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Mononuclear ruthenium complexes containing two different phosphines in *trans* position: II. Catalytic hydrogenation of C=C and C=O bonds

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Abstract

Bis(acetate) ruthenium(II) complexes of the general formula $Ru(CO)_2(OAc)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (OAc = acetate, X = CH_3O, CH_3, H, F or Cl), containing different phosphine ligands *trans* to P^nBu_3, have been employed as catalyst precursors for the hydrogenation of 1-hexene, acetophenone, 2-butanone and benzylideneacetone. For comparative purposes, analogous reactions have been performed using the homodiphosphine precursors $Ru(CO)_2(OAc)_2(P^nBu_3)_2$ and $Ru(CO)_2(OAc)_2(PPh_3)_2$. The catalytic activity of the heterodiphosphine complexes depends on the basicity of the triarylphosphine *trans* to P^nBu_3 as this factor controls, inter alia, the rate of formation of hydride(acetate), $Ru(CO)_2(H)(OAc)(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$, or dihydride, $Ru(CO)_2(H)_2(P^nBu_3)[(p\text{-}XC_6H_4)_3]$, complexes, by hydrogenation of the bis(OAc) precursors. The catalytic hydrogenation of the C=C double bond is best accomplished by homodiphosphine dihydride catalysts, while heterodiphosphine monohydrides are more efficient catalysts than the homo- and heterodiphosphine dihydrides for the reduction of the keto C=O bond.

Keywords: Hydrogenation; Phosphines; *Trans* effect; Ruthenium; Ketones; Alkenes

1. Introduction

Some of us have recently reported the synthesis of mononuclear ruthenium complexes of the formula $Ru(CO)_2(Y)(Y')(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ containing a P^nBu_3 ligand in *trans* position to triarylphosphines differently substituted in the *para* position of the aromatic ring (X = CH_3O, CH_3, H, F or Cl), and where Y and Y′ may be equal (OAc or H) or different from each other (OAc or H) (Scheme 1) [1,2]. The triarylphosphine ligands are kinetically labile in all complexes, due to an effective *trans* effect [3] caused by the greater basicity of the *trans* P^nBu_3 ligand. In particular, the existence of a *trans effect* was proved for the reactions of **1a**–**e** with hydrogen in benzene [2] (Scheme 1). Indeed, the formation of the dihydride complexes $Ru(CO)_2(H)_2(P^nBu_3)[(p\text{-}XC_6H_4)_3]$ (**2a**–**e**) is faster [2] and occurs at lower temperature as compared to the known homodiphosphine complexes $Ru(CO)_2(OAc)_2(PPh_3)_2$ (**4**) and $Ru(CO)_2(OAc)_2(P^nBu_3)_2$ (**5**) [4].

The formation of the dihydride complexes **2a**–**e** upon hydrogenation of the bis(OAc) precursors is apparently preceded by that of the monohydride compounds $Ru(CO)_2(H)(OAc)(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ (**3a**–**e**), but bis(OAc), dihydrides and monohydrides are in equilibrium, unless acetic acid is removed by treatment of the solution with an appropriate base such as Na_2CO_3 [2].

Since the homodiphosphine complexes **4** and **5** share many reactivity aspects with **1a**–**e**, especially as regards the reactions with H_2 [4], and have also been employed with success as catalysts for the homogeneous hydrogenation of alkynes [5], alkenes [5] and ketones [6], we decided to study analogous reactions using **1a**–**e**. The presence of two *trans* phosphines with different basicity in the latter

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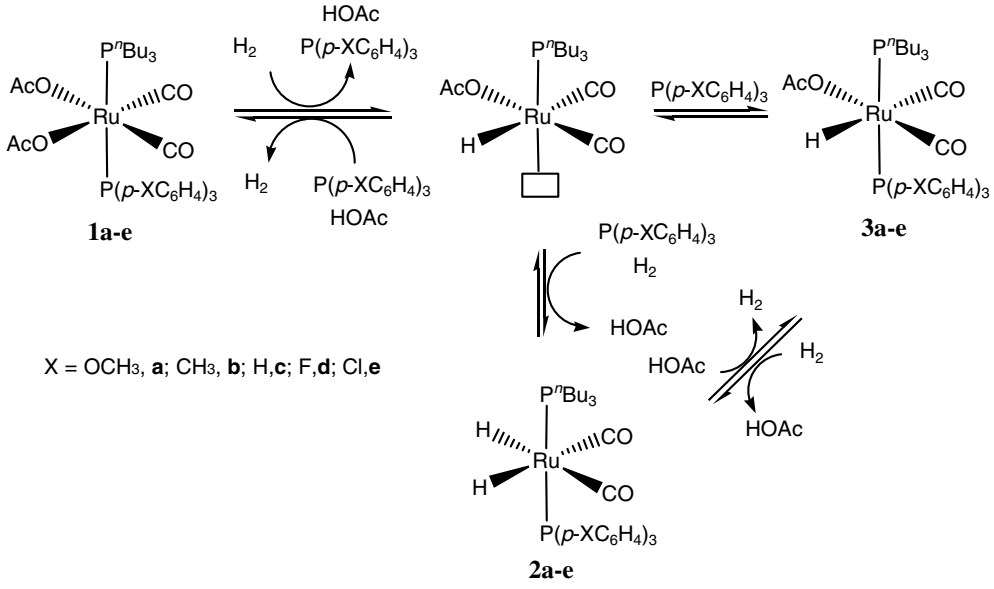


Scheme 1.

complexes and the possibility to vary the nucleophilicity of the P(p-XC_6H_4)$_3$ ligands [7], by changing the X substituent without affecting the steric properties (the cone angle does not vary within the triarylphosphines examined [8]), would create suitable conditions to evaluate the role of the *trans effect* in the catalytic reactions. This study would also provide information on the reaction mechanism, in particular as regards the occurrence of phosphine dissociation for substrate activation. This question is still a matter of debate for the hydrogenation of ketones or α,β-unsaturated ketones catalyzed by $Ru(CO)_2(H)_2(PPh_3)_2$ that has been reported to involve substrate-association by some authors [6] and phosphine-dissociation by other authors [9,10].

