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# Dimerization of 1-alkynes catalyzed by $RhCl(PMe_3)_3$. Isolation of the intermediate (alkynyl)(vinyl)rhodium(III) complexes

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## Abstract

The dimerization of 1-alkynes catalyzed by $RhCl(PMe_3)_3$ yields conjugated enynes I and II (I/II = 1.4–2.4), with a selectivity of 95–98%.

The data indicate that the reaction proceeds by alkyne insertion into the metal–hydride bond of the intermediate (alkynyl)(hydride)$Rh^{III}$ complexes VII, VIII to give the (alkynyl)(vinyl)$Rh^{III}$ species *cis*-$RhCl(PMe_3)_3(CH{=}CHC_3H_7)(C{\equiv}CC_3H_7)$ (IX) and *cis*-$RhCl(PMe_3)_3(CH_2{=}CC_3H_7)(C{\equiv}CC_3H_7)$ (X) which were isolated. The thermal decomposition of IX and X in solution gives the enynes I and II correspondingly.

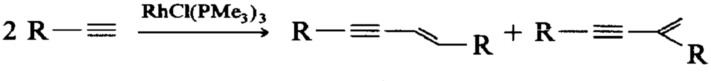
## Introduction

It has been reported that the $Rh^I$ complexes catalyze the dimerization of 1-alkynes [1–8] to give the conjugated (linear and branched) enynes; a branched isomer preponderates [2,4,5]. The $Rh^I$ triphenylphosphine complexes are most commonly used as catalysts in these reactions. The total selectivity to enyne formation is 65–75%, but alkyne trimerization also takes place [2,4,5].

Here we examine the dimerization of 1-alkynes catalyzed by $RhCl(PMe_3)_3$.

## Results and discussion

In the presence of $RhCl(PMe_3)_3$ dissolved in acetone, 1-alkynes are readily converted into a mixture of the enynes I and II; the linear isomer preponderates (I/II = 1.4–2.4). The alkyne conversion is 77–85% and the selectivity to the formation of I and II is 95–98% (see Table 1). The linear dimer has the *trans* configuration.



(I) (II)

$R = C_3H_7, C_4H_9, C_6H_{13}$

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Table 1

The dimerization of 1-alkynes catalyzed by $RhCl(PMe_3)_3$ [a]

| 1-Alkyne | 1-Alkyne conversion % | Yield of dimers [b] | | Mol (I + II)/ mol catalyst |
|---|---|---|---|---|
| | | I | II | |
| 1-Pentyne | 77 | 69 | 29 | 75 |
| 1-Hexyne | 81 | 57 | 41 | 79 |
| 1-Octyne | 85 | 59 | 39 | 84 |
| 1-Octyne | 38 | 57 | 38 | 36 |

[a] All reactions were performed with 16 mmol of 1-alkyne, 0.08 mmol of $RhCl(PMe_3)_3$, 1 ml of acetone, at 80 °C for 5 h. [b] GC yields; the isolated yields are 5–10% less. [c] In toluene (1 ml).

Under the conditions no dimers were obtained from phenylacetylene, ethyl propiolate and ethoxyacetylene.

Two mechanisms of the 1-alkynes catalytic dimerization have been postulated (Scheme 1): route (a) [1,5] and route (b) [9,10].

In mechanism (a) the $\pi$-coordinated alkyne in the alkynyl hydride intermediate **B** is inserted into the metal–carbon bond to give the vinyl hydride intermediates **C** and **D**. Route (b) involves the insertion of coordinated alkyne into the metal–hydride bond of **B** to give alkynyl vinyl species **E** and **F**.

There are no published data which would confirm the mechanisms depicted in Scheme 1. Moreover, there is a paucity of information about alkynyl hydride complexes of type **A** (M = Rh [11,12], Ir [13]). At the same time no examples of the complexes of **C**, **D**, **E** and **F** * have been reported.

We have determined the structure of the intermediates III–XI in the 1-pentyne dimerization reaction catalyzed by $RhCl(PMe_3)_3$ (Scheme 2) by NMR spectroscopy.

