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The role of $H_2Ru(CO)_2(PBu_3)_2$ in the activation of alkynes and alkenes☆

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Abstract

The reactivity of $H_2Ru(CO)_2(PBu_3)_2$ (**II**) with alkynes and an alkene has been investigated and compared with that of $Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**I**). Compound **II** is in fact formed from **I** under hydrogen pressure. The catalytic activity of both **I** and **II** in the hydrogenation of the same substrates has also been studied. A mechanism is suggested for this reaction based on the role of ruthenium hydridic intermediates which were identified in the reactivity studies.

Keywords: Catalytic activity; Hydrogenation; Ruthenium complexes; Activation of alkynes and alkenes

1. Introduction

Several tributylphosphine substituted Ru(I) or Ru(II) carbonylcarboxylates have been used to catalyse, in homogeneous phase, the hydrogenation of olefins [1–5] and other unsaturated substrates [4–10] both with hydrogen under pressure or by hydrogen transfer.

In order to collect information on the species catalytically active in these reactions we have investigated [11–13] the behaviour of these complexes under reaction conditions.

$Ru(CO)_2(MeCOO)_2(PBu_3)_2$ (**I**) is easily transformed, under hydrogen, into $H_2Ru(CO)_2(PBu_3)_2$ (**II**) according to an equilibrium reaction influenced by temperature, hydrogen pressure and acetic acid concentration. This equilibrium may be displaced towards the formation of **II** by neutralisation of acetic acid with solid Na_2CO_3 [11].

We report now the results of an investigation on the role of the hydride **II** in the hydrogenation of alkenes or alkynes. Similar investigations have already been performed with hydrides of ruthenium [14–23] and of other metals [16,24–35]. Among these, Mawby and coworkers have reported the reactivity of $H_2Ru(CO)_2(PMe_2Ph)_2$ with phenylethyne and 3,3-dimethylbutyne [20,21].

The detection of the intermediates, fairly easy in the case of the alkynes, is much more difficult with olefins because of the instability of the complexes involved.

2. Experimental

2.1. Instruments

Gas chromatographic analysis (GC) was performed with a Perkin-Elmer Sigma 1 system or a Perkin-Elmer 8320 instrument while gas chromatography mass spectroscopy (GC-MS) was carried out on a Carlo Erba QMD 1000 GC-MS data system or a Shimadzu GCMS-QP 2000. The packed columns used (2 m) were: PPG (polypropylene glycol LB550X (15%) on Chromosorb W), FFAP (' free fatty acids phase' (5%) on Chromosorb G AW-DMSC), OV1 (silicone (2.5%) on Chromosorb G AW-DMSC) while the capillary columns were Al_2O_3 PLOT (alumina on fused silica, 50 m, internal diameter 0.32 mm) AT™-1 (Alltech column, 30 m, internal diameter 0.25 mm) or SPB-1™ (a Supelco column, 30 m, internal diameter 0.25 mm).

Multinuclear NMR spectra were registered using a Varian VXR 300 spectrometer operating at 299.944 MHz for ^1H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P NMR spectra; tetramethylsilane was used as reference for ^1H and ^{13}C spectra. In ^{31}P NMR spectra downfield values from external H_3PO_4 (85%) were taken as positive. ^{13}C and ^{31}P NMR spectra were acquired

☆ This paper is dedicated to György Bor on the occasion of his 70th birthday.

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as proton decoupled spectra. IR spectra were recorded with an FT-IR Perkin-Elmer model 1760 spectrometer.

2.2. Materials

C_6H_6 was first refluxed on sodium metal, then distilled on $LiAlH_4$. Phenylethyne was distilled under nitrogen prior to use (b.p. 142 °C). 1-Deuterophenylethyne was prepared as reported by Beltrame et al. [36] (b.p. 142–143 °C).

All solvents and chemicals were reagent grade and generally used as received. All reactions and manipulations were performed under dry nitrogen by the Schlenk tube technique.

$[Ru(CO)_2(CH_3COO)_2(PBu_3)_2]$ (**I**) was prepared as described in the literature [37].

2.2.1. $[H_2Ru(CO)_2(PBu_3)_2]$ (II)

A solution of **II** (33 mM) in C_6D_6 (2 ml) was prepared by a slightly modified version of the procedure reported by Frediani et al. [11]. In a glass vial placed in a stainless-steel autoclave, under dry nitrogen, 45 mg of $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ (0.066 mmol), 600 mg of anhydrous Na_2CO_3 (5.661 mmol) and 2 ml of C_6D_6 were introduced. The autoclave was then sealed and hydrogen added up to 100 atm at 20 °C. The vessel was heated at 100 °C for 24 h. After cooling to room temperature, the gas was vented and a yellow solution recovered by filtration. The ^{31}P NMR spectrum, recorded on this solution, shows a singlet at 32.5 ppm. The IR spectrum (C_6D_6 solvent) showed, in the 2200–1800 cm^{-1} region, bands at 1990(vs) and 1949(vs) cm^{-1}. ^1H and ^{13}C NMR spectra agree with those previously reported [11].

2.3. Reactivity of $H_2Ru(CO)_2(PBu_3)_2$ with unsaturated organic substrates

Experiments with stoichiometric amounts of organic substrates were carried out in an NMR tube (diameter 5 or 10 mm) having a screw cap with a rubber septum. A nitrogen atmosphere was created in the tube then a solution of $H_2Ru(CO)_2(PBu_3)_2$ (**II**) of known concentration was introduced. The composition of the solution was controlled by ^1H and ^{31}P NMR spectroscopy. Organic substrates were added in a 1:1 molar ratio using a GC syringe and the evolution of the reaction was followed by ^{31}P NMR spectroscopy. When the conversion was appropriate IR, ^1H and ^{13}C NMR spectra were recorded together with GC and GC-MS analysis in order to identify and characterise the metallorganic complexes and the organic compounds present in solution. Some compounds were isolated by TLC.

2.3.1. $H_2Ru(CO)_2(PBu_3)_2$ and $PhC{\equiv}CH$

Phenylethyne (7.25 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (alkyne/Ru complex = 1/1 molar ratio) and the mixture monitored at room temperature.

A singlet at 23.8 ppm in the ^{31}P NMR spectrum, indicative of the alkynyl complex $HRu(CO)_2(C{\equiv}CPh)(PBu_3)_2$ (**III**), appeared soon. The conversion was 56% after 24 h. This complex was characterised by IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy (Tables 1–4) when the conversion was higher than 80% (after 48 h).

