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Chemoselective hydrogenation of α,β-unsaturated ketones to allylic alcohols, catalyzed by a mononuclear ruthenium complex containing *trans* P^nBu_3 and PPh_3 ligands

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Abstract

The ruthenium(II) bis(acetate) complex $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$ (OAc = acetate) containing two different *trans* phosphine ligands, has been employed as pre-catalyst for the chemoselective hydrogenation of α,β-unsaturated ketones to allylic alcohols. Analogous catalytic reactions with the homodiphosphine pre-catalysts $Ru(CO)_2(OAc)_2(P^nBu_3)_2$ and $Ru(CO)_2(OAc)_2(PPh_3)_2$ gave lower conversions and selectivities. Batch catalytic reactions and *operando* high-pressure NMR experiments have contributed to establish that the hydrogenation of the C=O group is performed by the heterodiphosphine monohydride $RuH(CO)_2(OAc)(P^nBu_3)(PPh_3)$ generated *in situ* by hydrogenation of the bis(OAc) precursor. PPh_3 unfastening from this monohydride complex is an essential condition for the occurrence of catalytic activity.

Keywords: Selective hydrogenation; Allylic alcohols; Ruthenium; *trans* Effect; HP-NMR

1. Introduction

In a recent work, we have examined the catalytic activity of ruthenium(II) bis(acetate) complexes of the formula $Ru(CO)_2(OAc)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ in the hydrogenation of alkenes and ketones [1]. These complexes contain a P^nBu_3 ligand in *trans* position to triarylphosphines bearing different substituents in the *para* position of the aromatic ring (X = CH_3O, CH_3, H, F, Cl) [2]. Due to an effective *trans* effect [3] caused by the greater basicity of P^nBu_3 as compared to any other *trans* triarylphosphine investigated, the latter is kinetically labile with formation of a free coordination site suitable for H_2 activation and substrate coordination [1,2].

As shown in Scheme 1, the hydrogenation of $Ru(CO)_2(OAc)_2(P^nBu_3)[P(p\text{-}XC_6H_4)_3]$ in benzene gives either monohydride or dihydride species with rates of formation and relative concentrations that depend on the basicity of the triarylphosphine. Notably, acetates, mono- and dihydrides are in equilibrium with each other under hydrogenation conditions unless acetic acid is removed by treatment of the reaction mixture with an appropriate base such as Na_2CO_3 [4].

Determining what ruthenium(II) species is prevalently formed under catalytic conditions turned out to be of crucial importance for driving both substrate conversion and selectivity. Indeed, alkene hydrogenation was found to preferentially involve dihydride catalysts, whereas ketone hydrogenation was best accomplished by monohydride catalysts [1]. This structure-chemoselectivity relationship is

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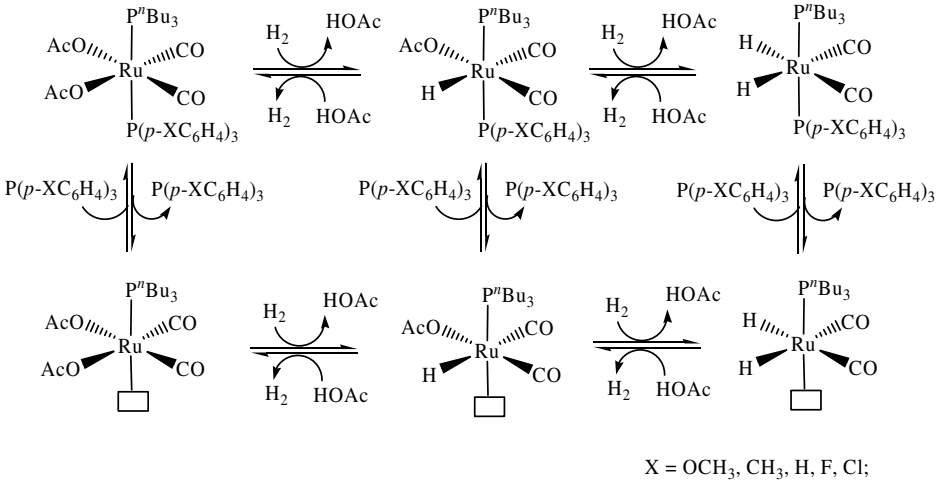
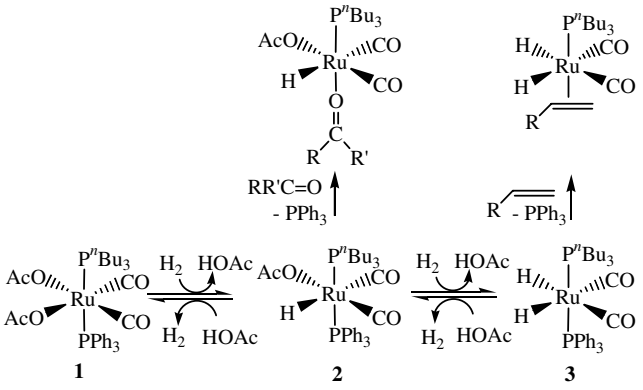


Scheme 1.



