Hydrogenation of Pentynes Catalysed by Substituted Derivatives of $H_4Ru_4(CO)_{12}$ with Phosphorus-Donor Ligands

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The catalytic hydrogenation under mild conditions of 1-pentyne and 2-pentyne in the presence of phosphine and phosphite substituted derivatives of $H_4Ru_4(CO)_{12}$ has been investigated. The initial rates of hydrogenation of both 1- and 2-pentyne with the monosubstituted derivatives were found to follow the trend: $P(OPh)_3 \cong P(OEt)_3 < PPh_3 \cong P(n\text{-}Bu)_3$. The initial rates of hydrogenation of 2-pentyne decrease with increasing substitution of the catalyst, while the opposite trend is observed for 1-pentyne. The specificity of all the catalysts investigated, towards the formation of cis-2-pentene and 1-pentene from 2-pentyne and 1-pentyne respectively, is similar and is improved as compared with that observed in the presence of $H_4Ru_4(CO)_{12}$. The experimental results are interepreted on the basis of the stability of the alkyne carbonylmetal intermediates and of the influence which increasing substitution on $H_4Ru_4(CO)_{12}$ plays on the formation of active sites. The complexity of this multistep process, however, does not allow a comprehensive rationalisation of the experimental data.

Introduction

In a previous communication we have described the catalytic activity of toluene solutions of H_4Ru_4-$(CO)_{12}$ in the hydrogenation, under mild conditions, of 1-pentyne and 2-pentyne [1]. We report here the effect on the activity and the selectivity, which can result in this process from the substitution of carbonyl groups of $H_4Ru_4(CO)_{12}$ with phosphines and phosphites.

A wide interest has, in fact, upsurged in this field of research and the application of cluster compounds as homogeneous catalysts is the subject of a very fast growing number of recent papers [2–9].

Experimental

$H_4Ru_4(CO)_{11}P(OEt)_3$ (Ia), $H_4Ru_4(CO)_{11}P(OPh)_3$ (Ib), $H_4Ru_4(CO)_{11}PPh_3$ (Ic), $H_4Ru_4(CO)_{11}P(n\text{-}Bu)_3$ (Id), $H_4Ru_4(CO)_{10}[P(OEt)_3]_2$ (IIa), $H_4Ru_4(CO)_{10}$-$[PPh_3]_2$ (IIc), $H_4Ru_4(CO)_9 [P(OEt)_3]_3$ (IIIa), H_4-$Ru_4(CO)_9[PPh_3]_3$ (IIIc) and $H_4Ru_4(CO)_8[P(OEt)_3]_4$ were prepared according to the procedures described previously [7]. The toluene, C. Erba pure grade, was dried on molecular sieves, distilled and saturated with dry hydrogen before use. 1-pentyne, Fluka pure grade and 2-pentyne, Merck Schuchardt pure grade, were distilled prior to use.

The kinetic experiments were run in glass vials equipped with a gc septum. The vials were connected to a vacuum line, filled with dry hydrogen at atmos-

TABLE I. Initial Rates of Hydrogenation of 1- and 2-Pentyne (55 mM) in Toluene at 80.0 °C in the Presence of $H_4Ru_4(CO)_{11}$ L Clusters (L = $P(OEt)_3$, PPh_3, $P(OPh)_3$, $P(n\text{-}Bu)_3$).