The IR, ^1H and ^{13}C NMR spectra also showed the signals due to the presence of styrene. A resonance, at 4.50 ppm in the ^1H NMR spectrum, may be attributed to free dihydrogen in solution. Ethylbenzene (4.0%), styrene (96.0%) and PBu_3 were present in solution, as shown by the GC analysis performed using an FFAP column at 80 °C for 40 min, then heated up to 200 °C at a rate of 10 °C/min, and kept at this temperature for 30 min. The identity of these products was determined by GC-MS analysis using an AT™-1 column at 40 °C for 10 min, then heated up to 220 °C at a rate of 15 °C/min then kept at this temperature for 5 min. MS ethylbenzene: $[M]^+ = 106(30)$, $[M-CH_2]^+ = 92(5)$, $[M-CH_3]^+ = 91(100)$, $[C_6H_6]^+ = 78(5)$, $[C_6H_5]^+ = 77(5)$, $[C_5H_5]^+ = 65(5)$, $[C_4H_3]^+ = 51(10)$; MS styrene: $[M]^+ = 104(100)$, $[M-CH_4]^+ = 88(20)$, $[M-C_2H_3]^+ = 77(15)$, $[C_4H_3]^+ = 51(15)$; MS PBu_3: $[M]^+ = 202(15)$, $[M-C_2H_5]^+ = 173(30)$, $[PHBu_2]^+ = 146(17)$; $[PH(Bu)(C_3H_6)]^+ = 131(18)$, $[PH(Bu)(C_2H_5)]^+ = 118(35)$, $[PH(Bu)(Me)]^+ = 104(40)$, $[PH(Bu)]^+ = 89(8)$, $[PH_2(Pr)]^+ = 76(100)$, $[PH_2(Et)]^+ = 62(60)$, $[PH(Et)]^+ = 61(20)$, $[C_4H_9]^+ = 57(10)$, $[C_4H_7]^+ = 55(15)$, $[C_3H_5]^+ = 41(20)$.

When the conversion of **II** into **III** was 91% more phenylethyne was added to reach a molar ratio of 10:1 with respect to the starting complex. A complete conversion of the dihydride into **III** at room temperature is then reached.

GC analysis performed on this solution after 7 days at room temperature on an OV1 column at 35 °C for 20 min, then heated to 280 °C at a rate of 10 °C/min and kept at this temperature for 15 min shows the

Table 1
IR spectral data of the new complexes: frequencies of the stretching bands in the 2200–1500 cm^{-1} region [a]

Compound	ν(C≡C)	ν(CO)	ν(COOEt)
III	2100(w)	2015(vs), 1960(vs)	
IV	2098(vw)	2015(vs), 1963(vs)	1680(s)
VI	2118(vw)	2009(vs), 1951(vs)	
VII	2041(vw)	2006(vs), 1955(vs)	
VIII		1992(w), 1953(vs), 1891(vs)	

[a] Frequencies in cm^{-1}; solvent C_6D_6; vs: very strong, s: strong, w: weak, vw: very weak.

Table 2
^{1}H NMR data of the new complexes [a]

Compound	*H*Ru	R–C≡C–	P(CH$_2$)$_3$*Me*	P(CH$_2$)$_2$*CH$_2$*	PCH$_2$*CH$_2$*	P*CH$_2$*
III	−6.54 (t) *J*(HP) = 21.7	7.20 (m, 3H, *Ph*C≡C−) 7.60 (m, 2H, *Ph*C≡C−)	0.91 (t) *J*(HH) = 7.3	1.35 (pq) *J*(HH) = 7.3	1.62 (m)	1.89 (m)
IV	−6.70 (t) *J*(HP) = 21.0	1.02 (t, 3H, OCH$_2$*Me*, *J*(HH) = 7.2) 4.00 (q, 2H, OC*H$_2$*Me, *J*(HH) = 7.2)	0.91 (t) *J*(HH) = 7.2	1.36 (pq) *J*(HH) = 7.2	1.57 (m)	1.82 (m)
V	−6.20 (t) *J*(HP) = 21.7	1.20 (t, 3H, OCH$_2$*Me*, *J*(HH) = 7.1) 4.20 (q, 2H, OC*H$_2$*Me, *J*(HH) = 7.1) 5.70 (m, 1H, C*H*H=C) 6.50 (m, 1H, CH*H*=C)	n.d.	n.d.	n.d.	n.d.
VI	−6.62 (t) *J*(HP) = 22.1	0.92 (m, 3H, C≡C(CH$_2$)$_3$*Me*) 1.80 (m, 4H, C≡CCH$_2$(*CH$_2$*)$_2$) 2.50 (m, 2H, C≡C*CH$_2$*)	0.94 (t) *J*(HH) = 7.2	1.39 (pq) *J*(HH) = 7.2	1.65 (m)	1.74 (m)
VII	−6.71 (t) *J*(HP) = 21.7	0.35 (s, 9H, *Me*$_3$Si)	0.94 (t) *J*(HH) = 7.2	1.41 (pq) *J*(HH) = 7.2	1.84 (m)	1.96 (m)
VIII		7.10 (m, 1H, H^p, C≡C*Ph*) 7.35 (m, 2H, H^m, C≡C*Ph*) 8.20 (m, 2H, H^o, C≡C*Ph*)	0.75 (m)	1.07 (m)	1.42 (m)	1.42 (m)

[a] Chemical shift in ppm and coupling constants in Hz; solvent C_6D_6; s: singlet, t: triplet, m: multiplet, pq: pseudoquartet.

Table 3
^{13}C NMR data of the new complexes[a]

Compound	$RC{\equiv}C$	$RC{\equiv}C$	Ru(*C*O)	Ru(*C*O)	$RC{\equiv}C$	$P(CH_2)_3Me$	$P(CH_2)_2CH_2$	PCH_2CH_2	PCH_2
III	110.8 (s)	111.4 (t) J(CP) = 18.9	199.1 (t) J(CP) = 10.7	201.5 (t) J(CP) = 10.1	n.d.	14.1 (s)	24.9 (t) J(CP) = 6.6	26.5 (s)	29.1 (t) J(CP) = 14.2
IV	104.4 (s)	120.7 (t) J(CP) = 20.1	198.5 (t) J(CP) = 7.6	201.1 (t) J(CP) = 10.9	14.4 (s, OCH_2Me) 59.7 (s, OCH_2) 153.6 (s, *C*OO)	13.9 (s)	24.5 (t) J(CP) = 6.6	26.2 (s)	28.6 (t) J(CP) = 14.5
V	n.d.	n.d.	n.d.		14.7 (s, OCH_2Me) 59.2 (s, OCH_2) 152.7 (s, *C*OO)	n.d.	n.d.	n.d.	n.d.
VI	107.0 (s)	90.9 (t) J(CP) = 21.1	199.5 (t) J(CP) = 8.3	201.3 (t) J(CP) = 10.3	13.9 (s, $CH_2(CH_2)_2Me$) 22.2 (s, $(CH_2)_2CH_2Me$) 22.7 (s, CH_2CH_2Et) 33.7 (s, $CH_2(CH_2)_2Me$)	14.1 (s)	24.8 (t) J(CP) = 6.5	26.4 (s)	28.8 (t) J(CP) = 14.4
VII	114.5 (s)	135.1 (t) J(CP) = 20.2	199.1 (t) J(CP) = 8.3	201.4 (t) J(CP) = 10.5	1.8 (s, Me_3Si)	14.2 (s)	24.7 (t) J(CP) = 6.5	26.2 (s)	28.7 (t) J(CP) = 14.4
VIII		113.9 (t) J(CP) = 4.8	211.3 (t) J(CP) = 12.7		125.6 (s, PhC≡CPh) 131.6 (s, PhC≡CPh) 131.8 (s, PhC≡CPh) 136.6 (s, PhC≡CPh)	13.9 (s)	24.6 (s)	25.9 (s)	26.7 (s)

[a] Chemical shift in ppm and coupling constants in Hz; solvent C_6D_6; s: singlet, t: triplet.