Scheme 2.

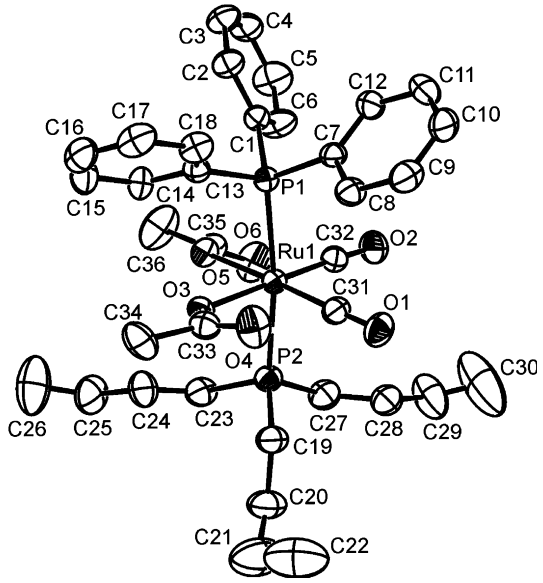


Fig. 1. ORTEP drawing of $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

shown in Scheme 2 for the complex $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$ (**1**), which was selected to carry out a preliminary study of the hydrogenation of an α,β-unsaturated ketone, namely *trans*-4-phenyl-3-buten-2-one (BZA) [1].

Under the experimental conditions employed to reduce alkenes and ketones, a rather low turn-over-frequency was observed (8.3 mol BZA converted (mol cat × h)$^{-1}$), but the selectivity in the corresponding allylic alcohol, *trans*-4-phenyl-3-buten-2-ol, was quite good (>91%). This finding was rather surprising as very few ruthenium complexes are known to catalyze the hydrogenation of α,β-unsaturated ketones with such a high chemoselectivity in allylic alcohol (>90%) [5]. Therefore, we decided to explore in a deeper way the ability of **1** to catalyze the hydrogenation of α,β-unsaturated ketones. The results of this study are reported in this paper, together with a crystallographic analysis of the catalyst precursor **1** as well as an *operando* high-pressure NMR investigation of selected catalytic reactions.

2. Results

2.1. Crystal structure determination of $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$

Suitable crystals of compound **1** were obtained by slow evaporation of a saturated *n*-hexane solution of the complex at room temperature. An ORTEP drawing of the molecular structure is presented in Fig. 1. Both, crystallographic data and selected geometrical parameters of compound **1** are given in Tables 1 and 2, respectively.

The ruthenium centre in **1** is octahedrally coordinated by two *cis* CO groups and two acetate ligands in the equatorial plane, while the apical positions of the octahedron are occupied by the phosphines. The deviation of the metal centre from the equatorial coordination plane, defined by the atoms O(3), O(5), C(31) and C(32) is of 0.0271(22) Å in direction of P(1). The difference of the Ru(1)–P bond lengths with the $Ru–PPh_3$ distance of 2.432(1) Å and the $Ru–P^nBu_3$

Table 1
Crystallographic data for **1**

Molecular formula	$C_{36}H_{48}O_6P_2Ru$
Formula weight (g mol^{-1})	739.75
Crystal colour, shape	White, prism
Crystal dimensions (mm)	$0.50 \times 0.50 \times 0.20$
T (K)	294(1)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.060(5)
b (Å)	29.674(5)
c (Å)	11.885(5)
α (°)	90.000
β (°)	98.145(5)
γ (°)	90.000
V (Å^3)	3861(2)
Z	4
$F(000)$	1544
ρ (calc.) (g cm^{-3})	1.273
λ(Mo Kα) (Å)	0.71072
μ (mm^{-1})	0.528
θ Range (°)	2.7–25.0
Index ranges	$-13 \leqslant h \leqslant 13$ $0 \leqslant k \leqslant 35$ $0 \leqslant l \leqslant 14$
Number of collected reflections	6752
Number of independent reflections	6752
Number of data/restrains/parameters	6752/3/411
Refinement method	Full-matrix least-squares on F^2
GOF on F^2	1.032
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0508, 0.1087
Final R_1, wR_2 indices (all data)	0.1181, 0.1291
Peak, hole in final difference map (e Å^{-3})	0.069, −0.483

