1 H), 2.71 (s, 3 H), 2.58 (m, 1 H), 1.81 (s, 3 H), 1.51 (m, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 338.81, 258.17, 202.61, 198.94, 198.67, 197.40, 136.36, 130.24, 128.10, 128.01, 69.70, 69.58, 55.95, 55.39, 40.09, 27.95.

The rearrangement of **7d** to **5d** was conducted in an NMR tube as follows: a small amount (ca. 30 mg) of complex **7d** was placed in a 5-mm NMR tube. The NMR tube was attached to a vacuum line, and benzene-d_6 (ca. 0.6 mL), which had been dried first with calcium hydride and then over sodium metal, was vacuum-transferred into the NMR tube. The contents of the NMR tube were subjected to several freeze–thaw–pump cycles, and then the tube was flame-sealed under vacuum. The progress of the rearrangement, which was conducted at 25 °C, was monitored by observing a decrease in the intensities of the resonances of **7d** with a concomitant increase in the intensities of the resonances of **5d**. Moreover, the solution changed color from an initial clear yellow to a final opaque brown-black. After 8 h only the NMR resonances for complex **5d** and $W(CO)_6$ were observed. ^1H NMR (C_6D_6): δ 7.77 (m, 6 H), 7.19 (m, 9 H), 5.30 (t, J = 7 Hz, 1 H), 3.33 (s, 3 H), 2.88 (br s, 5 H), 2.33 (m, 2 H), 2.02 (s, 3 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 257.50, 203.07, 199.59, 191.14 ($W(CO)_6$), 160.01, 136.45, 134.44, 130.15, 128.60, 128.44, 59.68, 55.24, 53.19, 39.89, 21.74.

$(CO)_5W[C(OCH_3)CH_2CH_2CH_2C(O)Si(CH_3)_3]$ (10a). Complex **5a** (100 mg, 0.2 mmol) was dissolved in 25 mL of chloroform, and then the solvent was removed under vacuum. The resulting residue was then allowed to stand under nitrogen at 0 °C for 8–10 weeks. After this period, ^1H NMR spectroscopy revealed that quantitative conversion to complex **10a** had occurred. The resulting residue was taken up in a minimum amount of methylene chloride and the solution transferred to a column of silica gel. Elution of the column with 50% methylene chloride/50% hexane, collection of all the yellow fractions, and then removal of the solvent under vacuum afforded **10a**: yellow oil; ^1H NMR ($CDCl_3$) δ 4.61 (s, 3 H), 3.17 (t, J = 7.7 Hz, 2 H), 2.62 (t, J = 7.2 Hz, 2 H), 1.73 (pentet, J = 7.5 Hz, 2 H), 0.20 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 336.20, 246.81, 203.14, 197.19, 70.46, 64.13, 47.03, 18.66, 1.37; MS (14.4 eV) m/e 510 (M^+, 0.6%), 454 (21), 426 (4), 398 (27), 370 (27), 342 (7). Anal. Calcd for $C_{14}H_{18}O_7SiW$: C, 32.95; H, 3.56. Found: C, 34.88; H, 3.89. The carbon analysis exceeded the acceptable limit because purification by distillation led to decomposition.

$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(O)Si(CH_3)_3]$ (10b). Complex **5b** (0.59 g, 1.1 mmol) was dissolved in a solvent mixture of THF (20 mL), methanol (30 mL), and water (5 mL). Then 5 drops of concentrated sulfuric acid was added with stirring for 24 h at 25 °C. The reaction mixture was then extracted several times with 50-mL portions of methylene chloride. The resulting combined organic extracts were washed several times with water, were then dried over anhydrous magnesium sulfate, and were finally filtered. The solvent was removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a column of silica gel. Elution of the column with 30% methylene chloride/70% hexane, collection of all the yellow fractions, and then removal of the solvent under vacuum afforded **10b** (0.46 g, 80%): orange-yellow oil; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 3.37 (s, 3 H), 2.97 (t, J = 8.8 Hz, 2 H), 2.71 (t, J = 6.2 Hz, 2 H), 1.55 (m, 2 H), 0.14 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 257.88, 247.81, 203.00, 198.90, 55.81, 53.38, 47.08, 41.20, 17.22, 1.31; MS (11.2 eV) m/e 523 (M^+, 0.5%), 495 (4), 467 (2), 439 (0.2). Anal. Calcd for $C_{15}H_{21}NO_6SiW$: C, 34.43; H, 4.05; N, 2.68. Found: C, 34.53; H, 4.04; N, 2.63.