Table 4
^{31}P NMR data of the new complexes [a]

Compound	δ (ppm)
III	23.8 (s)
IV	22.1 (s)
V	20.6 (s)
VI	25.5 (s)
VII	24.3 (s)
VIII	23.2 (s)
IX	24.4 (s)
X	26.1 (s)
XI	24.4 (s)

[a] Solvent C_6D_6; s: singlet.

presence of phenylethyne oligomers (dimers and trimers). These organic products were identified by GC-MS (using an AT™-1 column at 50 °C for 2 min then heated up to 280 °C at a rate of 15 °C/min and kept at this temperature for 8 min) as: 1,4-diphenylbutadiene (MS: $[M]^+ = 206(50)$, $[M-H]^+ = 205(25)$, $[M-Me]^+ = 191(17)$, $[M-PhCH_2]^+ = 115(55)$, $[C_7H_7]^+ = 91(100)$), 1,3-diphenylbutenyne (MS: $[M]^+ = 204(100)$, $[M-H]^+ = 203(85)$, $[M-H_2]^+ = 202(98)$, $[M-PhC_2]^+ = 101(32)$), (*Z*)-1,4-diphenylbut-3-en-1-yne (MS: $[M]^+ = 204(93)$, $[M-H]^+ = 203(90)$, $[M-H_2]^+ = 202(100)$, $[M-PhC_2]^+ = 101(62)$), (*E*)-1,4-diphenylbut-3-en-1-yne (MS: $[M]^+ = 204(97)$, $[M-H]^+ = 203(98)$, $[M-H_2]^+ = 202(100)$, $[M-PhC_2]^+ = 101(84)$), 1,2,4-triphenylbenzene (MS: $[M]^+ = 306(100)$) and 1,3,5-triphenylbenzene (MS: $[M]^+ = 306(100)$). The complete identification of these oligomers was performed, after their separation by TLC on an Al_2O_3 plate and n-pentane as eluent, by comparing their NMR spectra with those of authentic samples reported in the literature: (*Z*)-1,4-diphenylbut-3-en-1-yne ^1H NMR ($CDCl_3$): 6.01 (d, 1H, *J*(HH) 11.9 Hz, PhCH=C*H*), 6.77 (d, 1H, *J*(HH) 11.9 Hz, PhC*H*=CH), 7.36–7.62 (m, 8H, Ph), 7.96–8.06 (m, 2H, Ph) [38,39]; ^{13}C NMR ($CDCl_3$): 88.29 (PhC≡*C*), 95.90 (Ph*C*≡C), 123.4–128.9 (Ph), 131.5 (PhCH=*C*H), 136.6 (Ph), 138.71 (Ph*C*H=CH) ppm; (*E*)-1,4-diphenylbut-3-en-1-yne ^1H NMR ($CDCl_3$): 6.40 (d, 1H, *J*(HH) 16.9 Hz, PhCH=C*H*), 7.06 (d, 1H, *J*(HH) 16.9 Hz, PhC*H*=CH), 7.30–7.60 (m, 10H, Ph) [39]; 1,3,5-triphenylbenzene ^1H NMR ($CDCl_3$): 7.20–7.80 (m, 18H, Ph).

2.3.2. $H_2Ru(CO)_2(PBu_3)_2$ and $PhC{\equiv}CD$

Phenylethyne-1D (7.25 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (alkyne/Ru complex = 1/1 molar ratio) and the mixture monitored at room temperature.

The alkynyl complex $DRu(CO)_2(C{\equiv}CPh)(PBu_3)_2$ (**III**,D) showing, in the ^{31}P NMR spectrum, a singlet at 23.8 ppm, was formed with a conversion of 18% after 3.5 h. After 27.5 h the conversion was 58% by ^{31}P NMR and 34% by ^1H NMR spectroscopy. A resonance at 4.5 ppm, attributed to dihydrogen is present.

After 240 h, the conversion is 80% by ^{31}P NMR spectroscopy and 54% by integration of the ^1H NMR hydride resonances of **II** and **III**.

2.3.3. $H_2Ru(CO)_2(PBu_3)_2$ and $CH{\equiv}CCOOEt$

Ethyl propiolate (6.68 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (molar ratio alkyne/Ru complex = 1/1) and the evolution of the reaction at room temperature was followed by ^{31}P NMR spectroscopy.

A hydridoalkynyl complex $HRu(CO)_2(C{\equiv}CCOOEt)(PBu_3)_2$ (**IV**), showing a singlet at 22.1 ppm, and a hydridoalkenyl complex $HRu(CO)_2[C(COOEt){=}CH_2](PBu_3)_2$ (**V**), showing a singlet at 20.6 ppm, were formed (16% and 24%, respectively, after 6 h). The conversion of **II** reached 89% in 23 h at room temperature and 91% after 46 h; **IV** is the prevailing complex in solution. The conversion of **II** is the same after 16 days, while ethyl propiolate is completely transformed and the ratio **IV**/**V** is 3:1.

By comparing the evolution of the intensities of the significant signals in the IR, ^1H and ^{13}C NMR spectra obtained at various conversion degrees, a spectroscopic characterisation of **IV** and **V** in solution may be achieved (Tables 1–4).

Other signals present in the IR, ^1H and ^{13}C NMR spectra may be attributed to ethyl acrylate while a singlet at 4.50 ppm in the ^1H NMR spectrum may be due to dihydrogen dissolved in the solution.

The GC analysis on the solution made using an FFAP column at 35 °C for 10 min then heated to 200 °C at a rate of 10 °C/min and kept at this temperature for 20 min shows the presence of ethyl acrylate (8% of the starting alkyne) as the only hydrogenation product of the substrate present in solution. Products due to oligomerisation of the substrate are not present while traces of tri-n-butylphosphine are present. The GC-MS analysis on the reaction crude, performed using an SPB-1 column at 40 °C for 10 min then heated to 220 °C at a rate of 15 °C/min and kept at this temperature for 5 min confirms the presence of ethyl acrylate (MS: $[M]^+ = 100(5)$, $[M-H]^+ = 99(10)$, $[M-Me]^+ = 85(8)$, $[COOEt]^+ = 73(10)$, $[COOCH_2]^+ = 58(10)$, $[M-OEt]^+ = 55(100)$, $[M-EtOH]^+ = 54(8)$, $[OEt]^+ = 45(15)$, $[OC_2H_3]^+ = 43(10)$) and tri-n-butylphosphine in the organic phase.

2.3.4. $H_2Ru(CO)_2(PBu_3)_2$ and $BuC{\equiv}CH$

Hex-1-yne (7.58 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (molar ratio alkyne/Ru complex = 1/1). The evolution of the reaction at room temperature was then followed.

A new alkynyl ruthenium complex $HRu(CO)_2(C{\equiv}CBu)(PBu_3)_2$ (**VI**), showing a singlet at 25.5 ppm

in the ^{31}P NMR spectrum is formed. At room temperature the conversion reaches 19% after 9 h, 45% in 24 h, 62% after 60 h and 76% in 25 days. The new complex has been spectroscopically characterised through the IR, ^{1}H, ^{31}P and ^{13}C NMR spectra (Tables 1–4).

Other signals present in the IR, ^{1}H and ^{13}C NMR spectra may be attributed to hexenes (mixture of isomers) while a singlet at 4.50 ppm in the ^{1}H NMR spectrum may be due to dihydrogen dissolved in the solution.