Catalyst	Catalyst Concentration (mM)	Substrate	Initial Rate (mM h^{-1})	Initial Rate (mM h^{-1}) with CO (20 Torr)
(Ia) $H_4Ru_4(CO)_{11}P(OEt)_3$	0.39	2-pentyne	6.73	6.73
	0.39	1-pentyne	0.99	0.99
(Ib) $H_4Ru_4(CO)_{11}P(OPh)_3$	0.41	2-pentyne	5.85	5.80
	0.41	1-pentyne	0.81	0.80
(Ic) $H_4Ru_4(CO)_{11}PPh_3$	0.43	2-pentyne	8.74	5.51
	0.43	1-pentyne	1.76	1.88
(Id) $H_4Ru_4(CO)_{11}P(n\text{-}Bu)_3$	0.40	2-pentyne	9.33	3.45
	0.40	1-pentyne	1.76	1.70

TABLE II. Initial Rates of Hydrogenation of 1-Pentyne (55 mM) in Toluene at 80.0 °C in the Presence of H$_4$Ru$_4$(CO)$_{12-n}$L$_n$ Clusters (L = P(OEt)$_3$, PPh$_3$, P(OPh)$_3$, P(n-Bu)$_3$), with Hydrogen at Atmospheric Pressure.

| Catalyst		Catalyst Concentration (mM)	Initial Rate (mM h^{-1})	Initial Rate (mM h^{-1}) with CO (20 Torr)
(Ia)	H$_4$Ru$_4$(CO)$_{11}$P(OEt)$_3$	0.39	0.99	0.99
(Ic)	H$_4$Ru$_4$(CO)$_{11}$PPh$_3$	0.43	1.76	1.88
(IIa)	H$_4$Ru$_4$(CO)$_{10}$[P(OEt)$_3$]$_2$	0.41	1.58	1.53
(IIc)	H$_4$Ru$_4$(CO)$_{10}$[PPh$_3$]$_2$	0.39	1.88	1.22
(IIIa)	H$_4$Ru$_4$(CO)$_9$[P(OEt)$_3$]$_3$	0.39	2.97	1.57
(IIIc)	H$_4$Ru$_4$(CO)$_9$[PPh$_3$]$_3$	0.39	1.57	1.57

pheric pressure and sealed. The toluene solution of the catalyst was saturated with dry hydrogen and a measured volume was introduced into the vial with a high precision syringe. Substrate, ligand and carbon monoxide were similarly introduced into the vials. The reaction was carried out in a thermostatic bath at 80.0 °C. The composition of the solution at different reaction times was determined by gas chromatography at 55 °C on a 4 m column of 20% silicon oil 720 on Chromosorb P 60–80 mesh and at 25 °C on a 2 m column of 11% AgNO$_3$ and 21% phenylacetonitrile on Chromosorb P 60–80 mesh. The extent of pentyne hydrogenation was plotted as a function of reaction time and initial rates were evaluated from the tangent of the curve at t = 0. During these first initial steps the catalysts were not modified by the substrates as could be assessed by t.l.c. and i.r. spectra. On the contrary, after longer reaction times a modification of the catalysts could be observed.

Results and Discussion

The initial hydrogenation rates of 1-pentyne and 2-pentyne to pentenes, with hydrogen at atmospheric pressure, catalysed by toluene solutions of H$_4$Ru$_4$(CO)$_{11}$P(OEt)$_3$ (Ia), H$_4$Ru$_4$(CO)$_{11}$P(OPh)$_3$ (Ib), H$_4$Ru$_4$(CO)$_{11}$PPh$_3$ (Ic) and H$_4$Ru$_4$(CO)$_{11}$P(n-Bu)$_3$ (Id) are reported in Table I. The addition of the free ligand causes an initial inhibition which cannot, however, be ascribed to the dissociation of Ru–P bonds. A solution of H$_4$Ru$_4$(CO)$_{11}$P(OEt)$_3$ and free P(OPh)$_3$ (the molar ratio catalyst/free ligand is 2), in the presence of 1-pentyne or 2-pentyne under hydrogen, does not, in fact, give H$_4$Ru$_4$(CO)$_{11}$-P(OPh)$_3$, but only bisubstituted complexes. A similar behaviour has been reported in other processes catalysed by the same complexes [7–10] and with phosphinecobaltcarbonyl complexes [11]. For these systems it has therefore been suggested that the active sites are formed by Ru–CO ruptures and we assume