Table 2
Selected geometrical parameters for **1**

Bond lengths (Å)		Bond angles (°)	
Ru(1)–P(1)	2.432(1)	P(1)–Ru(1)–P(2)	172.68(5)
Ru(1)–P(2)	2.381(1)	O(3)–Ru(1)–O(5)	81.76(13)
Ru(1)–O(3)	2.076(3)	C(31)–Ru(1)–C(32)	87.30(20)
Ru(1)–O(5)	2.103(3)	P(1)–Ru(1)–O(3)	89.00(9)
Ru(1)–C(31)	1.873(6)	P(1)–Ru(1)–O(5)	84.31(10)
Ru(1)–C(32)	1.852(6)	P(1)–Ru(1)–C(31)	96.18(16)
C(31)–O(1)	1.145(6)	P(1)–Ru(1)–C(32)	93.33(16)
C(32)–O(2)	1.151(6)	P(2)–Ru(1)–O(3)	84.82(9)
		P(2)–Ru(1)–O(5)	90.91(10)
		P(2)–Ru(1)–C(31)	88.29(16)
		P(2)–Ru(1)–C(32)	92.67(16)
		Ru(1)–C(31)–O(1)	172.20(50)
		Ru(1)–C(32)–O(2)	174.40(50)

distance of 2.381(1) Å, reflects the *trans* influence exerted by P^nBu_3. Notably, the Ru–P(PPh_3) distance found in **1** is significantly elongated compared to analogous complexes exhibiting a *trans* $Ru(PPh_3)_2$ moiety, which show Ru–P distances ranging between 2.411(1) and 2.425(1) Å [6].

2.2. Hydrogenation of α,β-unsaturated ketones catalyzed by *1*

The α,β-unsaturated ketones scrutinized in this work are shown in Scheme 3. The hydrogenation reactions were initially carried out in toluene at 60 °C under 25 bar H_2 with a substrate to pre-catalyst ratio of 100.

Conversions and chemoselectivities for reactions lasting 3 h are reported in Table 3. This preliminary screening showed cyclohex-2-en-1-one and 3-methyl cyclohexen-1-one as the substrates showing the highest chemoselectivity. Therefore, cyclohex-2-en-1-one, that is less sterically congested than the 3-methyl derivative, was taken as model substrate for an in-depth study of the catalytic ability of **1**.

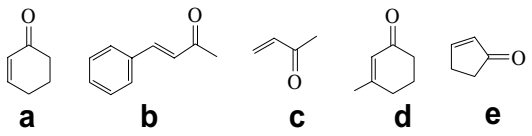
2.3. Operando high pressure NMR experiments

In an attempt of gaining information on the stability of the precursor **1** as well as intercepting organometallic species that might be involved in the hydrogenation of cyclohex-2-en-1-one catalyzed by this complex, an *operando* study was carried out by means of high-pressure (HP) NMR spectroscopy performed in a 10 mm-OD sapphire tube. A sequence of $^{31}P\{^1H\}$ NMR spectra acquired in C_6D_6 during a catalytic reaction is presented in Fig. 2.

The $^{31}P\{^1H\}$ NMR spectrum of the precursor (Fig. 2, trace a) showed the characteristic AB pattern of **1** [2a]. Substrate addition, followed by pressurization with 25 bar of H_2 did not change the spectrum (trace b). On heating this solution to 60 °C, several ruthenium hydride complexes were formed (trace c), among which we could identify, by comparison with authentic specimens, the monohydride $RuH(CO)_2(OAc)(P^nBu_3)(PPh_3)$ (**2**) [2b], the dihydride $RuH_2(CO)_2(P^nBu_3)(PPh_3)$ (**3**) [2b] and the homodiphosphine dihydrides $RuH_2(CO)_2(P^nBu_3)_2$ (**4**) [4a] and $RuH_2(CO)_2(PPh_3)_2$ (**5**) [4b] in a 3.0:22.0:1.0:7.0 ratio, respectively. A significant amount of the homodiphosphine complex $Ru(CO)_2(OAc)_2(P^nBu_3)_2$ (**6**) [4c] was also formed. A ^1H NMR spectrum acquired just after the last $^{31}P\{^1H\}$ NMR spectrum showed the formation of cyclohex-2-en-1-ol.