After a 93% conversion of **II**, hexane (0.7% of the starting alkyne) and hexenes (4.1% of the starting alkyne, mixture of isomers) and unreacted hex-1-yne (2.2% of the starting alkyne) were identified though GC analysis on the reaction crude using a PPG column at 35 °C for 20 min then heated up to 120 °C at a rate of 5 °C/min and kept at this temperature for 30 min. No oligomerisation products seemed to be present but a trace of tri-n-butylphosphine was detected. The hexenes mixture was evaluated through GC analysis using a capillary Al_2O_3 PLOT column at 140 °C for 1 min then heated up to 160 °C at a rate of 1 °C/min and kept at this temperature for 1 min (86.2% hex-1-ene, 8.7% *trans*-hex-2-ene, 5.1% *cis*-hex-2-ene) GC-MS analysis performed with an SPB-1 column at 35 °C for 15 min then heated up to 200 °C at a rate of 10 °C/min and kept at this temperature for 15 min confirms the identification of the products. (MS hexane: $[M]^+ = 86(15)$, $[M-Me]^+ = 71(10)$, $[C_4H_9]^+ = 57(100)$, $[C_4H_6]^+ = 56(50)$, $[C_4H_5]^+ = 55(5)$, $[C_3H_7]^+ = 43(85)$, $[C_3H_6]^+ = 42(40)$, $[C_3H_5]^+ = 41(75)$, $[C_3H_3]^+ = 39(30)$; MS hex-1-ene: $[M]^+ = 84(30)$, $[M-Me]^+ = 69(25)$, $[M-C_2H_4]^+ = 56(80)$, $[M-C_2H_5]^+ = 55(60)$, $[C_3H_7]^+ = 43(60)$, $[C_3H_6]^+ = 42(70)$, $[C_3H_5]^+ = 41(100)$; MS (*Z*)-, (*E*)-hex-2-ene: $[M]^+ = 84(30)$, $[M-Me]^+ = 69(25)$, $[M-C_2H_4]^+ = 56(25)$, $[M-C_2H_5]^+ = 55(100)$, $[C_3H_7]^+ = 43(15)$, $[C_3H_6]^+ = 42(60)$, $[C_3H_5]^+ = 41(55)$, $[C_3H_2]^+ = 39(45)$).

2.3.5. $H_2Ru(CO)_2(PBu_3)_2$ and $Me_3SiC{\equiv}CH$

Trimethylsilylethyne (9.33 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (alkyne/Ru complex = 1/1 molar ratio) and the evolution of the reaction at room temperature was then followed by ^{31}P NMR spectroscopy. A new alkynyl ruthenium complex $HRu(CO)_2(Me_3SiC{\equiv}C)(PBu_3)_2$ (**VII**), showing a singlet at 24.3 ppm, is rapidly formed. The conversion was 22% after 9 h, 58% after 33 h and reached 70% in 73 h. The IR, ^{1}H, ^{31}P and ^{13}C NMR spectra were obtained from a light brown solution after 10 days at room temperature, in which the conversion had reached 94% (Tables 1–4).

GC analysis was performed using a PPG column at 35 °C for 20 min then heated up to 120 °C at a rate of 5 °C/min and kept at this temperature for 20 min or by an FFAP column at 38 °C for 20 min, then heated up to 200 °C at a rate of 10 °C/min and kept at this temperature for 20 min. With reference to the starting alkyne, trimethylsilylethene (2.2%) and unreacted trimethylsilylethyne (3.8%) were present in the solution. GC-MS analysis, performed using an SPB-1 column at 35 °C for 15 min then heated up to 200 °C at a rate of 10 °C/min and kept at this temperature for 15 min, confirms the presence of the products reported. MS trimethylsilylethene: $[M]^+ = 100(5)$, $[M-H_2]^+ = 98(2)$, $[M-Me]^+ = 85(100)$, $[CH{\equiv}CSiMe_2]^+ = 83(2)$, $[SiMe_3]^+ = 73(15)$, $[HSiMe_2]^+ = 59(90)$; MS trimethylsilylethyne: $[M]^+ = 98(30)$, $[CH{\equiv}CSiMe_2]^+ = 83(100)$, $[SiMe_3]^+ = 73(15)$.

2.3.6. $H_2Ru(CO)_2(PBu_3)_2$ and $PhC{\equiv}CPh$

Diphenylethyne (11.76 mg, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (alkyne/Ru complex = 1/1 molar ratio). A new ruthenium complex $Ru(CO)_2(PhC{\equiv}CPh)(PBu_3)_2$ (**VIII**), showing a singlet at 23.2 ppm, in the ^{31}P NMR spectrum, is formed. At room temperature the conversion reaches 17% after 20 h and 24% in 30 h. The new complex **VIII** was spectroscopically characterised when the conversion of **II** reached 90% (the concentration of **VIII** in solution was 73%) through IR, ^{1}H, ^{31}P and ^{13}C NMR spectra (Tables 1–4). An unidentified product **IX** having a singlet in the ^{31}P NMR spectrum at 24.4 ppm (17%) was also present.

Cis-stilbene (10.4%), *trans*-stilbene (16.4%), diphenylethyne (73.2%) and tri-n-butylphosphine present in the solution were identified by GC analysis using an FFAP column at 50 °C for 5 min then heated up to 200 °C at a rate of 10 °C/min and kept at this temperature for 30 min. GC-MS analysis performed on the solution using an SPB-1 column at 50 °C for 2 min then heated up to 280 °C at a rate of 15 °C/min and kept at this temperature for 30 min confirms the identity of the products reported. MS *cis*-stilbene: $[M]^+ = 180(100)$, $[M-H]^+ = 179(60)$, $[M-H_2]^+ = 178(30)$, $[M-Me]^+ = 165(30)$, $[PhC]^+ = 89(20)$, $[C_6H_4]^+ = 76(20)$; MS *trans*-stilbene: $[M]^+ = 180(100)$, $[M-H]^+ = 179(100)$, $[M-H_2]^+ = 178(70)$, $[M-Me]^+ = 165(45)$, $[PhC]^+ = 89(25)$, $[C_6H_4]^+ = 76(15)$; MS diphenylethyne: $[M]^+ = 178(100)$, $[M-H]^+ = 177(5)$ $[M-H_2]^+ = 176(10)$; MS tri-n-butylphosphine: see above.

2.3.7. $H_2Ru(CO)_2(PBu_3)_2$ and $PhCH{=}CH_2$

Styrene (7.56 μl, 0.066 mmol) was added to a solution of **II** in C_6D_6 (2 ml) (alkene/Ru complex = 1/1 molar ratio) and the evolution of the reaction at room temperature was followed by ^{31}P NMR spectroscopy. The reaction rate at room temperature is very low. An 11% conversion of **II** is reached in 48 h when heating at

40 °C and two products are formed having, respectively, a singlet at 26.1 ppm (**X**, 5% yield) and a singlet at 24.4 ppm (**XI**, 6% yield).

The conversion of **II** reaches 13% after 13 h at 60 °C. Further heating at this temperature (25 h) even if the molar ratio olefin/ruthenium complex reaches 10 does not change the conversion of **II** but only the relative amount of the complexes **X** and **XI**. One of these complexes disappears after heating at 80 °C for 6 h.