that also in the hydrogenation of pentynes this mechanism is operative. Nonetheless it can be seen in Table I that the initial rate with (Ia) and (Ib) is practically unchanged in the presence of CO and only a small decrease of the rate is observed when L is PPh$_3$ and P(n-But)$_3$. This behaviour, however, does not necessarily disagree with the hypothesis suggested above, provided that the formation of the free sites on H$_4$Ru$_4$(CO)$_{11}$L is not the rate determining step. In this case the partial pressure of CO would display, at most, a small influence on the overall rate only with (Ic) and (Id), where the Ru–CO bond strength should be higher. We cannot, however, rule out that the unaltered hydrogenation rates with increasing CO partial pressure are to be ascribed to the formation of active sites by cleavages of metal–metal bonds, as has been recently hypothesized for some processes involving metal cluster compounds [11–13].

The rate of hydrogenation of pentynes with H$_4$-Ru$_4$(CO)$_{11}$L depends to some extent on the nature of L and slightly increases in the sequence:

$$P(OPh)_3 \cong P(OEt)_3 < PPh_3 \cong P(n-Bu)_3$$
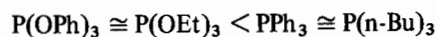
In agreement with the hypothesis reported above, this trend suggests that the rate determining step involves the formation of alkynecarbonylmetal intermediates, whose stability should increase with increasing basicity of L.

The catalytic activity of the H$_4$Ru$_4$(CO)$_{11}$L complexes is also affected by the nature of the substrate, 2-pentyne being hydrogenated with a significantly higher initial rate than 1-pentyne. In the hydrogenation of alkenes and alkynes catalysed by mono-metal complexes an opposite behaviour has been observed, because terminal unsaturated hydrocarbons are hydrogenated at higher rates than the internal isomers [15–16]. On the other hand, 1-alkenes have also been reported to show a very low hydrogenation rate, compared with the internal isomers and this behaviour has been ascribed to the formation of

TABLE III. Initial Rates of Hydrogenation of 2-Pentyne (55 mM) in Toluene at 80.0 °C in the Presence of $H_4Ru_4(CO)_{12-n}L_n$ Clusters (L = P(OEt)$_3$, PPh$_3$, P(OPh)$_3$, P(n-Bu)$_3$), with Hydrogen at Atmospheric Pressure.

Catalyst		Catalyst Concentration (mM)	Initial Rate (mM h^{-1})	Initial Rate (mM h^{-1}) with CO (20 Torr)
(Ia)	$H_4Ru_4(CO)_{11}P(OEt)_3$	0.39	6.73	6.73
(Ic)	$H_4Ru_4(CO)_{11}PPh_3$	0.43	8.74	5.51
(IIa)	$H_4Ru_4(CO)_{10}[P(OEt)_3]_2$	0.41	4.52	1.89
(IIc)	$H_4Ru_4(CO)_{10}[PPh_3]_2$	0.39	3.83	1.11
(IIIa)	$H_4Ru_4(CO)_9[P(OEt)_3]_3$	0.39	1.72	0.22
(IIIc)	$H_4Ru_4(CO)_9[PPh_3]$	0.39	2.23	0.22

stable organometallic complexes [17]. Therefore the lower activity of the $H_4Ru_4(CO)_{11}L$ complexes in the hydrogenation of 1-pentyne can be thought to be due to the higher stability of the alkynecarbonyl-metal intermediate. This can be correlated to the lower energy of the lowest unoccupied π^* orbital of 1-alkylacetylenes, compared with the internal isomers and to the higher stability observed in complexes prepared with 1-alkenes [18, 19].