2. Results and discussion

2.1. Reactivity of $Ru(CO)_2(OAc)_2(P^nBu_3)[P(C_6H_5)_3]$ (1c)

A previous study has shown that the P(p-XC_6H_4)$_3$ ligands in **1a**–**1e** are kinetically labile in solution so that small amounts of the homodiphosphine complexes $Ru(CO)_2(OAc)_2[P(p\text{-}XC_6H_4)_3]_2$ and **5** are invariably formed upon heating solutions of the heterodiphosphine precursors [2]. In an attempt of evaluating the phosphine equilibration process under the catalytic conditions of the present hydrogenation reactions, **1c** was heated in benzene at different temperatures and H_2 pressures. The products obtained were analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

2.1.1. Thermal stability of 1c

After a C_6D_6 solution of **1c** was heated under nitrogen at 80 °C for 3 h, a $^{31}P\{^1H\}$ NMR spectrum was acquired, showing the presence of the homodiphosphine products **4** and **5** in trace amount (<2%). The formation of the latter compounds became important (45%) only after heating at 100 °C for 24 h.

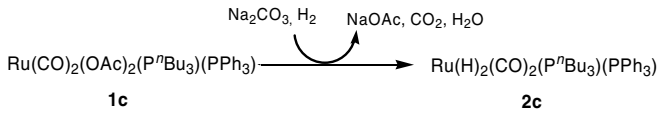
2.1.2. Reactivity of 1c with H_2

The reactions of **1c** with H_2 were carried out in C_6D_6 and the products obtained were identified by NMR spectroscopy (Table 1). In most reactions, anhydrous sodium carbonate was added to the reaction mixtures to neutralize the evolved acetic acid and ultimately make irreversible the formation of the dihydride **2c** (Scheme 2) [2]. The monohy-

Table 1
Product distribution with time and temperature upon hydrogenation of **1c** at 100 bar H_2

Entry	Reaction conditions		Products (%)[a]							
	T (°C)	Reaction time (h)	**1c**	**2c**	**3c**	**4**	**5**	**6**	**7**	**8**
1	20[b]	24	100	0	0	0	0	0	0	0
2	40[b]	16	0	84	0	1	6	7	2	0
3	60[b]	16	0	80	0	0	8	10	2	0
4	60[c]	24	0	60	18	0	11	9	0	2

[a] Calculated by ^{31}P NMR integration.
[b] In the presence of Na_2CO_3.
[c] Without Na_2CO_3.



Scheme 2.

dride $RuH(CO)_2(OAc)(P^nBu_3)(PPh_3)$ (**3c**) was intercepted only in the absence of Na_2CO_3.

At 20 °C, even with added Na_2CO_3, **1c** was fully stable for at least 24 h under 100 bar H_2 (entry 1). Only by heating to 40 °C, the complete conversion of **1c** was achieved to give **2c** in 84% yield together with the homodiphosphine acetates (7%) and the dihydrides $Ru(CO)_2(H)_2(PPh_3)_2$ (**6**) (7%) and $Ru(CO)_2(H)_2(P^nBu_3)_2$ (**7**) (2%) (entry 2). Increasing the temperature to 60 °C for 16 h did not improve appreciably the selectivity; a lower production of the dihydride **2c** was observed in fact, while all formed **4** was converted to the corresponding dihydride **6** (entry 3). These results are in agreement with the previously reported phosphine-redistribution reaction exhibited by **1c** to give **4** and **5**.

In the absence of Na_2CO_3 (entry 4), **2c** was still the major product (60%), but a significant amount (18%) of the monohydride **3c** was also formed together with **5** and **6** as well as an appreciable amount of the homodiphosphine monohydride $RuH(CO)_2(OAc)(PPh_3)_2$ (**8**). On leaving this reaction mixture at room temperature for 6 h under nitrogen, the amount of **3c** increased to 58% due to the reaction of **2c** with the free acetic acid present in solution.

2.2. Catalytic hydrogenation reactions

The catalytic performance of selected heterodiphosphine bis(acetate) complexes was investigated in the hydrogenation of 1-hexene, two ketones (acetophenone and butan-2-one) and the α,β-unsaturated ketone *trans*-4-phenyl-3-buten-2-one. No yield optimization was attempted, the study being exclusively centered on a comparison of the activity of the different catalyst precursors, in an attempt of relating catalytic activity and selectivity with the nature of the phosphine *trans* to P^nBu_3. The influence of some reaction parameters such as reaction time, temperature and H_2 pressure was evaluated for selected catalyst precursors. The substrate/catalyst ratio was fixed to 100:1, while the substrate conversion was determined by GC and GC–MS techniques.