The ^{1}H NMR spectra collected show very low signals at 2.47 ppm (q, J(HH) = 7.9 Hz) and 1.08 ppm (t, J(HH) = 7.9 Hz) attributed to ethylbenzene.

The presence of ethylbenzene, styrene and PBu_3 is proved by GC analysis using an FFAP column at 80 °C for 40 min then heated up to 200 °C at a rate of 10 °C/min and kept at this temperature for 30 min. The identity of these compounds has been confirmed by GC-MS analysis using an AT™-1 column at 40 °C for 10 min, heated to 220 °C at a rate of 15 °C/min and kept at this temperature for 5 min (MS spectra: see above).

2.4. Catalytic hydrogenation experiments

In a stainless steel autoclave (150 ml), evacuated of air, the catalytic precursor (1.48 mM), benzene (10 ml), the substrate selected (0.148 M) and hydrogen (50 atm) were introduced. The autoclave was placed in a thermostatic oil bath set at the desired temperature (±1 °C) and rocked for the prefixed time. At the end, the reactor was cooled and the gases vented out and the solution analysed by GC. The identity of the products was confirmed by GC-MS analysis. The GC and GC-MS operating conditions were the same used for the reactivity tests. For the results of these experiments, see Tables 7 and 8.

3. Results

3.1. Procedures

The reactivity of **II** with terminal (RC≡CH, where R = Ph, COOEt, C_4H_9, Me_3Si) or internal alkynes (PhC≡CPh) and an olefin ($PhCH=CH_2$) has been investigated using either stoichiometric amounts of the reagents or, in some cases, an excess of the organic substrate.

Solutions of **II** in C_6D_6 or C_6H_6 were prepared by reacting, in a high pressure autoclave, a solution of **I** with hydrogen under pressure (100 atm), at 100 °C, in the presence of an excess of anhydrous Na_2CO_3. At the end of the reaction the solid residue was eliminated by filtration. The conversion of **I** into **II** is complete under these conditions. The purity of the complexes could be checked by ^{31}P NMR spectroscopy.

Stoichiometric reactions have been followed by spectroscopic determinations performed under reaction conditions; C_6D_6 as solvent was employed when the evolution of the system was followed by ^{1}H NMR spectroscopy. In order to detect labile intermediates the reactants, in stoichiometric amounts, were mixed at low temperature and the evolution of the Ru complexes was followed by ^{31}P NMR spectroscopy. When the concentration of the new species was high enough it was characterised by FT-IR, ^{1}H and ^{13}C NMR spectroscopy.

The reaction crude was examined by GC and GC-MS to detect changes in the composition of the organic phase.

Catalytic tests were also performed using the same complexes in order to connect their reactivity with their catalytic activity.

3.2. Reactivity of $H_2Ru(CO)_2(PBu_3)_2$

3.2.1. With PhC≡CH

(a) Stoichiometric reaction

Equimolecular amounts of **II** and phenylethyne, in hydrocarbon solution, react already at room temperature. After 5 h 22% of **II** is converted into a new product; conversion reaches 56% in 24 h and exceeds 80% after 48 h. The new complex is a hydride, as indicated by the ^{1}H NMR at −6.54 ppm. Styrene is also present in solution as well as gaseous hydrogen.

^{1}H, ^{31}P, ^{13}C NMR and IR determinations suggest for the new complex the $HRu(CO)_2(C{\equiv}CPh)(PBu_3)_2$ (**III**) formulation and an octahedral structure having two phosphine molecules in *trans* and two carbonyl groups in *cis* positions (Fig. 1(a)).

Nothing can be said about the Ru–H stretching bands due to the presence of the strong CO stretchings in the same region.

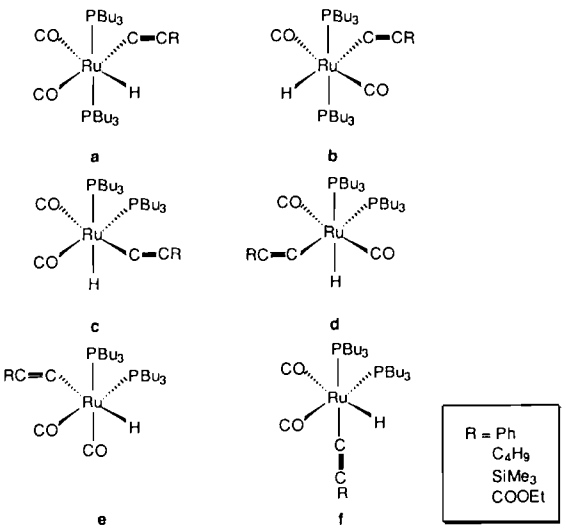


Fig. 1. Possible structures of $HRu(CO)_2(C{\equiv}CR)(PBu_3)_2$.

No indication could be obtained on the presence of an alkenyl complex. Phenylethyne is no more present in solution after 91% conversion of **II** while styrene, ethylbenzene (trace) and tri-n-butylphosphine may be detected. The starting alkyne is partially hydrogenated (9%) to styrene (96%) and ethylbenzene (4%).

(b) Excess of alkyne (1:10)

Complete conversion of **II** into the hydroacetylide **III** takes place at room temperature when using an excess of the alkyne (10:1). **III** is then the only ruthenium derivative present in solution.

Phenylethyne oligomers, mainly dimers and trimers, styrene, traces of ethylbenzene and of PBu_3, may be detected in solution besides the residual phenylethyne (Table 5). Phosphine is present in solution from the very beginning and its concentration remains approximately constant throughout.

(c) Deuterated substrate: PhC≡CD

New information has been obtained by reacting equimolecular amounts of PhC≡CD and **II**. The ^1H NMR spectrum registered at conversions below 20% shows the absence in **III** of the hydridic resonance and therefore suggest the formation of the rutheniumdeutero acetylide $DRu(CO)_2(C{\equiv}CPh)(PBu_3)_2$ (**III**, D). When the conversion exceeds 20% the hydridic absorption appears, but its intensity is lower than the one expected from the conversion of **II**.

Bray and Mawby [20] report the formation of $HRu(CO)_2(C{\equiv}CPh)(PMe_2Ph)_2$ in the reaction between $D_2Ru(CO)_2(PMe_2Ph)_2$ and phenylethyne.

3.2.2. With CH≡CCOOEt

Two new products **IV** and **V** are formed when reacting stoichiometric amounts of **II** and ethyl propiolate at room temperature. The rate of formation of the new complexes is reported in Table 6.

The ^1H, ^{31}P, ^{13}C NMR and IR data collected throughout the reaction suggest the $HRu(CO)_2(C{\equiv}CCOOEt)(PBu_3)_2$ formulation is assigned to **IV** having a structure analogous to that of **III** (Fig. 1(a)).

The formulation suggested for **V** is $HRu(CO)_2[C(COOEt){=}CH_2](PBu_3)_2$ with the two phosphine molecules in *trans* position and the two carbonyl groups in *cis* position according to the IR, ^1H and ^{31}P NMR data. The vinyl group in **V**, due to the addition of the hydride to the alkyne molecule, resonates at 6.50(m) and 5.70(m) ppm due to the geminal hydrogens of the olefin [17]. After two weeks at room temperature ethyl propiolate has disappeared, while **II** is still present (8%), and the **IV**/**V** ratio is 3/1. Ethyl acrylate (8% of the starting alkyne) may be detected in the reaction medium under these conditions but no oligomerisation products are found. Some free phosphine is also present.