When an excess of 1-pentyne was added to the $RhCl(PMe_3)_3$ solution at $-65\,^\circ C$ the trigonal bipyramidal $\pi$-complexes III and IV are immediately formed (experimental and calculated spectra of complex IV are depicted in Fig. 1). Under these conditions the equilibrium between initial $RhCl(PMe_3)_3$ and alkyne $\pi$-complexes is shifted towards III and IV ($RhCl(PMe_3)_3/(III + IV) = 0.2$). However, when the temperature was increased to $-35\,^\circ C$ this equilibrium was shifted to the initial $Rh^I$ complex ($RhCl(PMe_3)_3/(III + IV) = 1.5$).

A further rise in temperature, to $-10\,^\circ C$, converts the initial $RhCl(PMe_3)_3$ and the $\pi$-complexes III and IV into a mixture of the square pyramidal $\pi$-complexes V and VI and the (alkynyl)(hydride)$Rh^{III}$ complexes VII and VIII. Complexes VII and VIII are formed as a result of the oxidative addition of alkyne to $Rh^I$ in corresponding complexes V and VI. It should be noted, that the ratios V/VI and VII/VIII are both approximately 3/2, which approaches the ratio of I/II (see above). For this reason the $^{31}P$ chemical shifts listed in Table 2 for compounds V–VIII have been ascribed to the relevant phosphine ligands from the relative signal integrals in the $^{31}P\{^1H\}$ NMR spectra of the pairs V/VI, VII/VIII, and the final product ratio of I/II.

The $^1H$ NMR data are also consistent with the structures of the intermediate complexes (Scheme 2). Thus, the $^1H$ NMR spectrum of the reaction mixture of