All tests were performed twice in order to confirm the reproducibility of the experiments.

2.2.1. Hydrogenation of 1-hexene

The hydrogenation of 1-hexene catalyzed by either **1c** or **2c** was carried out in toluene at 50 bar H_2 for a reaction time of 3 h in the temperature range from 40 to 80 °C. The results obtained are reported in Table 2.

As a general trend, the conversion to *n*-hexane increased with the temperature and the dihydride **2c** proved invariably better than the bis(OAc) precursor **1c**, which is consistent with previous results obtained with the bis(P^nBu_3) couple **5/7** [5]. In order to observe a significant conversion to *n*-hexane, the temperature was increased to 80 °C (25.4% with **1c** and 40.8% with **2c**). At this temperature, however, extensive isomerization of 1-hexene occurred with a prevalence of *trans*- and *cis*-2-hexenes. Again, the dihydride catalyst was more efficient than the bis(OAc) precursor, yielding 55.8% of isomerized alkenes. It is noteworthy that the ratio between *n*-hexane and isomerized products increased with the temperature, consistent with a higher energy barrier to hydrogenation of internal double bonds as compared to the terminal one. An independent reaction at 80 °C in the presence of 1 equiv. of PPh_3 showed in either case a dramatic drop of the conversion (from 54.5% to 2.5% and from 96.6% to 33.2% for **1c** and **2c**, respectively). The same trend was observed for the isomerization reaction yielding *trans*-2-hexene.

A comparison of the catalytic activity of **1c** and **2c** versus that of the homodiphosphine complexes **4**, **5**, **6** and **7** under comparable experimental conditions is reported in Table 3.

Irrespective of the phosphine ligands, the catalytic activity of the dihydride complexes was higher than that of the corresponding bis(OAc) precursors. Among the latter, the bis(PPh_3) derivative **4** showed the highest conversion of 1-hexene, yet this was largely due to isomerized products,

Table 2
Hydrogenation of 1-hexene catalyzed by **1c** and **2c** at different temperatures

Catalyst	*T* (°C)	Conversion (%)	Reaction products composition (%)					
			n-Hexane	*trans*-3-Hexene	*trans*-2-Hexene	*cis*-3-Hexene	1-Hexene	*cis*-2-Hexene
1c	40	0.9	0.9	0	0	0	99.1	0
2c	40	12.2	4.7	0.9	2.4	1.1	87.8	3.1
1c	60	15.2	5.9	1.3	3.9	0.8	84.8	3.3
2c	60	59.0	8.1	2.5	28.2	0.9	41.0	19.3
1c	80	54.5	25.4	2.2	14.9	1.0	45.5	11.0
1c[a]	80	2.5	1.3	0	0.7	0	97.5	0.5
2c	80	96.6	40.8	11.2	29.0	2.3	3.4	13.3
2c[a]	80	33.2	25.6	1.0	3.0	0.8	66.8	2.8

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C; reaction time, 3 h.
[a] PPh_3 in excess: PPh_3/Ru molar ratio 2:1.

Table 3
Hydrogenation of 1-hexene catalyzed by selected hetero- and homodiphosphine complexes

Catalyst	Conversion (%)	Reaction products composition (%)					
		n-Hexane	*trans*-3-Hexene	*trans*-2-Hexene	*cis*-3-Hexene	1-Hexene	*cis*-2-Hexene
5	41.8	19.1	2.8	10.1	0.8	58.2	9.0
7	86.1	45.4	3.5	24.7	1.0	13.9	11.5
1c	54.5	25.4	2.2	14.9	1.0	45.5	11.0
2c	96.6	40.8	11.2	29.0	2.3	3.4	13.3
4	92.1	21.0	13.3	40.0	3.4	7.9	14.4
6	97.8	77.3	1.6	11.1	2.8	2.2	5.0

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C; reaction time, 3 h; *T*, 80 °C.

while **1c** was the most effective catalysts for the hydrogenation of the C=C double bond. It is worth noticing, however, that the experimental conditions of the reactions reported in Table 3 do not allow the complete transformation of the bis(OAc) complexes into the corresponding dihydrides (**2c**, **6** and **7**) (vide infra). Therefore, the highest activity of **1c** may be simply related to the faster formation of the dihydride **2c** according to the mechanism shown in Scheme 1. Consistent with this hypothesis, the use of the isolated dihydrides **2c**, **6** and **7** showed a reverse trend, the homodiphosphine catalysts being more active than **2c**, up to a 77.3% conversion into *n*-hexane obtained with **6**.

The influence of the X substituent in P(*p*-XC_6H_4)$_3$ on the hydrogenation of 1-hexene was evaluated using the bis(OAc) catalyst precursors **1a**–**1e** for a reaction lasting 6 h at 80 °C under 100 bar H_2 (Table 4). The catalytic activity of the heterodiphosphine complexes was compared to that of the homodiphosphine analogues **4** and **5**. The results obtained are reported in Table 4.

The reaction conditions chosen for these experiments guarantee the complete conversion of the bis(OAc) precusors into the corresponding dihydrides.