Table 5
Phenylacetylene oligomerisation in the presence of $HRu(CO)_2(C{\equiv}CPh)(PBu_3)_2$

Product	Yield (%)
1,4-Diphenylbutadiene	1.8
1,3-Diphenylbutenyne	2.7
(*Z*)-1,4-Diphenylbutenyne	7.9
(*E*)-1,4-Diphenylbutenyne	17.1
1,2,4-Triphenylbenzene	3.5
1,3,5-Triphenylbenzene	3.3

Catalytic precursor, 33 mM; substrate, 330 mM; C_6D_6, 2 ml; *T*, 25 °C. Reaction performed in an NMR sample tube.

Table 6
Organometallic complexes formed in the reaction between **II** and ethyl propiolate

Reaction time (h)	Yield (%)	
	IV	**V**
6	16	24
13	25	35
23	43	46
69	46	45

II, 33 mM; ethyl propiolate, 33 mM; C_6D_6, 2 ml; *T*, 25 °C. Reaction performed in an NMR sample tube.

3.2.3. With BuC≡CH

II reacts readily with hex-1-yne giving a new complex. After 9 h 20% of **II** is converted and the new product may be identified, through its ^1H NMR spectrum, as a hydride with two equivalent phosphines. Dihydrogen is also formed (resonance at 4.50 ppm). The conversion of **II** reaches 45% after 24 h and 62% after 60 h. Hex-1-ene is present in the reaction solution. The ^1H, ^{13}C, and ^{31}P NMR spectra suggest, for the new complex, the $HRu(CO)_2(C{\equiv}CBu)(PBu_3)_2$ (**VI**) formulation and the same structure as **III** and **IV** (Fig. 1(a)).

When the conversion of **II** is 93%, the residual alkyne is 2.2%, hexane is 0.7%, isomeric hexenes are 4.1% (3.5% hex-1-ene, 0.4% *trans*-hex-2-ene, 0.2% *cis*-hex-2-ene) but no oligomers of hex-1-yne are present.

3.2.4. With $Me_3SiC{\equiv}CH$

II reacts with stoichiometric amounts of trimethylsilylethyne at room temperature giving a new product having a singlet in the ^{31}P NMR spectrum.

After 9 h the conversion of **II** reaches 22% and the new complex may be identified as a hydride. After 10 days 94% of **II** is converted. The IR, ^1H, ^{31}P and ^{13}C NMR spectra suggest for this complex the formulation of an Ru(II) hydrido acetylide $HRu(CO)_2(C{\equiv}CSiMe_3)(PBu_3)_2$ (**VII**) having the same structure as the acetylide complexes (Fig. 1(a)). There is no evidence for the presence of an alkenyl complex. After 73 h, the residual alkyne is 3.8% and the alkene is 2.2% of the starting alkyne.

3.2.5. With PhC≡CPh

II readily reacts with PhC≡CPh (1:1) at room temperature giving a new product **VIII**. The conversion reaches 7% in 6 h. The ^{1}H NMR spectrum provides evidence for the coordination of diphenylethyne to ruthenium. No hydridic complex seems to be present in solution, only gaseous hydrogen. The conversion of **II** reaches 24% after 30 h.

The NMR and IR data registered when the conversion of **II** has reached 90% (24 days, the amount of **VIII** is 73%) suggest for **VIII** the formulation $Ru(CO)_2(PhC{\equiv}CPh)(PBu_3)_2$. Another unidentified product **IX** having a singlet in the ^{31}P NMR spectrum is also present (17%). The composition of the residual organic substrate is *cis*-stilbene (10.4%), *trans*-stilbene (16.4%) and unreacted diphenylethyne (73.2%). PBu_3 is also present.

3.2.6. With PhCH=CH$_2$

Styrene reacts with **II** at room temperature giving two new products, **X** and **XI**. The reaction rate is low, providing 11% conversion in 48 h at 40 °C. New hydridic signals are not detected but only the resonances due to the presence of ethylbenzene.

A slight increase in the formation of the new products is noticed working at 60 °C. The reactivity of the hydride with this olefin appears very low.

At 80 °C, with styrene in excess, further decomposition of the complex is obtained while free phosphine is detected in the reaction crude.

3.3. Structure of complexes

3.3.1. HRu(CO)$_2$(C≡CR)(PBu$_3$)$_2$

Both IR and NMR evidence suggest for all ruthenium hydroacetylide complexes an octahedral structure with two phosphine molecules in *trans* position and two carbonyl groups in *cis* position (Fig. 1(a)).

This structure in fact is in keeping with the presence of only one singlet in the ^{31}P NMR spectrum due to two equivalent phosphine molecules and a triplet (J(HP) = 21.0–22.1 Hz) in the hydride region of the ^{1}H NMR spectrum attributed to a hydridic hydrogen coupled with two equivalent phosphorous atoms. The two triplets in the ^{13}C NMR spectrum, between 198.5 and 201.4 ppm, are indicative of the presence of two non-equivalent carbonyl groups, one *trans* to the hydrogen, the other *trans* to the acetylide substituent, coupled with two equivalent phosphine molecules.

The spectroscopic evidence excludes the other possible structures (Fig. 1(b)–(f)).

An analogous structure has been reported by Bray and Mawby [20] for $HRu(CO)_2(C{\equiv}CPh)(PMe_2Ph)_2$.

3.3.2. HRu(CO)$_2$[C(COOEt)=CH$_2$](PBu$_3$)$_2$

The structure we can suggest for this complex is an octahedral one with two carbonyl groups in *cis* position, two phosphine ligands in *trans* position and the CH_2=CCOOEt group *cis* to the hydridic hydrogen (Fig. 2). The structure suggested is in keeping with the presence of a singlet in the ^{31}P NMR spectrum due to two equivalent phosphine ligands, with a triplet in the ^{1}H NMR spectrum due to an hydridic hydrogen coupled with two equivalent phosphines in *cis* position (J(HP) = 21.7 Hz). The presence of the geminal vinyl hydrogens, giving the absorptions at 5.70 and 6.70 ppm in the ^{1}H NMR spectrum, confirms the above structure and excludes the presence of the alternative ligand (CH=CHCOOEt). Further evidence helping to establish a more detailed structure could not be obtained.

3.3.3. Ru(CO)$_2$(PhC≡CPh)(PBu$_3$)$_2$

The presence of a triplet at 113.9 ppm (J(CP) = 4.8 Hz) in the ^{13}C NMR spectrum may be due to the carbon atoms of the triple bond coordinated to the metal, symmetrically coupled with two equivalent phosphine ligands, while the triplet at 211.3 ppm (J(CP) = 12.7 Hz) may be attributed to the presence of the carbonyl groups coupled with the phosphine ligands. The equivalence of the two phosphines agrees with the presence of a singlet in the ^{31}P NMR spectrum of this complex.

All these data suggest for $Ru(CO)_2(PhC{\equiv}CPh)(PBu_3)_2$ an octahedral or a trigonal bipyramidal structure where the two phosphine molecules are in apical *trans* positions, the two carbonyl groups in *cis* position, while the molecule of diphenylethyne is placed in the free positions of the octahedra or in the equatorial plane of the trigonal bipyramid. The alkyne in the octahedral structure may provide a metallocycle complex, while in the second case there is a coordinative bond between the triple bond and the metal.