On heating the reaction mixture at 60 °C for 3 h, the $^{31}P\{^1H\}$ NMR pattern did not appreciably change (trace d). The signals of the hydride species were observed also upon cooling down the sapphire tube to room temperature (trace e). A ^1H NMR spectrum acquired under the conditions of the $^{31}P\{^1H\}$ NMR spectrum shown in trace d of Fig. 2 confirmed the formation of these hydride complexes (Fig. 3).

The NMR picture of the present catalytic system is consistent with the slow conversion of the precursor **1** into catalytically active species. Indeed, the most abundant species under catalytic conditions, even after 3 h at 60 °C (trace d), was still the precursor **1**. Notably, the organic product



Scheme 3.

Table 3
Hydrogenation of different α,β-unsaturated ketones catalyzed by **1**[a]

Substrate	Conversion (%)	Selectivity (%)		
		A	B	C
(a)	33.1	6.6	90.3	3.1
(a)[b]	60.5	5.2	85.1	9.7
(b)	19.9	12.0	87.7	0.3
(c)	34.8	32.9	60.6	6.5
(d)	8.4	6.3	91.0	2.7
(d)[b]	14.2	5.8	90.7	3.5
(e)	9.8	14.8	74.7	10.5

[a] Reaction conditions: **1**, 0.015 mmol; cyclohex-2-en-1-one, 1.50 mmol; solvent, toluene (4 ml); reaction time, 3 h; temperature, 60 °C; $p(H_2)$, 25 bar at 20 °C.
[b] Reaction time, 24 h. A, saturated ketone; B, unsaturated alcohol; C, saturated alcohol.

composition of the HP-NMR experiment was comparable to that obtained in batch conditions with catalyst **1** (Table 3).

The substitution of **1** with the monohydride **2**, generated by treatment of the dihydride **3** with 1 equiv. of HOAc (see Section 4) [1], in an HP-NMR experiment of cyclohex-2-en-1-one hydrogenation (60 °C, 25 bar H_2) showed the fast transformation of **2** into the corresponding dihydride (**3**) (Scheme 2) as well as a lower chemoselectivity in allylic alcohol (*vide infra*).

2.4. Influence of different reaction parameters on the hydrogenation of cyclohex-2-en-1-one catalyzed by *1*

Tables 4 and 5 report data relative to both conversion and chemoselectivity of cyclohex-2-en-1-one hydrogenation by **1** as a function of the H_2 pressure and of the reaction temperature, respectively. A reaction temperature of 60 °C and a hydrogen pressure ranging from 5 to 25 bar represented an optimum compromise between an excellent chemoselectivity and an acceptable conversion. In fact, more drastic reaction conditions, though increasing the conversion, resulted in a lower chemoselectivity. Based on a previous study on the hydrogenation of alkenes and ketones by **1** [1], the negative influence of higher H_2 pressures and temperatures can be rationalized in terms of an increased concentration of the dihydride complex $RuH_2(CO)_2(P^nBu_3)(PPh_3)$ (**3**), which is a selective catalyst for the hydrogenation of the C=C bond (Scheme 2) [1].

2.5. Hydrogenation of cyclohex-2-en-1-one by different ruthenium(II) pre-catalysts

As shown by the HP-NMR experiments, the plain hydrogenation of **1** gives **2** and **3** as major products together with the bis(OAc) complexes $Ru(CO)_2(OAc)_2(P^nBu_3)_2$ (**6**) and $Ru(CO)_2(OAc)_2(PPh_3)_2$ (**7**) and their