Irrespective of the catalyst precursor, a nearly complete conversion of 1-hexene was obtained, the only difference being the *n*-hexane/isomerized hexenes ratio. The highest yield in *n*-hexane (98.5%) was obtained with the bis(PPh_3) complex **4**, followed by **1c** with a 81.1% conversion. In the heterodiphosphine complexes series, the production of *n*-hexane increased in the order **1e** < **1d** < **1b** < **1a** < **1c**, which reflects, at least for the first four members, a direct correlation between the basicity of P(*p*-XC_6H_4)$_3$ and the ability of the corresponding catalysts to hydrogenate 1-hexene. Indeed, the lowest yield in *n*-hexane (53.7%) was obtained using **1e** that is the catalyst with the least basic P(*p*-XC_6H_4)$_3$ ligand [7]. On the other hand, the latter complex and its close member **1d** were the most efficient for the isomerization of 1-hexene to *trans*-2-hexene, which suggests a preferential anti-Markovnikov hydride migration for the catalyst precursors containing the least basic P(*p*-XC_6H_4)$_3$ ligand.

The results reported in Table 4 suggest a dual role for the P(*p*-XC_6H_4)$_3$ ligand in the hydrogenation of 1-hexene. Provided that phosphine unfastening, facilitated by less basic phosphines, is required for H_2 activation (Table 2), product removal (hydride-alkyl reductive elimination) would be best accomplished by more basic phosphines. Within this picture, the best performance of the catalyst **1c** might simply be due to the specific properties of PPh_3.

The influence of reaction parameters such as hydrogen pressure and reaction time, in the 1-hexene hydrogenation, was evaluated using **1a** as catalyst precursor (Table 5).

According to this study, the best experimental conditions for the conversion of 1-hexene to *n*-hexane catalyzed by **1a** are a H_2 pressure of 100 bar and a temperature of 80 °C. Interestingly, these are also the best conditions for the complete transformation of **1a** into the dihydride **2a**.

2.2.2. Hydrogenation of ketones

The hydrogenation of acetophenone was studied making use of the catalyst precursors **1c** and **2c**. For comparative purposes, reactions under identical experimental conditions were carried out with the homodiphosphines

Table 4
Hydrogenation of 1-hexene catalyzed by **1a-e** and **4**–**5**

Catalyst	Conversion (%)	Reaction products composition (%)					
		n-Hexane	*trans*-3-Hexene	*trans*-2-Hexene	*cis*-3-Hexene	1-Hexene	*cis*-2-Hexene
5	99.3	58.3	7.8	24.1	1.9	0.7	7.2
1a	99.6	78.4	4.5	12.5	1.0	0.4	3.2
1b	99.3	70.8	6.2	16.4	1.3	0.7	4.6
1c	99.5	81.1	4.8	10.5	0.3	0.5	2.8
1d	99.3	60.8	7.8	22.3	1.9	0.7	6.5
1e	99.0	53.7	6.4	28.3	2.1	1.0	8.5
4	99.9	98.5	0.3	0.9	0.0	0.1	0.2

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 100 bar at 20 °C; reaction time, 6 h; *T*, 80 °C.

Table 5
Hydrogenation of 1-hexene catalyzed by **1a**: influence of the hydrogen pressure and the reaction time

$p(H_2)$ (bar)	Reaction time (h)	Conversion (%)	Reaction products composition (%)					
			n-Hexane	*trans*-3-Hexene	*trans*-2-Hexene	*cis*-3-Hexene	1-Hexene	*cis*-2-Hexene
50	3	54.0	29.0	0.9	15.3	0.0	46.0	8.8
	6	98.8	41.7	10.6	33.3	2.9	1.2	10.3
	24	99.0	41.7	11.3	33.4	2.7	1.0	9.9
100	3	99.7	72.3	5.9	16.3	1.2	0.3	4.0
	6	99.6	78.4	4.5	12.5	1.0	0.4	3.2
	24	99.9	97.6	0.7	1.3	0.0	0.1	0.3

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; *T*, 80 °C.

bis(OAc)/dihydride couples **4/6** and **5/7**. Initially a reaction temperature of 80 °C was selected, just to have a reliable comparison with the hydrogenation reactions of 1-hexene catalyzed by the same complexes (vide infra). The results obtained are reported in Table 6.

From a perusal of Table 6, one may readily realize that **1c** is by far the best catalyst, yielding a conversion of 28.3% to 2-phenylethanol at 80 °C. As a general trend, the bis(OAc) precursors were more efficient catalysts than the dihydrides, which contrasts with the results of 1-hexene hydrogenation. It is therefore probable that the two reactions proceed via different active species and eventually different catalytic mechanisms. The higher conversion observed for **1c** as compared to **2c** is a clear indication that the active species along the hydrogenation of acetophenone is intermediate between the bis(acetate) and the dihydride. In view of the reactivity of **1c** and related homo- and heterodiphosphines acetates with H_2 [2,4a,4b] (see Scheme 1), the likely candidate is the monohydride **3c**. An active role of the latter species in the catalytic cycle is also suggested by catalytic reactions performed at lower temperature at which the dihydrides are barely formed [2]. Indeed, decreasing the temperature first to 60 °C, then to 40 °C, did not change the order of reactivity as **1c** was still more efficient than **2c**. Like for 1-hexene hydrogenation, the addition of an excess of PPh_3 to the reaction mixture catalyzed by **1c** caused a dramatic drop of the conversion from 28.3% to 2.7%. These results and the higher catalytic activity of **1c** respect to **4** and **5** suggest that also the reduction of ketones requires the decoordination of a phosphine ligand to start the catalytic cycle.