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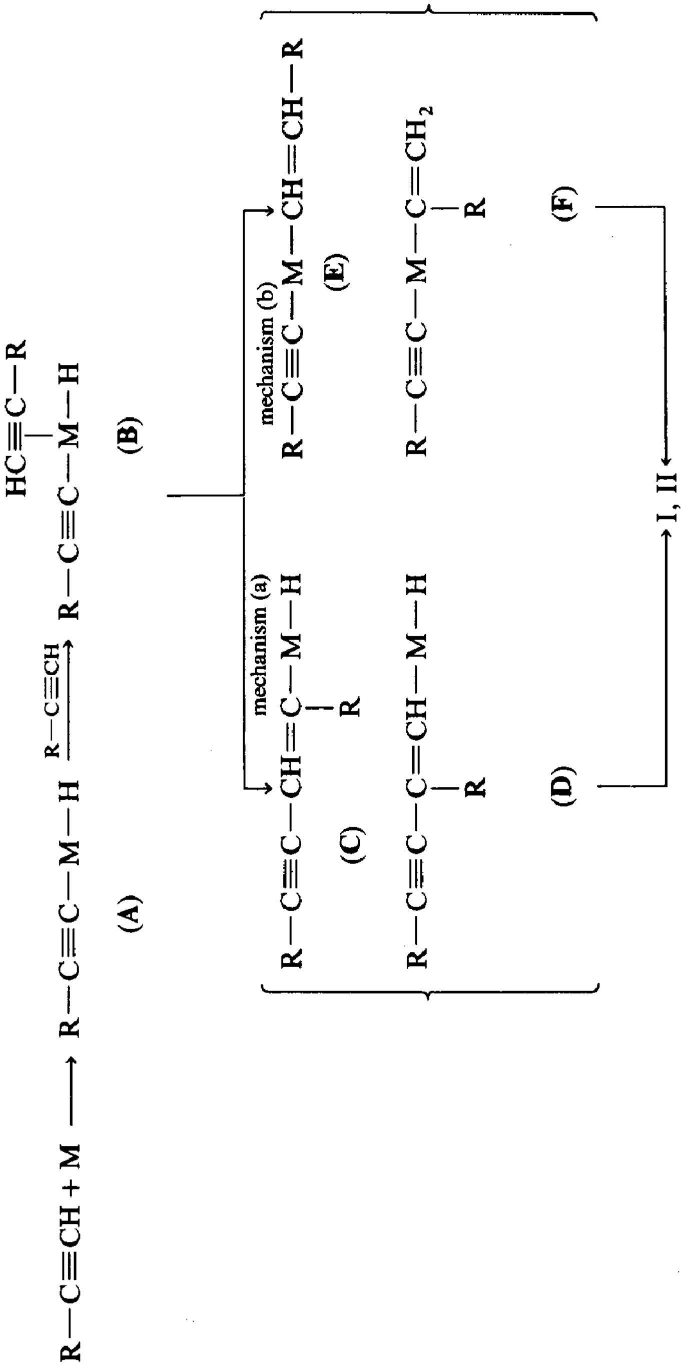
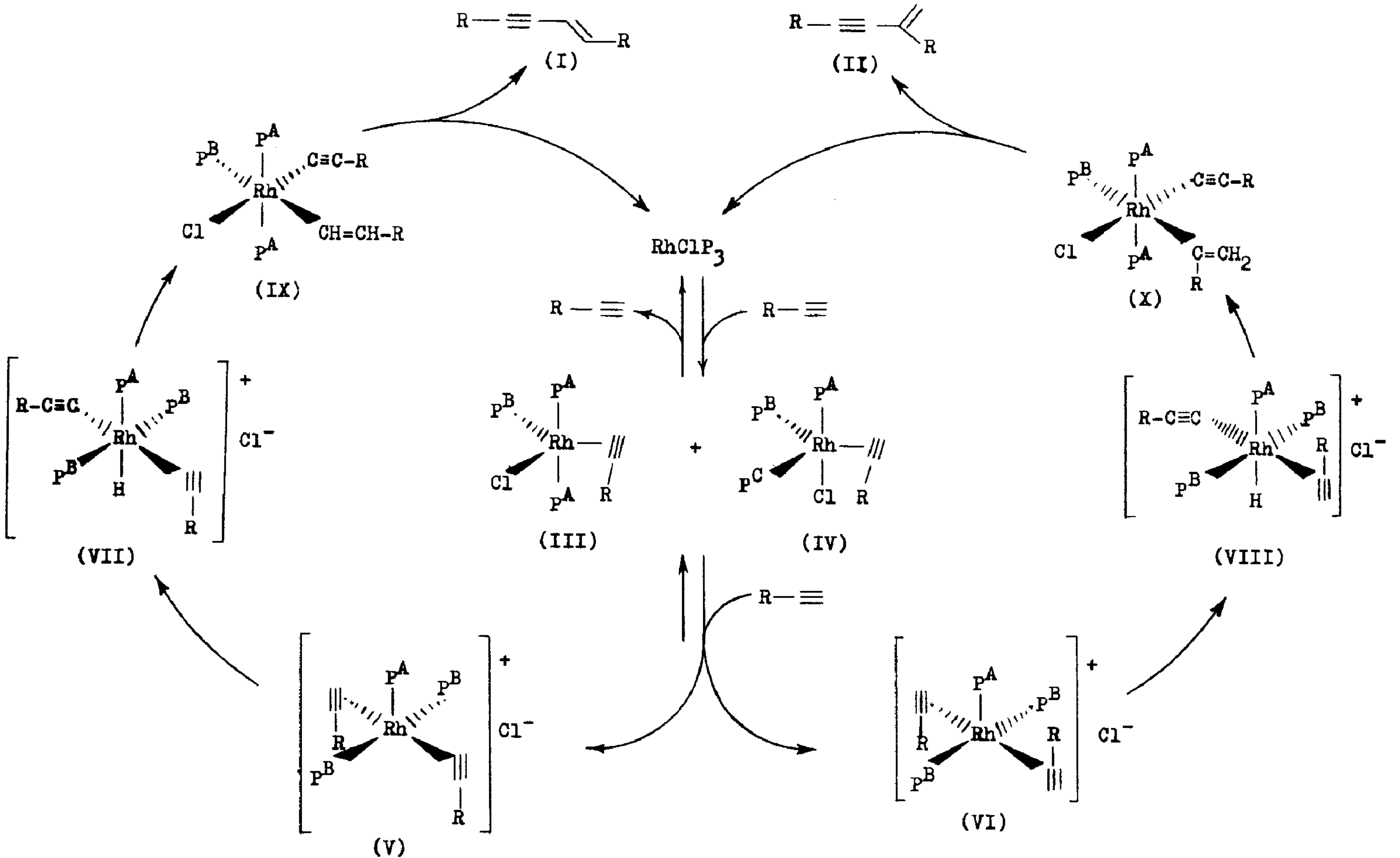
* Recently $Pt^{II}$ complexes of this type (**F**) were reported [14].