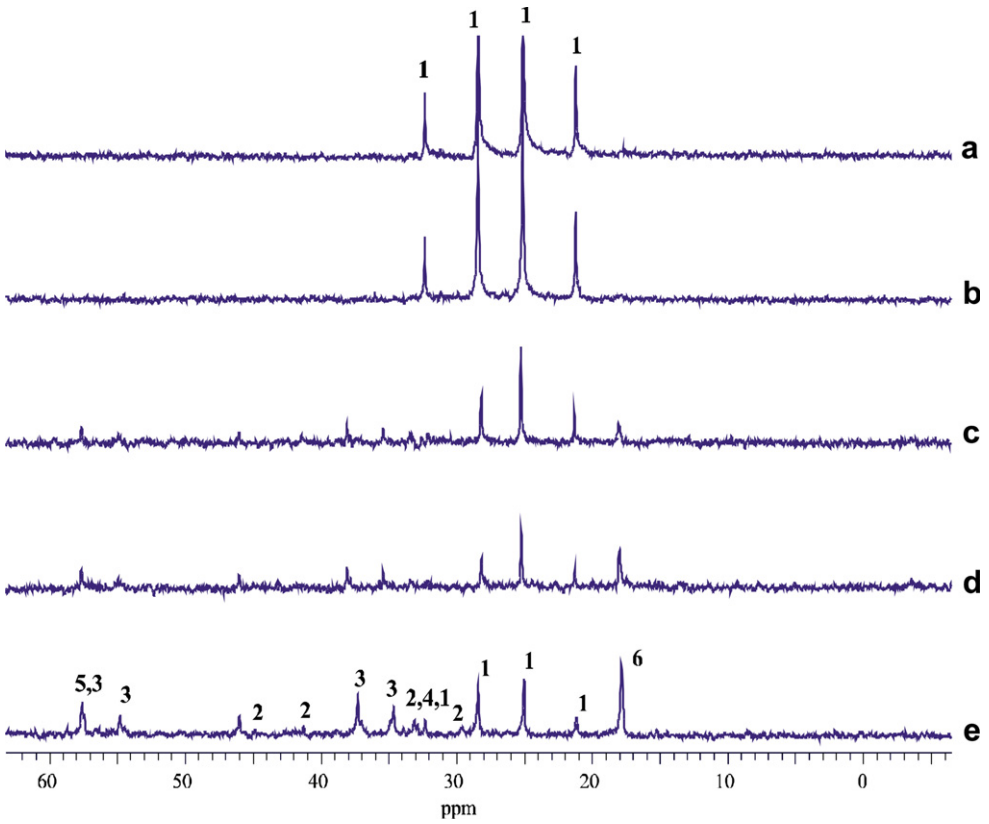


Fig. 2. Selected sequence of $^{31}P\{^1H\}$ HP-NMR spectra for a catalytic reaction carried out in C_6D_6 with **1**. Solution of **1** at room temperature (trace a); after addition of cyclohex-2-en-1-one and pressurization with 25 bar of H_2 at room temperature (trace b); after heating to 60 °C (trace c); after 3 h at 60 °C, spectrum at 60 °C (trace d); after cooling to room temperature (trace e).

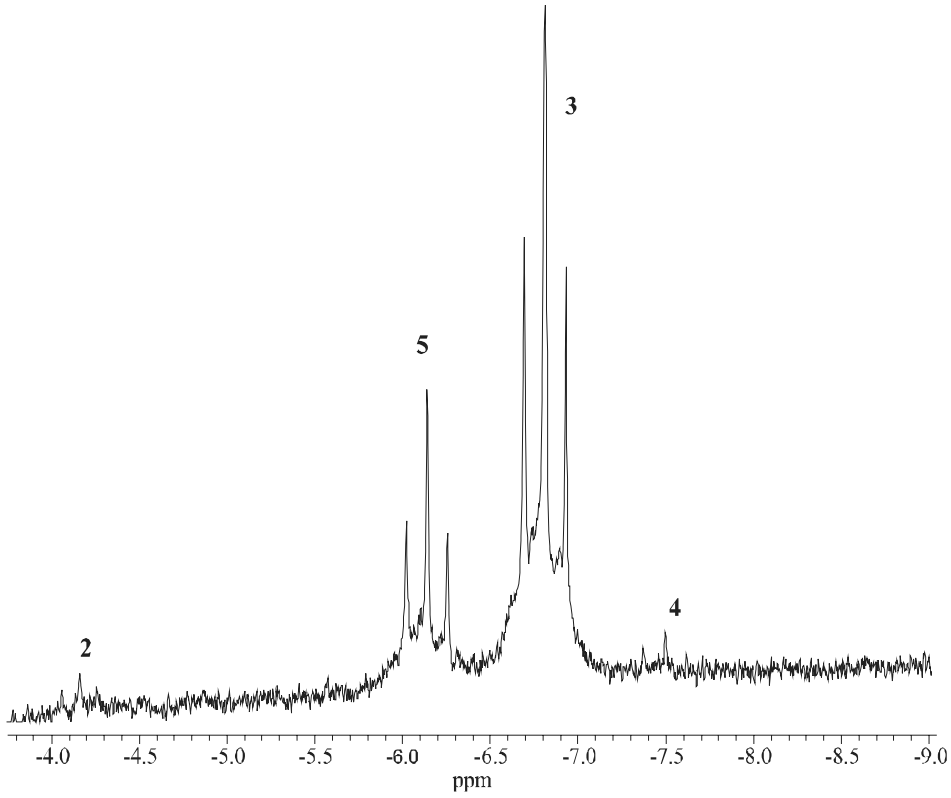


Fig. 3. ^{1}H NMR spectrum of the Ru–H region, acquired under the same conditions as in the $^{31}P\{^{1}H\}$ NMR spectrum shown in Fig. 2, trace d.

corresponding dihydrides **4** and **5** [1,2,4]. Just to have an idea of the possible contribution of these species to the catalysis outcome using **1** as catalyst precursor, each complex was synthesized [2,4,7] and independently employed to catalyze the hydrogenation of cyclohex-2-en-1-one. The results obtained are reported in Table 6. Some reactions with mono- and dihydrides were carried out by adding 1 or 2 equiv. of acetic acid in an attempt of mimicking the catalytic mixtures where this acid is formed by reaction of the bis(OAc) precursor with H_2 (Scheme 2).