A screening of the catalytic properties of the various heterodiphosphine complexes studied in this work was performed for 2-butanone. The results obtained are reported in Table 7.

Besides confirming the results obtained for acetophenone (Table 6), the activity trend exhibited by **1a–e** for 2-butanone reduction showed that the catalytic activity increases with the basicity of the phosphine *trans* to P^nBu_3, which seemingly contrasts with $P(p\text{-}XC_6H_4)_3$ dissociation as a preliminary step to H_2 addition.

In an attempt of obtaining further information on the possible reaction mechanisms involved in ketone hydrogenation by the present heterodiphosphine complexes, a number of reactions were carried out with the catalyst precursor **1a**, varying systematically experimental parameters such as temperature, hydrogen pressure and reaction time.

Interestingly, decreasing the hydrogen pressure from 100 to 20 bar, at even temperature (80 °C) and time (3 h), increased the conversion to 2-phenyl ethanol from 24.3% to 33.4% (Fig. 1). This result is consistent with our assumption that the monohydrides rather than the dihydrides are the preferred catalysts for the reduction of ketones, although a catalytic role of the dihydrides cannot be ruled out (Table 6).

The influence of the temperature on the productivity was evaluated both at 20 and 50 bar H_2 (Fig. 2). From 60 to 80 °C, the conversion increased with the temperature,

Table 6
Hydrogenation of acetophenone by selected homo- and hetereodiphosphine complexes

Catalyst	Conversion (%)		
	40 °C	60 °C	80 °C
1c	7.5	18.1	28.3
1c[b]			2.7
2c	2.4	6.5	10.3
4			9.7
6			3.0[a]
5			16.8
7			2.1

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; reaction time, 3 h; $p(H_2)$, 50 bar at 20 °C.
[a] Taken from the literature [6].
[b] PPh_3 in excess: PPh_3/Ru molar ratio 2:1.

Table 7
Hydrogenation of 2-butanone by hetereodiphosphine complexes

Catalyst	Conversion (%)
1a	28.1
1b	27.5
1c	24.6
1d	24.5
1e	19.6
4	4.9
5	11.3

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; reaction time, 3 h; $p(H_2)$, 50 bar at 20 °C; *T*, 80 °C.

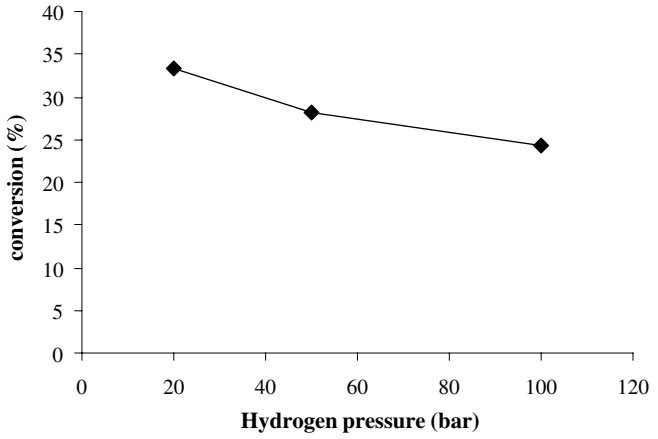


Fig. 1. Hydrogenation of 2-butanone with **1a**: dependence on the hydrogen pressure. *Conditions*: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; *T*, 80 °C; reaction time, 3 h.

whereas it decreased at 100 °C. Again, this finding is consistent with a higher concentration of the less active dihydride **2a** at 100 °C. The detrimental effect of a too large concentration of **2a** would oppose the positive effect of the higher temperature, in fact.

Finally, when the reaction time was increased from 3 to 6 h and then to 24 h for reactions carried out at 60 or 80 °C under 50 bar H_2, the productivity did not increase proportionally with time like if other less reactive ruthenium species would form (Table 8).

In the absence of kinetic measurements, it would be highly speculative to draw out any conclusion from these experiments, yet the results do not contrast the hypothesis that the concentration of the dihydride **2a** increases with time at the expense of the more active monohydride $RuH(CO)_2(OAc)(P^nBu_3)[P(p\text{-}CH_3OC_6H_4)_3]$ (**3a**).

Experiments in the temperature range from 60 to 100 °C with **1a** and isolated **2a** (Table 8) confirmed that the hydrogenation of 2-butanone is best accomplished by the bis(OAc) precursor, while the productivity trend suggested the hydroacetate **3a** as the catalytically active species (Scheme 1).

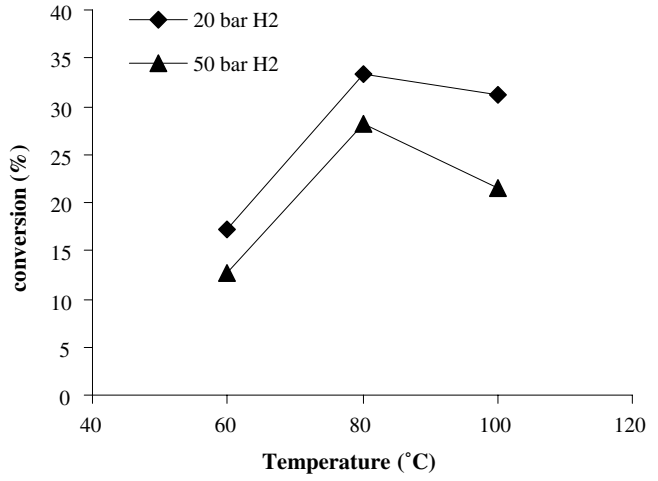


Fig. 2. Hydrogenation of 2-butanone with **1a**; dependence on the temperature. *Conditions*: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; reaction time, 3 h.