The recovery of the alkyne by thermal decomposition of the complex seems to support the proposed structure in which this molecule appears unaltered.

3.4. Catalytic hydrogenation of alkynes and alkenes

The formation of hydrogenation products of the alkynes and alkenes used when testing the reactivity of **I** and **II**, prompted us to investigate the catalytic activity of these complexes in the hydrogenation of the above substrates.

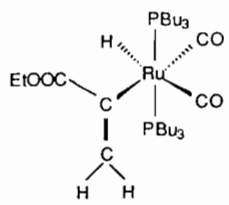


Fig. 2. Structure attributed to HRu(CO)$_2$[C(COOEt)=CH$_2$](PBu$_3$)$_2$.

Table 7
Hydrogenation of PhC≡CH catalysed by phosphine substituted ruthenium carbonyl complexes. Influence of temperature on the reaction products composition (%)

T (°C)	Products	Catalytic precursor	
		I	II
80	ethylbenzene	8.9	27.5
	styrene	15.1	36.8
60	ethylbenzene	0.9	12.8
	styrene	1.0	19.7
50	ethylbenzene	trace	9.1
	styrene	trace	11.1

Catalytic precursor, 1.48 mM; substrate, 0.148 M; benzene, 10 ml; $p(H_2)$, 50 atm at 20 °C; reaction time, 3 h.

The working conditions for these tests were chosen with the aim of stressing the differences, if present, in the activities of these two complexes. Isochronous tests were therefore performed under 50 atm of hydrogen at 80 °C (Table 7). Under these conditions there is only a limited transformation of **I** into **II**.

When **II** is used as catalytic precursor the conversion obtained is higher than when in the presence of **I**, both in the hydrogenation and, when possible, in the isomerisation of the substrate.

In order to see if the reaction took place in the presence of **I** a series of hydrogenation tests was then performed at progressively lower temperatures, so that the transformation of **I** into **II** would become difficult or would not take place at all. The results reported in Table 7 show that the activity of the system provided by **I** rapidly decreases and falls to zero at 50 °C. The hydride **II** evidently is a necessary precursor if not the catalytically active species itself.

At the end of the experiments carried out at 50 °C with phenylethyne and **I**, the diacetate ruthenium complex **I** is recovered unaltered. At 80 ° C **I** is still the prevailing ruthenium complex present in solution. When working in the presence of **II** consistent amounts of $HRu(CO)_2(C{\equiv}CR)(PBu_3)_2$ are found in the final solution.

In the solutions recovered from the hydrogenation tests on olefins and the internal alkyne, in the presence of **II**, the prevailing ruthenium derivatives detected are the unaltered hydride and small amounts of the complex containing the coordinated unsaturated ligand.

4. Discussion

4.1. Reactivity of I and II with alkenes and alkynes in stoichiometric amounts

The dihydride **II** when reacted with terminal alkynes gives rise to the formation of a ruthenium hydroacetylide, hydrogen and some olefin.

The main reaction is the one leading to the hydroacetylide with evolution of hydrogen. Four possible paths may be suggested for it (Scheme 1):

(i) an oxidative addition of the carbon–hydrogen bond of the ethyne to the metal atom followed by the reductive elimination of hydrogen;

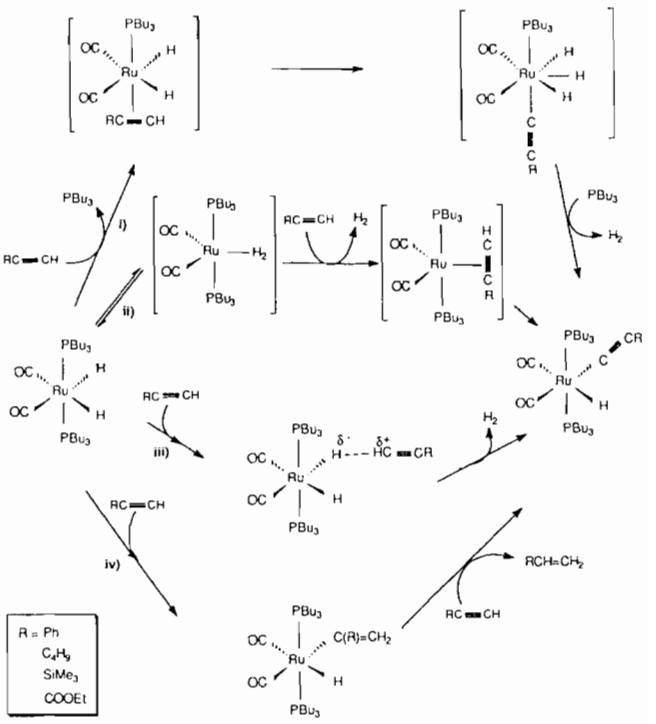
(ii) a reductive elimination of dihydrogen followed by an oxidative addition of the alkyne;

(iii) an acid–base reaction between the hydride and the alkyne with elimination of hydrogen;

(iv) insertion of an alkyne on an Ru–H bond to form an alkenyl complex followed by the formation of an alkene and a rutheniumalkynyl complex.

Path (i). One of the ligands, the phosphine, for instance, is temporarily removed from its site to allow the coordination of the alkyne. The oxidative addition of the carbon–hydrogen bond then takes place with formation of the hepta-coordinated intermediate of Ru(IV) (Scheme 1, path (i)). Ru(IV) metallo-organic intermediates have been previously reported [40,41]. Hepta- and even octa-coordinated Ru(IV) complexes have been suggested by Helliwell et al. [17] for a similar reaction between phenylethyne and a ruthenium monohydride. This path does not seem to contribute substantially to the formation of alkenylruthenium complexes because if it did the formation of **III**,D could not be explained.

Path (ii). The detection of only the deuteroacetylide ruthenium complex in the initial stages of the reaction between the dihydride **II** and 1-deuterophenylethyne



Scheme 1.

is clear proof of the elimination of the hydridic hydrogens from the complex without scrambling with deuterium from phenylethyne. In this case the coordination site necessary to allocate the ethyne ligand is made free by the reductive elimination of the hydridic hydrogens and not by the loss of the phosphine. The insertion of PhC≡CD on the intermediate containing dihydrogen as ligand then takes place through the loss of dihydrogen followed by the oxidative addition of the carbon–deuterium bond onto the metal. This hypothesis has been reported by Bray and Mawby [20]. At a higher conversion, in our case, scrambling between dihydrogen in solution and the deuteroacetylide becomes relevant and makes the interpretation of the results questionable.

Path (*iii*). An acid–base interaction between the hydridic hydrogen of **II** and the acid hydrogen of RC≡CH may give a dihydrogen complex having the alkyne as the counter-ion and, through a subsequent displacement of dihydrogen, the formation of the hydridoacetylide complex. A similar mechanism has been suggested to be operative in the reaction between the dihydride **II** and acetic acid [42] or in the reaction between phenylethyne and a ruthenium monohydride [23]. In the last case an alkynylruthenium dihydrogen complex has been isolated and characterised. The initial formation of **III**,D in our experiments however, rules out this hypothesis.