In Tables II and III the hydrogenation initial rates of 1-pentyne and 2-pentyne with toluene solutions of (Ia), (IIa), (IIIa), (Ic), (IIc) and (IIIc) are reported. 1-pentyne is hydrogenated at an initial rate (Table II) which changes according to the sequence:

$$(Ia) < (IIa) < (IIIa), (Ic) < (IIc) < (IIIc),$$
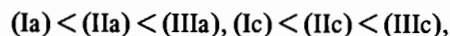
whereas the opposite sequence is observed with 2-pentyne (Table III):

$$(Ia) > (IIa) > (IIIa), (Ic) > (IIc) > (IIIc)$$
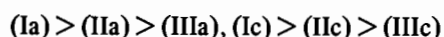
The hydrogenating activity of the complexes with a different number of substituted carbonyl groups is differently affected by the partial pressure of carbon monoxide. With the same catalyst, moreover, the influence of CO changes with the nature of the substrate. As shown in the Tables II and III the activity of (Ia) is unchanged and that of (Ic) is slightly decreased by the addition of CO with both the substrates. In the hydrogenation of 1-pentyne with (IIa), (IIc) and (IIIc) the initial rate is not significantly affected by the carbon monoxide and only with (IIIa) does an evident decrease take place. Conversely, the hydrogenation rate of 2-pentyne is slowed down, when the catalyst is a bisubstituted complex as (IIa) or (IIc) and a larger decrease is observed with (IIIa) and (IIIc).

The trend observed in the hydrogenation of 1-pentyne is similar to that shown by the same catalysts in the isomerisation of dimethylmaleate to dimethylfumarate [10, 20] and the behaviour displayed in the hydrogenation of 2-pentyne is strictly related to that observed in the isomerisation of linear pentenes [7].

The sequence of the hydrogenation initial rates of 2-pentyne with $H_4Ru_4(CO)_{12-n}L_n$ [n = 1,2,3, L = PPh$_3$, P(OEt)$_3$, P(OPh)$_3$] seems to be a consequence both of the strengthening of the Ru–CO bonds with increasing substitution on the metal cluster [21] and of steric effects. It is unlikely that the coordination of the substrate takes place on a substituted Ru(CO)$_2$L unit, because L increases the Ru–CO bond strengths mainly within the Ru(CO)$_2$L unit and also because the bulkiness of L creates a steric hindrance. This is particularly evident with $H_4Ru_4(CO)_8$-$[P(OEt)_3]_4$, which does not give any detectable amount of pentenes under experimental conditions similar to those used with the other complexes and hydrogenates about 2% of 2-pentyne only after several hours at 110 °C.

Oppositely, the dissociation of the Ru–CO bonds and the coordination of the alkyne to the free sites do not play a significant role in the hydrogenation of 1-pentyne, as shown by the results of Table II. On the other hand, we could not investigate separately the different steps of this multistep process and if a single step is not greatly prevailing over the others it is impossible to evaluate the relevance in the overall process of the stability of the alkynecarbonyl-metal intermediate or of the hydrogen addition to this intermediate. The attempts to obtain indirect information on the hydrogen addition to the coordinated alkyne were unsuccessful. The hydrogenation rate of 1- and 2-pentyne was, in fact, greatly reduced both in the presence of weak acids and bases.