Table 8
Hydrogenation of 2-butanone catalyzed by **1a** or **2a**: influence of the temperature and reaction time

Catalyst	Time (h)	Conversion (%)		
		60 °C	80 °C	100 °C
1a	3	12.7	28.1	21.4
1a	6	23.0	38.3	
1a	24	36.0	46.2	
2a	3	5.7	6.3	13.0

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C.

The formation of **3a** in catalytic hydrogenation conditions as well as its disappearance with time and with increasing H_2 pressure was proved by $^{31}P\{^1H\}$ NMR spectroscopy. Two different reactions were performed using **1a** in C_6D_6. At the end of each reaction, Na_2CO_3 was added to neutralize the acetic acid formed. After 3 h at 80 °C with a H_2 pressure of 20 bar, the ruthenium complexes **1a**, **2a** and **3a** were produced in a 3:3:1 ratio. After 24 h at 80 °C with a H_2 pressure of 100 bar, only **2a** and **3a** were present in a 3:1 ratio.

The results obtained and the complicated chemistry of the present catalytic systems do not allow one to draw out any unambiguous conclusion on ketone hydrogenation. Having said this, the better performance of the heterodiphosphine catalysts **1a**–**e** as compared to the homodiphosphine catalysts **4**–**5** may be ascribed to the more facile decoordination of the *trans* triarylphosphine ligands. However, the basicity of the latter must be finely tuned to get the best performance: when the nucleophilicity of the $P(p\text{-}XC_6H_4)_3$ ligand is reduced too much as is the case of **1e** (Table 7), then the conversion of the more active monohydride complexes into the less active dihydrides is favored (Scheme 1) with a detrimental effect on the overall catalytic activity. On the other hand, the removal of the alcohol product from the metal center, which is an important catalysis step, may be favored by more nucleophilic phosphines.

2.2.3. Hydrogenation of trans-4-phenyl-3-buten-2-one (BZA)

Intrigued by the results obtained for the hydrogenation of C=C and C=O double bonds, we decided to investigate the reduction of a substrate containing both functional groups [11]. *trans*-4-Phenyl-3-buten-2-one (BZA) was selected as model substrate and its catalytic hydrogenation was attempted using **1c** and **2c** as heterodiphosphine precursors and **4**, **5**, **6** or **7** as homodiphosphine precursors. The results obtained are reported in Table 9.

The highest conversion (25.5%) and selectivity (91.3% of *trans*-4-phenylbut-3-en-2-ol (**D**)) were obtained with the heterodiphosphine bis(OAc) complex **1c**, while the corre-

Table 9
Hydrogenation of *trans*-4-phenyl-3-buten-2-one by hetero- and homodiphosphine complexes

Catalyst	Conversion (%)	Selectivity (%)			
		A	**B**	**C**	**D**
5	1.8	11.1	11.1	11.1	66.7
7	5.4	37.0	13.0	0.0	50.0
1c	25.5	6.7	1.6	0.4	91.3
2c	13.0	17.7	3.1	1.5	77.7
4	2.1	23.8	4.8	4.8	66.6
6	4.4	81.9	13.6	4.5	0.0

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C; reaction time, 3 h; *T*, 60 °C. **A**: 4-phenylbutan-2-one; **B**: *trans*-4-phenyl-3-buten-2-one; **C**: 4-phenylbutan-2-ol; and **D**: *trans*-4-phenyl-3-buten-2-ol.

sponding dihydride **2c** was less active yielding only 13.0% of hydrogenated products and also less selective (77.7% **D**). Almost negligible conversions of BZA were achieved with the homodiphosphine compounds **4**–**7**. However, the results obtained with latter catalysts deserve a comment as they can contribute to rationalize the different behavior of the homo- and heterodiphoshime complexes. Unlike the heterodiphosphine compounds, the homodiphosphine dihydride compounds **6** and **7** proved more active than the bis(OAc) derivatives. A net change in selectivity was observed with the bis(PPh_3) dihydride **6** that gave 81.9% of the saturated ketone 4-phenylbutan-2-one (**A**).

Overall, the results obtained for BZA confirm the data obtained for alkenes and ketones, with the heterodiphosphine precursors being more selective for C=O reduction and the homodiphosphine precursors, in particular compound **6**, being more selective for C=C reduction. The combined activity/selectivity data reported in Table 9 also confirm that the hydrogenation of the heterodiphosphine complex **1c** leads to the formation of two catalytically active species: the monohydride **3c**, suited for the reduction of C=O bonds, and the dihydride **2c**, suited for the reduction of the C=C bond.

The influence of temperature and reaction time on the hydrogenation of BZA was evaluated for **1c** and **2c**. Indeed, the highest chemoselectivity for the C=O reduction (94.4%) was obtained in the presence of **1c** after 24h at 40 °C with a conversion of 28.8% (Table 10).