Acknowledgment. We wish to thank the Bureau of General Research (Kansas State University) for support of this research and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer (Northern Illinois University). We also wish to thank Pressure Chemical Co. for their generous gift of tungsten hexacarbonyl.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, and least-squares plane results (4 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Selective Hydrogenation of α,β-Unsaturated Aldehydes in Aqueous Organic Two-Phase Solvent Systems Using Ruthenium or Rhodium Complexes of Sulfonated Phosphines

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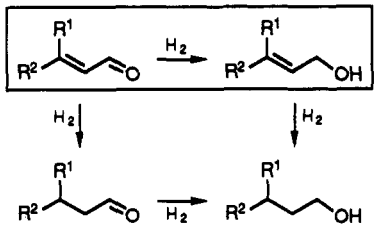
Selective hydrogenation of α,β-unsaturated aldehydes catalyzed by metal–sulfonated phosphine complexes prepared in situ is reported. The regioselectivity in the reduction was found to depend markedly on the nature of the metal used (Ru or Rh). Others factors controlling the activity and selectivity in the case of the ruthenium–sulfonated phosphine system were also investigated. ^{31}P and ^1H NMR experiments were carried out to explain the behavior of the mixture $RuCl_3$/TPPTS (TPPTS = tris(*m*-sulfophenyl)phosphine trisodium salt) in water. A possible mechanism that could accommodate these results is discussed.

Introduction

α,β-Unsaturated aldehydes are known to be valuable intermediates in the field of fragrance and flavor chemistry,[1] and very often the multistep synthesis to new products involves the selective reduction of the carbonyl function. Hydrogenation of the carbon–carbon double bond is readily achieved under mild conditions with high selectivity[2] whereas catalytic reduction of the aldehyde group remains a challenging problem (Scheme I).

Scheme I



(1) (a) Bauer, K.; Garbe, D. *Common Fragrance and Flavor Materials*; VCH: New York, 1985. (b) Bauer, K.; Garbe, D. *Ullman Encyclopedia*, 3rd ed.; VCH: New York, 1988; Vol. A11, p 141.

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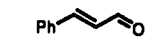
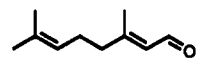
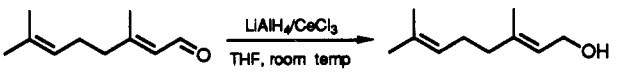
Table I. Catalytic Hydrogenation of Various α,β-Unsaturated Aldehydes

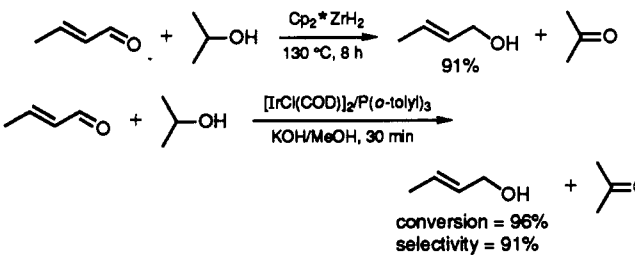
substrate	catalyst	P_{H_2}, bar	T, °C	time, h	yield, %	selectivity,[a] %	ref
 2-butenal	$Ru(CF_3CO_2)(CO)(PPh_3)_2$	15	160	6	85	60	9b
	$RuCl_2(PhP(CH_2CH_2PPh_2)_2$	34	100	1,6	54	38	12
	$Os(H)(Br)(CO)(PPh_3)_3$	1	100	1	100	50	10b
 2-phenyl-2-propenal	$[IrCl(COD)]_2 + PPh_2Cy$	30	100	2	98	96	11a
 3,7-dimethyl-2,6-octenal	$HRuCl(PPh_3)_3$	50	30	20	99	95	9a

[a] Selectivity in allylic alcohol.

