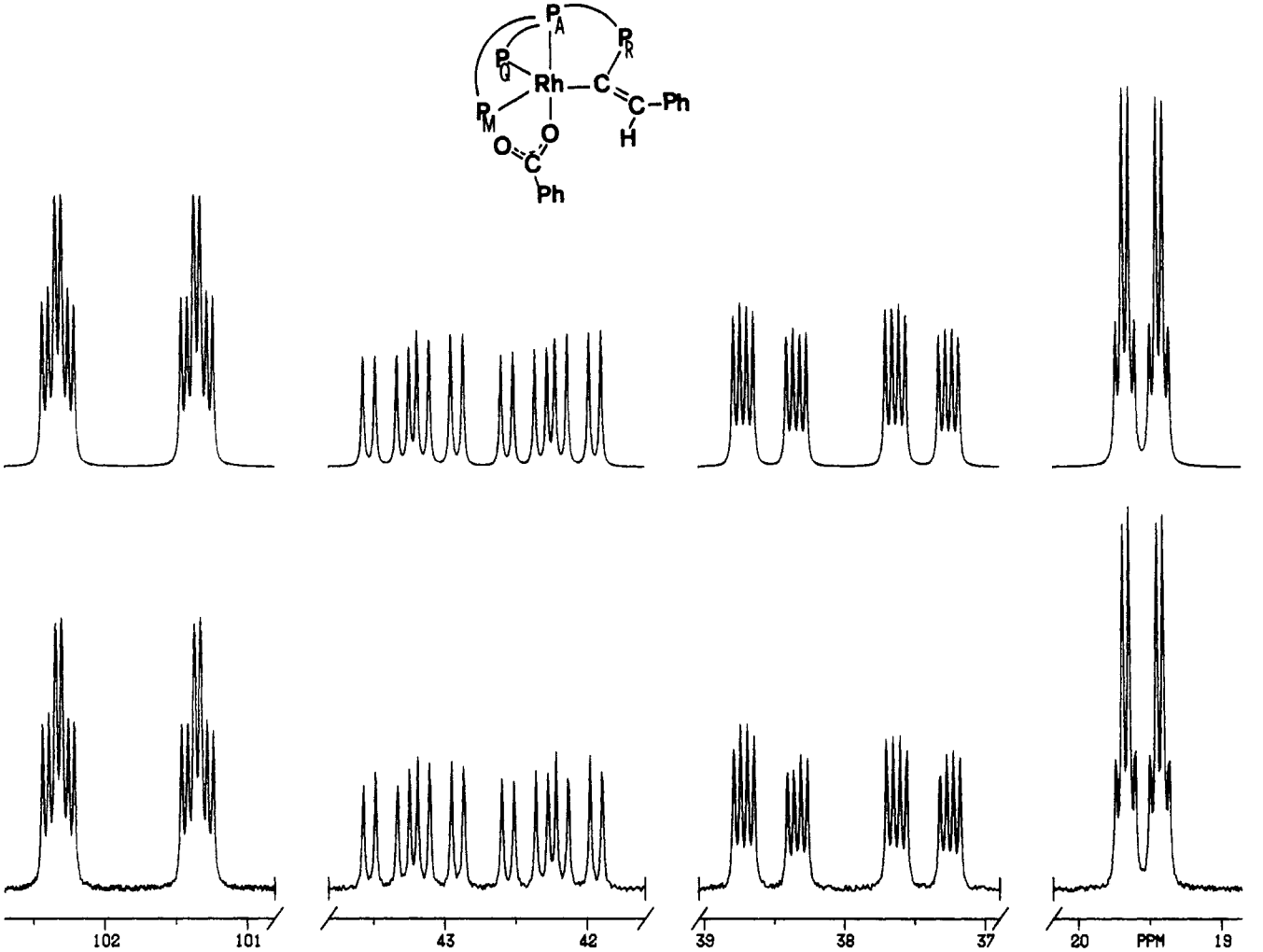


Figure 1. Experimental (lower) and computed (upper) $^{31}P\{^1H\}$ NMR spectra of 11 (121.42 MHz, acetone-d_6, 293 K, 85% H_3PO_4 reference).