Increasing the temperature of the reactions catalyzed by **1c**, the conversion to hydrogenated products increased, but also the selectivity in **D** decreased, as expected for higher concentrations of the dihydride **2c** in the reaction mixtures. Consistently, when isolated **2c** was used as catalyst, a low selectivity was observed in the temperature range from 40 to 80° C even after 24 h. Only at 100 °C, the system became quite active (100% conversion after 24 h) and fairly selective, yielding exclusively 61.8% of saturated alcohol **C** together with 38.2% of saturated ketone **A**.

The influence of the H_2 pressure was evaluated using **1c** in reactions lasting 3 h at 60 °C (Table 11). As expected, increasing the pressure to 100 bar the conversion increased

Table 10
Hydrogenation of *trans*-4-phenyl-3-buten-2-one catalyzed by **1c** or **2c**: influence of the temperature and of the reaction time

Catalyst	*T* (°C)	Time (h)	Conversion (%)	Selectivity (%)			
				A	**B**	**C**	**D**
1c	40	3	9.6	5.2	0.0	2.1	92.7
1c	40	24	28.8	4.2	1.0	0.4	94.4
1c	40	48	36.3	6.9	4.1	0.8	88.2
1c	60	3	25.5	6.7	1.6	0.4	91.3
1c	60	24	35.8	9.5	0.8	2.5	87.2
1c	60	48	37.0	9.2	0.8	1.1	88.9
1c	80	3	30.5	12.4	1.3	2.0	84.3
1c	80	24	50.1	12.4	0.6	3.0	84.0
1c	80	48	82.4	30.7	0.2	20.3	48.8
1c	100	3	62.0	41.3	0.5	11.6	46.6
1c	100	24	98.7	34.0	0.0	49.3	16.7
2c	40	3	4.3	16.3	9.3	2.3	72.1
2c	40	24	15.0	12.7	4.0	1.3	82.0
2c	60	3	13.0	17.7	3.1	1.5	77.7
2c	60	24	40.6	34.7	1.2	9.6	54.5
2c	80	3	21.2	30.7	0.5	7.5	61.3
2c	80	24	57.1	29.6	0.7	15.4	54.3
2c	100	3	37.9	57.3	1.3	8.2	33.2
2c	100	24	99.9	38.2	0.0	61.8	0.0

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C. **A**: 4-phenylbutan-2-one; **B**: *trans*-4-phenyl-3-buten-2-one; **C**: 4-phenylbutan-2-ol; and **D**: *trans*-4-phenyl-3-buten-2-ol.

to 28.2%, yet the best selectivity in **D** was obtained in the hydrogen pressure range from 5 to 50 bar, likely due to a smaller concentration of the dihydride **2c**.

Two catalytic reactions, with **1c** and **2c**, were carried out in the presence of a twofold excess of PPh_3 (PPh_3/Ru complex = 2:1). As shown in Table 12, a remarkable decrease in the productivity was observed with either catalyst in the presence of added PPh_3. It is worth noticing, however, that the added PPh_3 did not remarkably affect the selectivity of **1c**, whereas the selectivity in **D** decreased from 77.7% to 30.0% in the case of **2c**, with a concomitant increase in the production of the saturated ketone **A**. Again, these results are consistent with an initial and mandatory phosphine-dissociation for H_2 activation and with a different

Table 11
Hydrogenation of *trans*-4-phenyl-3-buten-2-one catalyzed by **1c**: influence of the hydrogen pressure

$p(H_2)$ (bar)	Conversion (%)	Selectivity (%)			
		A	**B**	**C**	**D**
5	17.4	5.7	2.3	0.0	92.0
20	21.4	6.5	2.8	1.4	89.3
50	25.5	6.7	1.6	0.4	91.3
100	28.2	12.4	1.4	1.8	84.4

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; reaction time, 3 h; *T*, 60 °C. **A**: 4-phenylbutan-2-one; **B**: *trans*-4-phenyl-3-buten-2-one; **C**: 4-phenylbutan-2-ol; and **D**: *trans*-4-phenyl-3-buten-2-ol.

Table 12
Hydrogenation of *trans*-4-phenyl-3-buten-2-one catalyzed by **1c** and **2c**: influence of the PPh_3 excess

Catalyst	Conversion (%)	Selectivity (%)			
		A	**B**	**C**	**D**
1c	25.5	6.7	1.6	0.4	91.3
1c[a]	3.5	5.8	2.8	2.8	88.6
2c	13.0	17.7	3.1	1.5	77.7
2c[a]	2.0	40.0	15.0	15.0	30.0

Conditions: Substrate, 1.50 mmol; catalyst, 15.0 μmol; toluene 4 ml; $p(H_2)$, 50 bar at 20 °C; reaction time, 3 h; *T*, 60 °C. **A**: 4-phenylbutan-2-one; **B**: *trans*-4-phenyl-3-buten-2-one; **C**: 4-phenylbutan-2-ol; and **D**: *trans*-4-phenyl-3-buten-2-ol.
[a] PPh_3/Ru molar ratio 2:1.

selectivity of the active species formed from **1c** or **2c** in these reaction conditions.