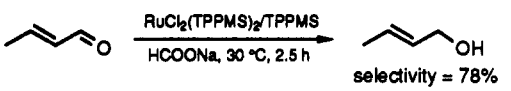
Most popular of the selective reducing agents are the various metal hydrides, mainly those of boron and aluminum.[3,4]



Among other reducing procedures available, we can mention the following: (a) the Meerwein–Pondorf–Verley type reduction of carbonyl groups catalyzed by group IVA metals[5] or transition metals.[6]



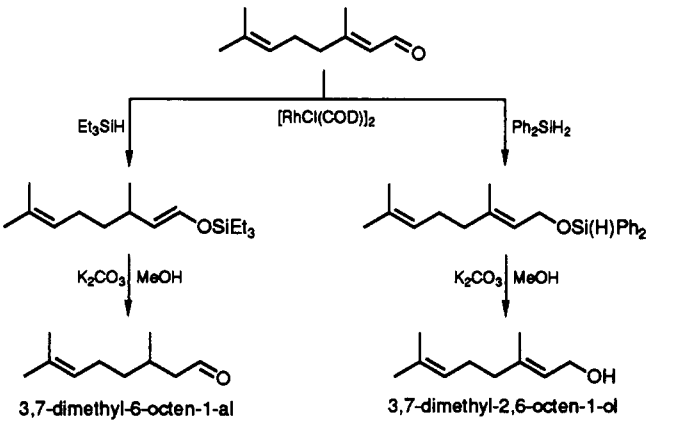
Both primary and secondary alcohols may serve as hydrogen donors. Recently, F. Joo et al. reported the selective reduction of unsaturated aldehydes in aqueous phase with a water-soluble ruthenium catalyst.[7]



TPPMS = (sulfophenyl)diphenylphosphine sodium salt

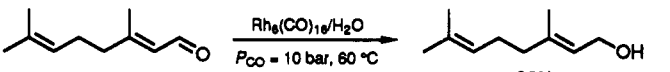
The main disadvantage of such a technique holds to the formation of sodium carbonate during the course of the reaction leading to a basic medium, which may cause degradation of the ligand and deactivation of the catalyst.

(b) Transition-metal-catalyzed hydrosilylation has been described as an efficient method of reduction, provided the proper choice of silane is made.[8] Monohydrosilanes lead to 1,4-addition in contrast to dihydrosilanes (1,2-addition).



(c) Catalytic hydrogenation is by far the most attractive way to carry out the reduction with respect to economical and industrial process considerations. As shown in Table I, a few examples are reported for the formation of unsaturated alcohols. While high regioselectivity was obtained with 3-phenyl-2-propenal (cinnamaldehyde) and 3,7-dimethyl-2,6-octadienal (citral), 2-butenal (crotonaldehyde) gave poor results.

It has been shown that rhodium catalysts lead to decarbonylation[13] unless the reaction is carried out under water–gas shift conditions with the cluster $Rh_6(CO)_{16}$.[14]



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In this paper we will describe a full account of our research on the highly selective reduction of α,β-unsaturated aldehydes catalyzed either by ruthenium or rhodium sulfonated phosphine complexes under biphasic conditions. This work was directed toward the following goals: (1) to reach the highest selectivity and (2) to solve the eternal problem in homogeneous catalysis, namely the catalyst recycling.

Experimental Section

Materials and Products Analysis. $RuCl_3 \cdot 3H_2O$, $[RhCl(COD)]_2$, and $[IrCl(COD)]_2$ were purchased from Strem Chemicals. Other ruthenium catalysts including TPPTS–ruthenium complexes were prepared according to known methods;[36] all organic solvents were purified by standard techniques and stored under argon prior to use. Argon and hydrogen were used as received without purification. TPPTS was synthesized by sulfonation of PPh_3.[15] Other reagents and products were commercially available or supplied by "Rhône-Poulenc Animal Nutrition".

^1H and ^{31}P NMR spectra were recorded respectively with tetramethylsilane and 85% phosphorous acid as standard.

The products of the reaction were identified by GC and mass analysis. Gas chromatography was run on a Varian 3700 instrument equipped with a Rheoplex 400 Chromosorb PAW packed column. The peaks were identified by comparison with authentic samples and GC/MS techniques. The gas chromatograph was calibrated to calculate concentrations of products on a mole percent basis.