Path (*iv*). This path is relevant when reacting **II** with ethyl propiolate. In this case both the hydroacetylide **IV** and the hydroalkenyl complex **V** have been detected in solution, while dihydrogen is evolved and the corresponding olefin is formed. The rate of formation of ethyl acrylate increases when the build-up of the alkenyl complex in solution ceases. This also may be taken as an indication of the involvement of this complex in the formation of the olefin. This reaction path is operative also with the other alkynes and helps to rationalise their hydrogenation to the corresponding alkenes.

The insertion of the carbon–carbon triple bond on the ruthenium–hydrogen bond leads to the formation of the hydroalkenyl complex which, by the reaction with the free alkyne, gives rise to a molecule of olefin and a molecule of hydroacetylide.

The hydroacetylide therefore may be formed in two different ways: by the straight reaction between **II** and the alkyne, with formation of dihydrogen, or by the reaction of the alkyne with the hydroalkenyl derivative.

The hydroalkenyl intermediate, identified when reacting ethyl propiolate with **II** cannot be detected when using the other terminal alkynes. The formation of the olefin, however, must take place through such an intermediate in all cases. Probably with these last alkynes the concentration of this species must be too low to be detected.

The greater amount of the hydroacetylide formed compared with that of the olefin is a clear indication that the formation of the hydroacetylide proceeds mainly by the direct reaction between **II** and the terminal alkyne.

When reacting **II** with diphenylethyne a complex is formed containing a coordinate alkyne molecule, besides dihydrogen and small amounts of *cis*-and *trans*-stilbene. The hydrogenation of this substrate may take place through the addition of the ruthenium–hydrogen bond to the alkyne with formation of the hydroalkenyl derivative, followed then by olefin elimination and formation of $Ru(CO)_2(PhC{\equiv}CPh)(PBu_3)_2$ by reaction with a second molecule of alkyne.

A similar mechanism may rationalise the formation of ethylbenzene by reaction of **II** with styrene (Scheme 2). The number of moles of styrene and of the dihydride converted are the same. The spectral data obtained do not allow any suggestion on the structure of the intermediates involved. There is no evidence of the presence of hydridic hydrogens.

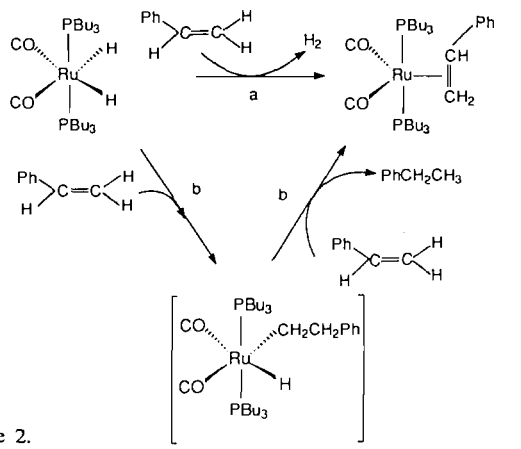
There are some indications of the presence of a penta-coordinated ruthenium complex containing an olefin bound to the metal.

4.2. Reactivity of II with an excess of alkynes

When reacting **II** with an excess of phenylethyne (1:10) oligomerisation of the organic substrate takes place with prevalent formation of alkenynes: (*Z*)-and (*E*)-1,4-diphenylbutenynes (Table 5). According to the literature report [17], the formation of these products may be due to the insertion of the alkyne on the ruthenium–carbon bond of the hydroacetylide, although the formation of a hydroalkenyl complex cannot be excluded.

4.3. Catalytic activity

The hydroalkenyl and hydroalkyl species seem to be the intermediates involved in the hydrogenation, respectively, of the triple and of the double bond when using these catalysts. Their reaction with molecular hydrogen sets the hydrogenation product free and restores the catalytically active hydridic species.



Scheme 2.

Table 8
Hydrogenation of organic unsaturated substrates catalysed by phosphine substituted ruthenium carbonyl complexes. Reaction product composition (%)

Substrate	Product	Catalytic precursor	
		I	II
PhC≡CH	ethylbenzene	8.9	27.5
	styrene	15.1	36.8
$EtO_2CC{\equiv}CH$	ethyl acrylate	0	10.8
BuC≡CH	hexane	19.1	45.4
	hex-1-ene	20.4	36.7
	trans-hex-2-ene	1.2	2.2
	cis-hex-2-ene	1.1	1.8
$Me_3SiC{\equiv}CH$	trimethylsilylethene	14.9	21.1
	trimethylsilylethane	32.6	53.9
PhC≡CPh	diphenylethane	2.1	32.9
	cis-stilbene	4.4	5.3
	trans-stilbene	6.2	61.3
$PhCH{=}CH_2$	ethylbenzene	23.2	33.6
$BuCH{=}CH_2$	hexane	20.2	58.3
	trans-hex-2-ene	18.5	32.3
	cis-hex-2-ene	9.3	7.5
cis-PhCH=CHPh	diphenylethane	0.9	8.5
	trans-stilbene	14.9	90.0
trans-PhCH=CHPh	diphenylethane	1.4	2.2
	cis-stilbene	0.4	0.6

Catalytic precursors, 1.48 mM; substrate, 0.148 M; benzene, 10 ml; $p(H_2)$, 50 atm at 20 °C; T, 80 °C; reaction time, 3 h.

The catalytic activity of **I** is much lower than that of **II** (Tables 7 and 8). Evidently **II** is the catalytically active species and the transformation of **I** into **II**, by reaction with hydrogen, is an equilibrium reaction, affected by the presence of acetic acid in solution.

The results of the hydrogenation of diphenylethyne are interesting. Only 32.9% of the triple bond is completely hydrogenated to paraffin, while the remaining substrate is almost all found as olefin: 92% of this olefin is in the *trans* form. From Table 8 we may see that *trans*-stilbene is neither isomerised nor hydrogenated in the presence of this catalytic system. *Cis*-stilbene is only slowly hydrogenated and mainly isomerised to the *trans* form. These data suggest that the hydrogenation of the alkyne to paraffin is mainly carried out without the formation of free alkene: the *trans*-alkene formed remains practically unreacted while the *cis*-alkene is mainly isomerised to the *trans* form.

Complex **II**, probably for steric reasons, reacts with greater difficulty with the *trans*- than with the *cis*-olefin.

5. Conclusions

The reactivity of $H_2Ru(CO)_2(PBu_3)_2$ with both alkynes and alkenes and its catalytic hydrogenation activity give a clear indication of its role in the mechanism of this last reaction. The activation of the organic substrate takes place by insertion of the C–C multiple bond onto the Ru–H bond. The evidence collected suggests a mechanism for the hydrogenation of these substrates.

Terminal alkynes are much more reactive than the internal ones and the olefins. When reacting a terminal alkyne, complexes containing coordinated double or triple bonds could not be detected but only the relatively stable ruthenium hydroacetylide.

Using ethyl propiolate the alkenyl complex, probable intermediate in the hydrogenation to ethyl acrylate, was detected. The formation of the olefin from an alkyne must in any case take place through a very reactive alkenyl intermediate.

The reactivity of the dihydride with an olefin is lower than that with an internal alkyne. For both reactions we may suggest the formation of an Ru(0) pentacoordinated complex in which the unsaturated substrate is coordinated to the metal atom by the double or triple bond, respectively. A hydroalkyl or hydroalkenyl intermediate is then formed which, by reaction with the residual substrate, releases the hydrogenation product with formation of the more stable Ru(0) species.

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