3. Conclusions

The ruthenium(II) heterodiphosphine complexes $Ru(CO)_2(OAc)_2(P^nBu_3)(PR_3)$ ($R = p\text{-}XC_6H_4$) and the homodiphosphine complexes $Ru(CO)_2(OAc)_2(PR_3)_2$ ($R = Ph$, ^{n}Bu) catalyze the hydrogenation of C=C and C=O groups, showing different activity (and chemoselectivity when both groups are present in the substrate). Irrespective of the $P(p\text{-}XC_6H_4)_3$ ligand, the hydrogenation of 1-hexene by the heterodiphosphine precursors is slow and incomplete even under very high H_2 pressure, likely due to effective isomerization to internal alkenes. For C=C hydrogenation, the homodiphosphine catalysts are definitely much more efficient. The reverse trend is observed for the hydrogenation of the C=O group from ketones or α,β-unsaturated ketones, the heterodiphosphine precursors being more active than the homodiphosphine ones. Notably, the hydrogenation of *trans*-4-phenyl-3-buten-2-one by the heterodiphosphine catalysts can occur with excellent selectivity in the corresponding allylic alcohol, *trans*-4-phenyl-3-buten-2-ol (>90%), which is surprisingly high for ruthenium complexes [11a,12].

The different activity and selectivity exhibited by the heterodiphosphine and homodiphosphine precursors is difficult to interpret as in either system the decoordination of a phosphine ligand is mandatory for any catalytic activity. However, it has been established that the catalytic hydrogenation of the C=C double bond is best accomplished by homodiphosphine dihydride catalysts, while heterodiphosphine monohydrides are more efficient catalysts than both homo- and heterodiphosphine dihydrides for the reduction of the keto C=O bond. The formation of mono- and dihydride species is faster for the heterodiphosphine complexes than for the homodiphosphine ones, which reflects the *trans* effect exerted by P^nBu_3.

Current studies in our laboratories are presently aimed at finding the proper conditions for the selective formation of either monohydride or dihydride intermediates as either species controls activity and substrate/product selectivity.

4. Experimental

4.1. Materials

All non-catalytic reactions and manipulations were performed under dry nitrogen in Schlenk tubes. C_6D_6 (99.8%), sodium carbonate (99.5%), 2-butanone and *trans*-4-phenylbut-3-en-2-one were reagent grade and used without further purification. Toluene was purified and stored using the method reported in the literature [13]. Acetic acid was distilled under nitrogen prior to use (b.p. 118 °C). 1-Hexene was purified by elution through a neutral Al_2O_3 (70-230 mesh) chromatographic column, then distilled and stored under nitrogen. Acetophenone was distilled prior to use (b.p. 82 °C/15 mm Hg).

The complexes **1a**–**1e** [2], **4** [14] and **5** [15] were synthesized according to the literature methods. The complexes **2a**–**2e** [2], **6** [4c] and **7** [5] were similarly prepared following known procedures, except for using toluene as solvent.

4.2. Instruments

^{1}H NMR spectra were recorded at 399.92 MHz on either a Varian Mercury 400 spectrometer or at 199.985 MHz on a Varian VXR 200 spectrometer, using the solvent residual peak as reference. $^{31}P\{^1H\}$ NMR spectra were registered at 121.421 MHz on a Varian VXR 300 instrument, using H_3PO_4 (85%) as external standard: downfield values were taken as positive. All $^{31}P\{^1H\}$ NMR spectra were acquired using a broad-band decoupler.

4.3. Catalytic reactions – general procedure

In a glass vial placed in a stainless-steel autoclave a toluene solution (4.0 ml) containing the catalyst (1.50×10^{-5} mol) and the substrate (1.50×10^{-3} mol) was introduced under dry nitrogen. The autoclave was sealed and pressurized with H_2 to the desired pressure. The reactor was heated at the desired temperature with stirring. At the end of each reaction, the autoclave was cooled to room temperature and the residual gas was vented off. The product composition was determined by GC using pure compounds as standards.

The following GC methods were employed:

1-Hexene: a Chrompack capillary column Al_2O_3/Na_2SO_4 PLOT (length: 50 m, diameter: 0.45 mm) was kept at 130 °C for 25 min, then heated up to 200 °C at a rate of 30 °C min^{-1}. Finally, it was maintained at this temperature for 50 min.

The other GC analyses were performed with packed columns (length: 2 m, diameter: 1/8″).

Acetophenone: a CW 20M column was kept at 60 °C for 10 min, then heated to 160 °C at a rate of 5 °C min^{-1}. Finally, it was maintained at this temperature for 30 min.

2-Butanone: a PPG column was heated at 50 °C.

trans-4-Phenylbut-3-en-2-one: a FFAP column ('free fatty acids phase' supported on Chromosorb G AW-

DMCS 5%) was kept at 50 °C for 2 min, then heated to 140 °C at a rate of 10 °C min^{-1}. Finally, it was maintained at this temperature for 40 min.

4.4. Thermal stability of *1c*

A C_6D_6 (0.75 ml) solution of **1c** (22.193 mg, 3.0×10^{-5} mol) was introduced into a NMR tube and heated at the desired temperature. The conversion of **1c** was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

4.5. Reactivity of *1c* with H_2

A C_6D_6 (0.75 ml) solution of **1c** (22.193 mg, 3.0×10^{-5} mol) was introduced under nitrogen into a glass contained in a stainless-steel autoclave (150 ml). In some reactions anhydrous sodium carbonate (150 mg, 1.45 mmol) was added. Then the autoclave was closed and pressurized with hydrogen (100 bar). The autoclave was placed in a thermostatic oil bath set at the desired temperature and rocked for the desired time. At the end, the reactor was cooled, the gases vented off and the solution, recovered under nitrogen, was filtered to eliminate any suspended solid, and analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

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