A perusal of the results reported in Table 6 shows that the homodiphosphine complexes **6** and **7** are scarcely active and chemoselective, which reflects the importance of phosphine unfastening from the precursor for the activation of both H_2 and substrate [1,2,4]. Rather low substrate conversion was also achieved with the corresponding dihydrides **4** and **5** in the presence of acid, which, by the way, are more selective for the hydrogenation of the C=C bond [1].

Either in the presence or in the absence of added acid, the monohydride **2** was much less active than the bis(OAc) precursor **1**. This result can be accounted for by the fact that **2** is a direct precursor to **3** (Scheme 2) which, besides being a scarce catalyst, is better suited for the hydrogenation of the C=C double bond. The opposite chemoselectivity of the mono- and dihydride species is clearly shown by the fact that the addition of 1 equiv. of acid to a solution of **3** shifts the hydrogenation selectivity from the C=C group (>95%) to the C=O group (>74%).

Table 4
Cyclohex-2-en-1-one hydrogenation by **1**: Dependence of the conversion and chemoselectivity on the H_2 pressure[a]

$p(H_2)$ (bar)	Conversion (%)	Selectivity (%)		
		A	B	C
5	21.1	3.6	95.3	1.1
5[b]	63.5	10.6	82.6	6.8
10	28.0	4.5	93.5	2.0
25	33.1	6.6	90.3	3.1
25[b]	60.5	5.2	85.1	9.7
50	38.2	5.9	87.6	6.5

[a] Reaction conditions: **1**, 0.015 mmol; cyclohex-2-en-1-one, 1.50 mmol; solvent, toluene (4 ml); reaction time, 3 h; reaction temperature, 60 °C; $p(H_2)$, hydrogen pressures at 20 °C.
[b] Reaction time, 24 h. A, saturated ketone; B, unsaturated alcohol; C, saturated alcohol.

Table 5
Cyclohex-2-en-1-one hydrogenation by **1**: Dependence of the conversion and chemoselectivity on the temperature[a]

T (°C)	Conversion (%)	Selectivity (%)		
		A	B	C
50	11.6	3.7	95.4	0.9
60	21.1	3.6	95.3	1.1
70	28.2	8.1	89.3	2.6

[a] Reaction conditions: **1**, 0.015 mmol; cyclohex-2-en-1-one, 1.50 mmol; solvent, toluene (4 ml); reaction time, 3 h; reaction temperature, 60 °C; $p(H_2)$, 5 bar at 20 °C. A, saturated ketone; B, unsaturated alcohol; C, saturated alcohol.

Table 6
Hydrogenation of cyclohex-2-en-1-one catalyzed by different ruthenium(II) pre-catalysts[a]

Catalyst	CH_3COOH (equiv.)	Conversion (%)	Selectivity (%)		
			A	B	C
1	–	33.1	6.6	90.3	3.1
6	–	5.1	23.3	73.5	3.2
7	–	1.2	52.0	29.9	18.1
2	–	16.6	19.6	75.6	4.8
2	1	14.9	18.9	76.8	4.3
3	–	2.7	95.7	0.0	4.3
3	1	13.4	20.8	74.6	4.6
3	2	15.8	20.0	74.8	5.2
4	2	16.0	61.3	30.5	8.2
5	2	1.3	74.5	9.8	15.7

[a] Reaction conditions: precatalyst, 0.015 mmol; cyclohex-2-en-1-one, 1.50 mmol; solvent, toluene (4 mL); reaction time, 3 h; reaction temperature, 60 °C; $p(H_2)$, 25 bar at 20 °C. A, saturated ketone; B, unsaturated alcohol; C, saturated alcohol.