Scheme 1



P = PMe$_3$ , R = n-Pr

Scheme 2

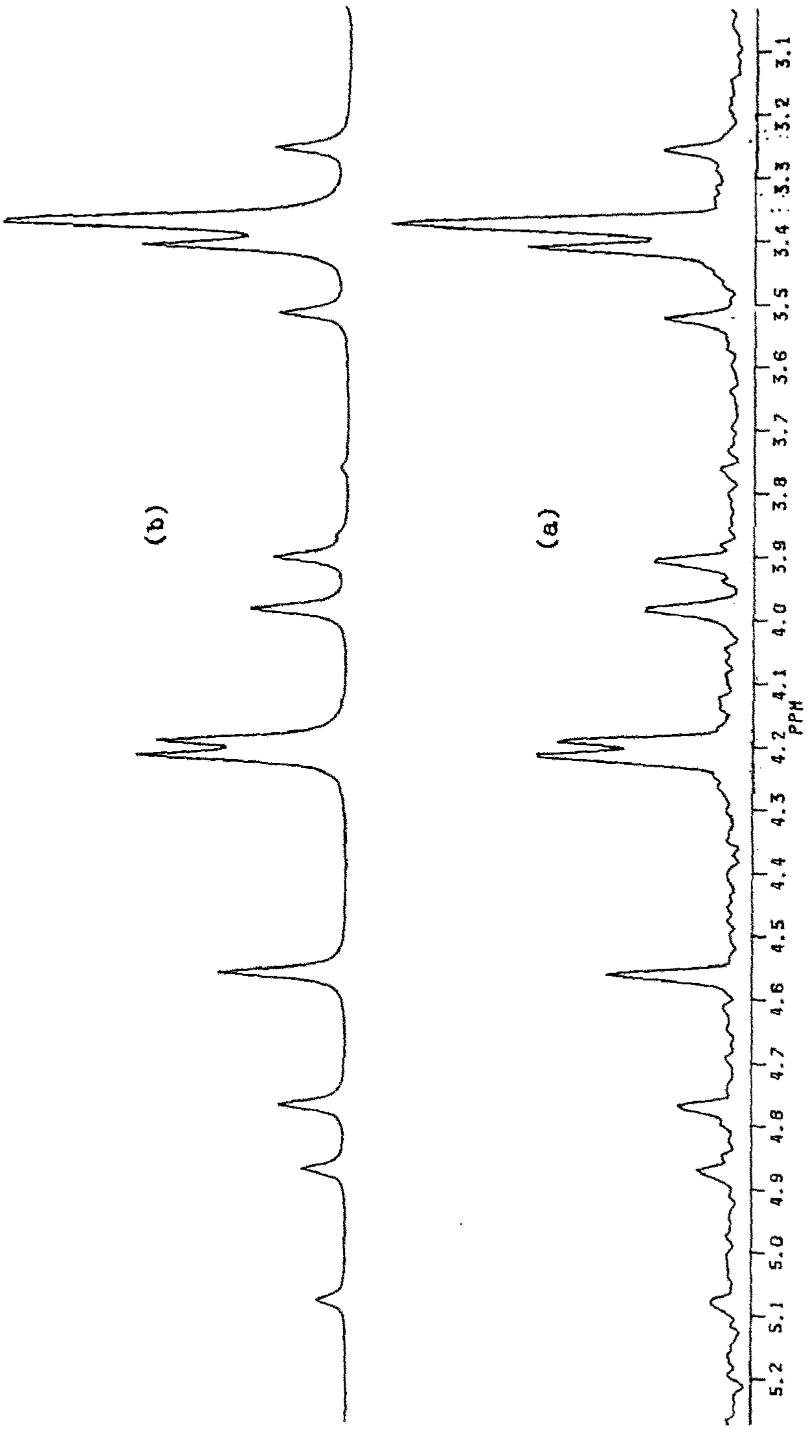


Fig. 1. Observed (a) and calculated (b) $^{31}P\{H\}$ spectrum of complex IV.