The most interesting result of the application of these substituted derivatives of $H_4Ru_4(CO)_{12}$ in the hydrogenation of pentynes concerns the selectivity to the specific formation of one alkene, which is greatly increased by the substitution of carbonyl groups. Starting from 1-pentyne and 2-pentyne, 1-pentene and 2-*cis*-pentene respectively represent 60% of the total pentenes until 50% of the pentyne has been hydrogenated. The distribution of the
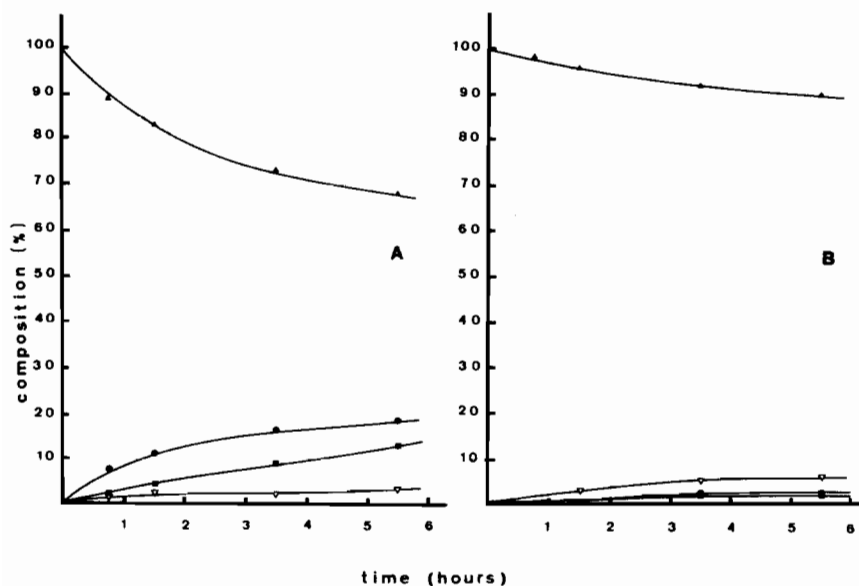
time (hours)

Fig. 1. Hydrogenation of: A) 2-pentyne and B) 1-pentyne catalysed by $H_4Ru_4(CO)_{11}P(OEt)_3$. ▲ pentyne, ● 2-*cis*-pentene, △ 1-pentene, ■ 2-*trans*-pentene.
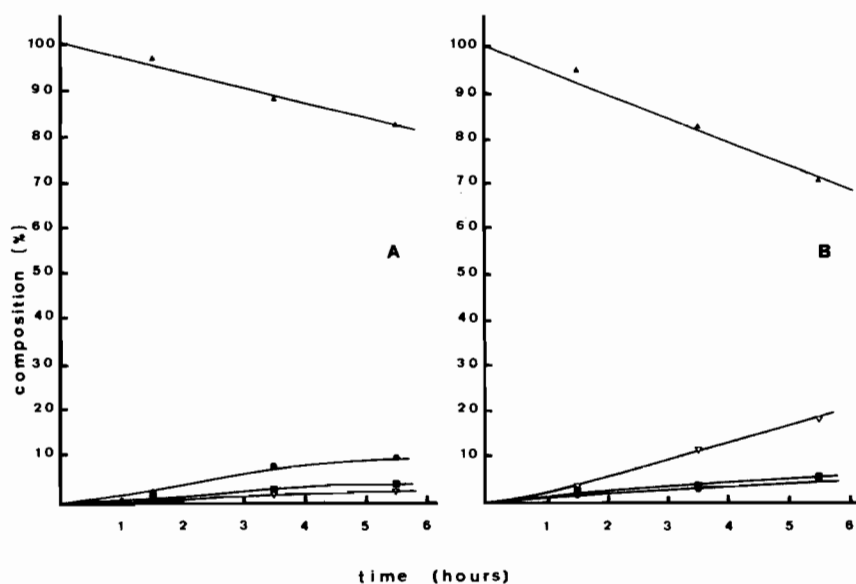

time (hours)

Fig. 2. Hydrogenation of: A) 2-pentyne and B) 1-pentyne catalysed by $H_4Ru_4(CO)_9[P(OEt)_3]_3$. ▲ pentyne, ● 2-*cis*-pentene, △ 1-pentene, ■ 2-*trans*-pentene.

products during the hydrogenation of 1- and 2-pentyne catalysed by (Ia) and (IIIa) is reported in Figs. 1 and 2. This selectivity can be ascribed to the competition for the catalyst between alkynes and alkenes and this is also supported by the observation that no hydrogenation of alkenes to pentane can be detected as long as some alkyne is present. This selectivity, however, seems to be almost independent of the nature of the ligand and of the number of substituted CO groups.

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