Table 7
Effect of the acetic acid concentration and of added PPh_3 on the hydrogenation of cyclohex-2-en-1-one by **1**[a]

Added reagent (equiv)	Conversion (%)	Selectivity (%)		
		A	B	C
–	33.1	6.6	90.3	3.1
HOAc (2)	25.0	3.9	93.1	3.0
HOAc (31)	16.9	5.6	93.1	1.3
PPh_3(1)	4.1	10.4	79.1	10.5

[a] Reaction conditions: **1**, 0.015 mmol; cyclohex-2-en-1-one, 1.50 mmol; solvent, toluene (4 ml); reaction time, 3 h; reaction temperature, 60 °C; $p(H_2)$, 25 bar at 20 °C. A, saturated ketone; B, unsaturated alcohol; C, saturated alcohol.

2.6. Influence of the addition of either acetic acid or PPh_3 on the hydrogenation of cyclohex-2-en-1-one catalyzed by **1**

Since the hydrogenation of **1** produces free HOAc, that remains in the catalytic mixture, some reactions were performed in the presence of this acid. The results obtained are reported in Table 7. The conversion of cyclohex-2-en-1-one decreased remarkably just by adding two equiv. of acid and decreased further on to 16.9% by addition of a large excess of acid (31 equiv.). In contrast, the chemoselectivity was not affected significantly by addition of acid. The observed trend is in line with the increasing stability of the bis(OAc) complex **1** vs. the monohydride **2** in the presence of added acid (see Scheme 2).

A much more remarkable effect on the catalytic activity was observed by addition of 1 equiv. of PPh_3 to the catalytic mixture. Indeed, the conversion dropped from 33.1% to 4.1% and the selectivity in allylic alcohol decreased from 90.3% to 79.1%. These results are in line with previous results for the hydrogenation of alkenes and ketones by **1** [1], and are consistent with the occurrence of the equilibria shown in Schemes 1 and 2 according to which PPh_3 unfastening is mandatory for H_2 activation as well as for generating a free coordination site to accommodate the substrate.

3. Conclusions

The heterodiphosphine complex $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$ is capable of generating an effective chemoselective catalyst for the hydrogenation of α,β-unsaturated ketones to allylic alcohols under relatively mild experimental conditions.

Batch catalytic reactions and *operando* high-pressure NMR experiments have contributed to establish that the hydrogenation of the C=O group is performed by the heterodiphosphine monohydride $RuH(CO)_2(OAc)(P^nBu_3)(PPh_3)$ generated *in situ* by hydrogenation of the bis(OAc) precursor. However, PPh_3 unfastening from this monohydride complex is an essential condition for the occurrence of catalytic activity.

A drawback of the present ruthenium(II) catalyst is represented by the generally low conversions as only a fraction of the ruthenium is effectively used in the catalysis cycle. For this reason, any practical application of *trans*-heterodiphosphine ruthenium(II) complexes in catalytic hydrogenation reactions will require to modify the molecular structure of the precursors so as to have a large concentration of catalytically active ruthenium species. Preliminary results with increasing concentrations of $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$ do not seem to provide a clue to solve the problem of the low productivity as even by increasing the catalyst amount from 0.015 to 0.045 mmol only a 4% increase in the conversion to allylic alcohol was achieved.

4. Experimental

4.1. Materials

All non-catalytic reactions and manipulations were performed under dry nitrogen in Schlenk tubes. The ruthenium(II) complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** were synthesized following reported procedures [2,4,7].

Commercial methyl vinyl ketone (99%), BZA (99%), PPh_3 (98%), C_6D_6 (99.6%) and trifluoroacetic acid were used without further purification. Cyclohex-2-en-1-one (⩾95%), 3-methyl-cyclohex-2-en-1-one (98%) and 2-cyclopenten-1-one (98%) were purified by distillation under vacuum and stored under nitrogen. Toluene was purified and stored using a standard procedure. Acetic acid was distilled under nitrogen prior to use (b.p. 118 °C).

4.2. Instruments

IR spectra were recorded on a FT-IR Perkin–Elmer Spectrum BX model, using the Spectrum v. 3.02.02 program. The solutions were analyzed using CaF_2 cells having 0.1 mm path.

^1H NMR spectra were recorded at 399.92 MHz on a Varian Mercury 400, using the solvent residual peak as reference. $^{13}C\{^1H\}$ NMR spectra were collected at

100.57 MHz on a Varian Mercury 400, using solvent residual peak as reference. $^{31}P\{^1H\}$ NMR spectra were registered at 121.421 MHz on a Varian VXR 300, using H_3PO_4 (85%) as external standard: downfield values were taken as positive. All $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were acquired using a broad band decoupler.