Table 2

$^{31}P\{^1H\}$ NMR data of complexes III–XI [a]

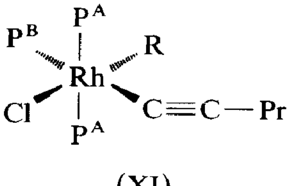
| Complex | $\delta^{31}P$/ppm | | $^1J$(Rh–P)/Hz | | $^2J$(P–P)/Hz |
|---|---|---|---|---|---|
| | $P^A$ | $P^B$ | $P^A$ | $P^B$ | |
| III | 0.09 | −14.34 | 100.9 | 148.6 | 39.9 |
| IV [b] | 4.15 | 3.70 | 151.3 | 99.0 | |
| V [c] | −5.25 | −13.54 | 93.9 | 95.3 | 32.7 |
| VI [c] | −5.36 | −13.67 | 94.2 | 95.0 | 32.8 |
| VII [c] | −24.34 | −5.66 | 95.4 | 68.4 | 28.9 |
| VIII [c] | −24.36 | −5.68 | 95.4 | 68.6 | 22.9 |
| IX | −9.05 | −23.09 | 98.4 | 68.2 | 27.0 |
| X | −8.71 | −23.01 | 99.2 | 66.2 | 26.1 |
| XI | −8.23 | −17.02 | 96.8 | 89.9 | 33.3 |

[a] Toluene-$d_8$, −35 °C. [b] $\delta(P^C) = 3.72$ ppm, $^1J(Rh\text{–}P^C) = 92.0$; $^2J(P^A\text{–}P^B) = -34.0$; $^2J(P^A\text{–}P^C) = -30.7$; $^2J(P^B\text{–}P^C) = 37.0$ Hz. [c] $T = -10$ °C.

RhCl(PMe$_3$)$_3$ and 1-pentyne (toluene-$d_8$, −10 °C) clearly shows the availability of complexes with Rh–H bonds VII and VIII ($\delta$ (H–Rh) = −8.97 ppm ($^1J$(Rh–H) = 15.5; $^2J(H\text{–}P_{trans}) = 213.7$; $^2J(H\text{–}P_{cis}) = 15.5$ Hz).

A further temperature increase, to +25 °C, causes the appearance of the (alkynyl)(vinyl)Rh$^{III}$ complexes IX and X in a ratio of 3/2 owing to the insertion of a coordinated alkyne into the Rh–H bond (at this temperature complexes V and VI are absent in solution). These compounds are the first ever examples of the (alkynyl)(vinyl)Rh$^{III}$ complexes. They have been isolated from the solution in a crystalline form. Complexes IX and X are stable in solution at room temperature, but when they are heated in toluene solution to 50 °C reductive elimination occurs to give the conjugated enynes I and II in the ratio I/II = 3/2, equal to that of IX/X. The direct observation of a reductive elimination reaction of this type has previously only been described for an (alkynyl)(vinyl)platinum$^{II}$ complex [14].

The $^{31}P\{^1H\}$ NMR spectra of complexes IX and X are very similar and indicate the presence of two *trans* phosphine ligands ($P^A$) with $\delta$ −9 ppm ($J$(Rh–P) 100 Hz) in both complexes (cf. [12,15]) (Table 2). The chemical shifts of the phosphorus atoms *cis* to the two others ($P^B$) are −23 ppm. In similar alkynyl hydride complexes, such as [*cis*-HRh(PMe$_3$)$_4$(C≡C(CH$_2$)$_2$OH)]Cl [12], $\delta$ values for the trimethylphosphine ligands in trans to the hydrogen atom and the alkynyl group are −29 and −18 ppm, respectively, thus the chemical shifts of the phosphorus atom ($P^B$) in complexes IX and X have intermediate values. Since the $\sigma$-donor ability falls in the order H > CH=CHR > C≡CR [16], a chemical shift of −23 ppm in $^{31}P\{^1H\}$ NMR spectra of these complexes must be attributed to the PMe$_3$ *trans* to the alkenyl group ($P^B$). Moreover, the $^{31}P\{^1H\}$ NMR spectrum of IX and X shows the presence, in toluene-$d_8$ solution at −35 °C, of a small amount (less than 3%) of the alkynyl vinyl complex, XI. In this complex, an isomer of IX and X, the alkynyl group and the phosphine ligand ($P^B$) are *trans* to each other the $^{31}P$ chemical shift is −17 ppm (cf. ref. 12).