spectrum exhibits a doublet of pseudotriplets at 5.62 ppm (1 H, J_1 = 11.2 Hz, J_2 = 9.1 Hz), which falls in the proper region of vinylphosphonium hydrogens.[11] In the absence of selective ^{31}P decoupling experiments, it is hard to discriminate between the possible coupling connections. However, it sounds likely that the largest coupling is $J(HP_R)$.[11]

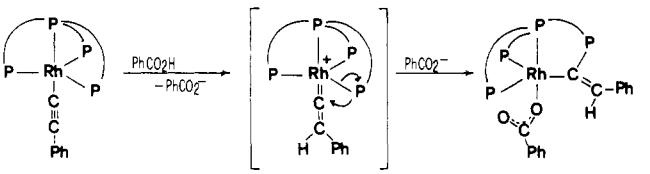
A reasonable mechanism for the formation of **11** is the one that implies the initial protonation of **9** at the acetylide C_β atom to give a vinylidene intermediate,[11,9a] followed by nucleophilic attack by a terminal PPh_2 group of PP_3 at the electron-deficient vinylidene C_α atom (Scheme VI). As a result, an electronically and coordinatively unsaturated vinylidene complex forms that is stabilized by a benzoate anion via coordination.

By treatment of either the vinylphosphonium complex **11** or the vinylidene **12** in toluene with excess of HC≡CPh or HC≡C-*n*-C_3H_7 even at reflux temperature, no apparent reaction involving alkynes was observed. The vinylphosphonium compound remains intact, whereas the vinylidene decomposes according to a thermal pathway already reported.[11] Therefore we conclude that the σ-acetylides are a dead end as far as the catalytic reaction leading to enol esters is concerned.

Conclusions

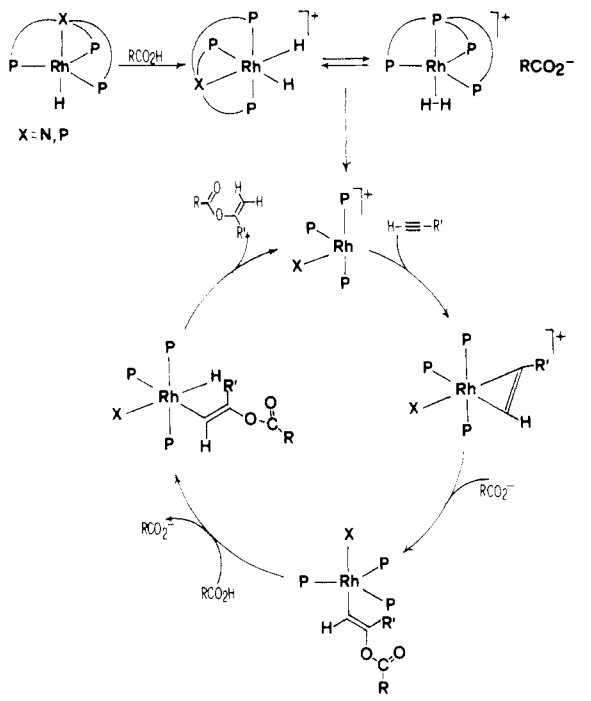
Surveying the experimental results presented in the previous sections, one may readily infer that the first step of the interaction between **1** or **2** and carboxylic acid/1-alkyne mixtures is the protonation of the Rh(I) center. As a result, the OCT Rh(III) dihydrides are obtained. Whatever the mechanism through which H_2 is eliminated from the latter compounds when they are treated with 1-alkynes (simple displacement of H_2 or hydrogen transfer to alkyne),[13] the 16-electron fragments $[(L)Rh]^+$ evidently form at a certain stage of the reactions. Indeed, only the presence of such species may explain the subsequent formation of the *cis*-(hydride) acetylide complexes (see Scheme V). In fact, the coordinatively and electronically unsaturated $[(L)Rh]^+$ systems are known to interact with 1-alkynes forming π-alkyne adducts that are thermodynamically unstable in ambient temperature solutions and slowly convert to the *cis*-(hydride) acetylide derivatives via irreversible insertion across the sp CH bond (Scheme VII). The π-alkyne complexes can be isolated at low temperature. At least in principle, however, the kinetic π-alkyne products may be chemically trapped by reaction with nucleophiles.[15] In this eventuality, the nucleophile is