Hydrogenation Procedure. A typical run was carried out in a glass-lined stainless steel autoclave (125 cm^3), which provided agitation by rocking (200 cycles/min). Hydrated ruthenium chloride, TPPTS, water, substrate, and the desired organic solvent were successively introduced under inert atmosphere into the ampule, which then was placed in the autoclave. The reactor was purged several times with nitrogen before setting the required hydrogen pressure. During the run, the hydrogen pressure was kept constant by continuous feeding from a high-pressure reservoir. As the reaction proceeded, the decline of the hydrogen pressure within the reservoir was recorded. At the end of the uptake, the autoclave was cooled down and vented carefully. The two-phase system was decanted and the aqueous layer washed several times with the organic solvent. The combined organic layers were analyzed by gas chromatography.

Example of Product Isolation. 3-Methyl-2-butenal (42 g, 0.5 mol) was hydrogenated in a 300-mL stainless autoclave at 50 °C and 20 bar. After the hydrogen uptake ceased (50 min), the autoclave was cooled with stirring and vented carefully. The reaction mixture was poured in a 250-mL separatory funnel and the reactor rinsed two times with 10-mL portions of water. The organic layer was separated and the aqueous phase washed with 3 × 25 mL of dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and distilled under atmospheric pressure to yield 43.3 g (bp = 140 °C) of 3-methyl-2-buten-1-ol (isolated yield = 96.5%) identified by NMR, MS, and microanalysis techniques.

Table II. Catalytic Hydrogenation of 3-Methyl-2-butenal to 3-Methyl-2-buten-1-ol[a]

run	catalyst	P_{H_2}, bar	T, °C	time, h	conversion, %	selectivity (prenol)
1	$H_2Ru(PPh_3)_4$	1	50	6	0	0
2	$H_2Ru(PPh_3)_4$	30	50	2, 5	100	91
3	$RuCl_2(PPh_3)_3$	30	50	3	81	80
4	$HRuCl(CO)(PPh_3)_3$	30	50	3	33	38
5	$HRu(OAc)(PPh_3)_3$	30	50	7	60	73
6	$RuCl_3 \cdot 3H_2O$	20	35	6	9	77
7	$RuCl_3/4PPh_3$	20	35	9	69	93

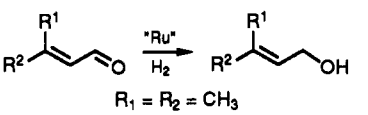
[a] Conditions: Ru = 0.5 mmol; substrate = 20 mmol; IprOH/H_2O (95/5) = 15 mL.

Kinetics. The kinetics were run in a 300-mL stainless steel autoclave equipped with a turbine-type impeller. Known amounts of $RuCl_3$ and TPPTS along with 100 mL of KH_2PO_4/NaOH (buffer pH = 7) were introduced in the reactor under nitrogen atmosphere. The mixture was hydrogenated at 20 bar and 50 °C for 1 h. Then the autoclave was cooled down, vented carefully, and purged with nitrogen, and the substrate (0.5 mol) was syringed inside. After sealing, the temperature and hydrogen pressure were set at the desired values. Stirring began while the run temperature was reached. During the reduction, samples were withdrawn from the reaction mixture at desired intervals and submitted to GC analysis.

The experimental conditions are the following. Effect of agitation speed: P_{H_2} = 20 bar; 50 °C; $RuCl_3 = 5 \times 10^{-4}$ mol; TPPTS = 18×10^{-3} mol; stirring rate = variable; buffer, pH = 7 (KH_2PO_4/NaOH), = 100 mL; 3-methyl-2-butenal = 0.5 mol; prereduction = 20 bar; 50 °C; 1 h. Influence of ligand concentration: P_{H_2} = 20 bar; 50 °C; $RuCl_3 = 5 \times 10^{-4}$ mol; TPPTS = variable; stirring rate = 2000 rpm; buffer, pH = 7 (KH_2PO_4/NaOH), = 100 mL; 3-methyl-2-butenal = 0.5 mol; prereduction = 20 bar; 50 °C; 1 h. Influence of the hydrogen pressure: P_{H_2} = variable; 50 °C; $RuCl_3 = 5 \times 10^{-4}$ mol; TPPTS = 18×10^{-3} mol; buffer, pH = 7 (KH_2PO_4/NaOH), = 100 mL; 3-methyl-2-butenal = 0.5 mol; stirring rate = 2000 rpm; prereduction = 20 bar; 50 °C; 1 h. Influence of ruthenium concentration: P_{H_2} = 20 bar; 50 °C; $RuCl_3$ = variable; TPPTS = 18×10^{-3} mol; stirring rate = 2000 rpm; buffer, pH = 7 (KH_2PO_4/NaOH), = 100 mL; 3-methyl-2-butenal = 0.5 mol; prereduction = 20 bar; 50 °C; 1 h.