P = PMe$_3$

R = —CH=CH—Pr or —C(=CH$_2$)Pr

(XI)

Thus, the obtained data indicate that the dimerization of the 1-alkyne, catalyzed by $RhCl(PMe_3)_3$, follows mechanism (b); the insertion of alkyne into a metal–hydride bond in the intermediate **B** (Scheme 1).

## Experimental

The $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a "Bruker AM 300" spectrometer in $CDCl_3$ and $C_6D_5CD_3$, TMS as internal standard and 85% $H_3PO_4$ as external standard. The IR spectra were recorded with a Specord M 80 instrument as thin layers or as CsI pellets. The GC analysis was carried out in LHM-8MD(5) using a 200 × 0.3 cm column with 15% of 1,2,3-tris($\beta$-cyanoethoxy)propane on a Chromosorb P. All operations were carried out under argon. Solvents and initial reagents were dried and degassed before use. $RhCl(PMe_3)_3$ was prepared as described previously [17].

*Dimerization of 1-alkynes.* A mixture of 0.03 g (0.08 mmol) of $RhCl(PMe_3)_3$, 16 mmol of alkyne and in 1 ml of the relevant solvent was heated for 5 h in a sealed glass tube at 80 °C. Then the reaction mixture was analysed by GC. The products were isolated by vacuum distillation. The spectral features of the dimers were similar to those described previously [5,18]. The results are listed in Table 1.

*The study of the mechanism of 1-alkynes dimerization.* The reactions were monitored by NMR spectroscopy. 0.2 g (3.0 mmol) of 1-pentyne were placed in a 10 mm ⌀ NMR tube, cooled to $-80\,^\circ C$ and then a solution of 0.037 g (0.1 mmol) of $RhCl(PMe_3)_3$ in 3 ml of toluene-$d_8$ was added at the same temperature. The tube was placed in the spectrometer and the $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded at $-65$, $-35$, $-10$ and $+25\,^\circ C$ (data are listed in Table 2).

*Synthesis of the complexes IX and X.* 0.14 g (2 mmol) of 1-pentyne and 3 ml of acetone were added to 0.037 g (0.1 mmol) of $RhCl(PMe_3)_3$ at $-30$ to $-40\,^\circ C$. The resulting orange solution was then heated to room temperature and left to stand for 1 h. The pale yellow solution was evaporated in vacuo and the residue was dried at room temperature for 3 h. A mixture of complexes IX and X (IX/X = 3/2) was isolated in quantitative yield. The $^{31}P\{^1H\}$ NMR spectra data are listed in Table 2. $^1H$ NMR ($\delta$, ppm, toluene-$d_8$, $-35\,^\circ C$): 0.99 (m, 6H, $CH_3$); 1.26 (m, 27H, $PMe_3$); 1.38 m; 1.48 m; 1.85 m; 2.27 m; 2.78 m (all $CH_2$); 5.8–6.3 (m, =CH). IR spectrum of the mixture of IX and X in Nujol ($\nu$, $cm^{-1}$): 2128w, 1640w, 1282m, 945s, 860m, 725m, 675m, Found: C, 45.62; H, 8.53; Cl, 7.14. $C_{19}H_{43}ClP_3Rh$ calcd.: C, 45.38; H, 8.62; Cl. 7.05%.

*Decomposition of the complex IX and X.* A mixture of complexes IX and X (0.04 g; prepared as described above) in toluene solution in a ratio of 2/3 (3 ml) was heated for 30 min at 50 °C and analyzed by GC. Only enynes I and II (I/II = 63/37) were found in the reaction mixture once the reaction was complete.

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