High-pressure NMR experiments were performed on a Bruker ACP 200 spectrometer operating at 200.13 and 81.01 MHz for ^1H and $^{31}P\{^1H\}$ NMR, respectively. The 10 mm-o.d. sapphire tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at ICCOM-CNR (Firenze, Italy) [8]. *Caution*: *Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.*

The reaction mixtures were analyzed with a Shimadzu GC-14A gas chromatograph equipped with a packed column (length 2 m, diameter, 3.17 mm) and a flame ionization detector. A column of the type FFAP ('free fatty acids phase' supported on Chromosorb G AW-DMCS 5%) was used to analyze the hydrogenation products of the α,β-unsaturated ketones studied in this work, except for methyl vinyl ketone for which a PPG column (Polypropylenglicol LB-550-X 15% supported on Chromosorb W) was employed.

GC-MS spectra were collected using a Shimadzu GC-17A QP5050A instrument.

Elemental analyses were performed with a Perkin–Elmer 2400 Series II CHNS/O analyzer.

4.3. Catalytic reactions

4.3.1. General procedure

Typically, in a glass vial placed in a stainless-steel autoclave, previously evacuated by a vacuum pump, were introduced 4.0 ml of a toluene solution containing the catalytic precursor (1.5×10^{-5} mol) and the substrate (1.5×10^{-3} mol) under dry nitrogen. The autoclave was then pressurized at room temperature with H_2, placed in a thermostatic oil bath at the desired temperature (±1 °C) and rocked for the desired time. At the end of the reaction, the autoclave was cooled to room temperature and the gaseous contents were vented off. The product composition of the solutions was analyzed by GC-MS and by GC using pure compounds as standards.

4.4. Operando high-pressure NMR studies in C_6D_6

4.4.1. High pressure NMR study with $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$ with or without substrate

Complex **1** (15.5 mg, 0.025 mmol) was dissolved in a Schlenk tube containing degassed C_6D_6 (1.8 ml). The resulting solution was then transferred under nitrogen into a sapphire NMR tube, which was introduced at room temperature into the NMR probe. $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired at room temperature. Then the sapphire tube was removed from the NMR probe-head and cyclohex-2-en-1-one (72.6 μl, 0.75 mmol) was added, followed by pressurization with 25 bar of H_2 at room temperature. The tube was placed into the NMR probe and $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired in 10 °C steps from room temperature to 60 °C. The tube was kept for 3 h at 60 °C, before cooling it again to room temperature.

An analogous study in the absence of substrate was carried out applying the same experimental conditions.

4.4.2. High pressure NMR study with $RuH(CO)_2(OAc)(P^nBu_3)(PPh_3)$ in the presence of substrate

The dihydride **3** (18.0 mg, 0.025 mmol) was dissolved in a Schlenk tube containing degassed C_6D_6 (1.8 ml). To this solution was added HOAc (1.4 μl, 0.025 mmol) and the obtained solution was stirred for 2 days at room temperature. The solution was transferred under nitrogen into a 10 mm-OD sapphire NMR tube. $^{31}P\{^1H\}$ and ^1H NMR spectra showed the complete conversion of **3** into the monohydride **2** already at room temperature. To this solution were sequentially added under nitrogen HOAc (1.4 μl, 0.025 mmol) and cyclohex-2-en-1-one (72.6 μl, 0.75 mmol). The sapphire tube was pressurized with H_2 (20 bar) at room temperature and $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired at the same temperature. The NMR tube was then heated to 60° C and maintained at this temperature for 20 min. During this time **2** was transformed quantitatively into **3**. The NMR tube was cooled to room temperature and the gas was released. A GC-MS analysis of the solution showed the formation of the allylic alcohol (75%) together with the saturated ketone (15%) and the saturated alcohol (4%).

4.5. X-ray data collection and structure determination of $Ru(CO)_2(OAc)_2(P^nBu_3)(PPh_3)$

A suitable single crystal of **1** was analyzed with an Enraf Nonius CAD4 automatic diffractometer with Mo Kα radiation (graphite monochromator) at room temperature. Unit cell parameters were determined from a least-squares refinement of the setting angles of 25 carefully centred reflections. Crystal data and data collection details are given in Tables 1 and 2, respectively. Lorentz-polarization and absorption corrections were applied [9a]. Atomic scattering factors were taken from Ref. [9b] and an anomalous dispersion correction, real and imaginary part, was applied [9c]. The structure was solved by direct methods and refined by full-matrix F^2 refinement. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and hydrogen atoms were introduced in their calculated positions applying a riding model with thermal parameters 20% larger than those of the respective carbon atoms. All calculations were performed on a PC using the WINGX package [9d] with SIR-97 [9e], SHELX-97 [9f] and ORTEP-3 [9g] programs.

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Appendix A. Supplementary material

CCDC 609254 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.006.

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