Scheme VII



(15) (a) Reger, D. L.; McElligot, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5932. (b) Reger, D. L.; Mintz, E.; Lebioda, L. *Ibid.* **1986**, *108*, 1940. (c) Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305.

Scheme VIII



expected to preferentially attack the substituted acetylene carbon atom.[16]

Within this context, it is worth reporting that $[(PP_3)Rh(H)_2](PhCO_2)$ in toluene reacts with an equivalent mixture of $PhCO_2H$ and $HC{\equiv}CPh$ at reflux temperature, producing the benzoate complex $[(PP_3)Rh(O_2CPh)]$ and enol esters. Under the same conditions, the tetraphenylborate salt **3** quantitatively converts to the *cis*-(hydride) acetylide **5**.

It is therefore reasonable to propose the cycle shown in Scheme VIII to describe the present synthesis of enol esters. This involves the Rh(I) monohydrides **1** or **2** as catalyst precursors and the 16-electron systems $[(L)Rh]^+$ as real catalysts. The Rh(I) σ-alkenyl complexes that may form upon nucleophilic attack by carboxylate at η^2-alkyne are ready to be protonated at the metal by a second molecule of carboxylic acid.[9] As a result, Rh(III) *cis*-(hydride)(alkenyl) derivatives form, which are known to be unstable with respect to the reductive elimination of alkene (see Scheme III).[16] In this way, the 16-electron fragments $[(L)Rh]^+$ are regenerated and the catalysis cycle can continue.

In nice accord with the proposed catalysis cycle, we have found that the TBP Rh(I) chlorides $[(L)RhCl]^3$ (L = PP_3, NP_3) do not catalyze the addition of carboxylic acids to 1-alkynes. The compounds are protonated by carboxylic acids, but the resulting *cis*-(hydride) chlorides $[(L)Rh(H)Cl]^+$ are quite stable with respect to the reductive elimination of HCl and do not react with 1-alkynes even under drastic conditions. In contrast, the σ-methyl derivative $[(PP_3)RhMe)]^3$ (**13**) is a catalyst precursor for the synthesis of enol esters, yielding an isomeric product distribution essentially identical with that found for the monohydrides **1** and **2**. Interestingly, however, the complete conversion of the benzoic acid/propyne mixture into (benzoyloxy)propene requires, under similar conditions, a much longer reaction time (19 h instead of 4 h). We ascribe the lower activity of **13** to an induction period since the protonation by benzoic acid to give the *cis*-(hydride)(methyl) intermediate $[(PP_3)Rh(H)Me]^+$ is not as fast as the analogous reaction of the monohydrides **1** and **2**.

In the absence of detailed kinetic measurements, it is not possible to precisely address the question of the rate-determining step of the catalysis cycle shown in Scheme VIII, although two reactions only may play this role, i.e., the $[(L)Rh(H)_2]^+ \rightarrow [(L)Rh]^+$ conversion (this practically corresponds to the catalyst precursor → catalyst conversion) and the nucleophilic attack by carboxylate at the η^2-alkyne intermediates. In this respect, it is worth noticing that the latter reaction has been suggested as the key step in the synthesis of enol esters catalyzed by $RuCl_2(PPh_3)(p\text{-cymene})$. In particular, it was shown that a carboxylate group bonded to ruthenium does not add to the alkyne.[2f]

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(16) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligot, P. J. *Organometallics* **1984**, *3*, 134.