Results and Discussion

Preliminary Results. The behavior of several ruthenium complexes for the selective hydrogenation of 3-methyl-2-butenal (prenal) in 3-methyl-2-butenol (prenol) has been examined. The results are summarized in Table II.



$R_1 = R_2 = CH_3$

From these data, we can conclude that the wide range of selectivity depends on the metal environment. Interestingly, run 7 shows that the simple association of ruthenium chloride and triphenylphosphine is an efficient catalyst for this reduction. The presence of the phosphine is necessary to avoid degradation of ruthenium into metallic particles. The reasonably high regioselectivity with some ruthenium catalysts prompted us to extend the study to the water-soluble phosphine in order to carry out the reaction under biphasic conditions and thus offer a possible solution to the catalyst recovery problem.

Biphasic Homogeneous Catalysis. Organometallic compounds are particularly attractive because of the possibility of varying their ligands to obtain desired activity and selectivity. From the industrial standpoint, homo-

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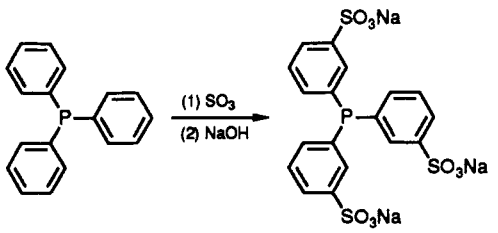
Table III. Solvent Dependence of the Biphasic Reduction of 3-Methyl-2-butenal[a]

organic solvent	time, min	conversion, %	selectivity in prenol, %
cyclohexane	80	99	92
toluene	70	96	96
chloroform	70	84	96
ethyl acetate	75	93	96

[a] Conditions: $RuCl_3$ = 0.1 mmol; TPPTS = 0.5 mmol; substrate = 20 mmol; water/organic solvent = 5 mL/5 mL.

geneous catalysts are difficult to use because they are not readily separable from the products that are formed in the same phase. However, advantages in activity and selectivity have led to methods to overcome the separation problems. One possibility is to carry out the reaction in a biphasic medium such that one phase contains the product and the other phase the catalyst (metal and ligand). According to this concept, Rhône-Poulenc has developed homogeneous catalysis in aqueous phase with the use of an original ligand: TPPTS (tris(*m*-sulfophenyl)-phosphine trisodium salt). The sulfonation of the aryl group[15] confers on the phosphine an extremely high solubility in water and inextractibility into common organic solvents.



Numerous applications using this ligand in the field of homogeneous catalysis have been reported so far such as hydrocyanation,[15] telomerization of dienes,[16] hydroformylation of alkenes,[18] or 1,4-addition of active methylene derivatives to conjugated dienes.[19] Among them, hydroformylation (Ruhrchemie/Rhône-Poulenc process) and nucleophilic addition to 1,3-diene (Rhône-Poulenc Animal Nutrition[20]), both catalyzed by Rh/TPPTS, gained industrialization.

Concerning the homogeneous catalyzed hydrogenation in aqueous phase, much of the work was done with the monosulfonated triphenylphosphine (TPPMS) complexed to rhodium[21] or ruthenium.[21,22] Patin et al. studied the olefin-catalyzed hydrogenation with the Rh(III)/TPPTS system[23] and reported the redox reaction between the high-valent rhodium and the phosphine leading to the formation of colloidal rhodium particles.

3-Methyl-2-butenal Biphasic Catalyzed Hydrogenation. By analogy with the $RuCl_3/PPh_3$ system, we tested the efficiency of the $RuCl_3$/TPPTS mixture in water for the selective reduction of 3-methyl-2-butenal to 3-methyl-2-buten-1-ol. The reaction was carried out under hydrogen pressure in a biphasic medium water/immiscible organic solvent. The data from Table III clearly demonstrate a nondependence of the 3-methyl-2-buten-1-ol selectivity on the solvent. At the end of the reaction, the reaction mixture was strictly biphasic, the aqueous phase being reddish and the organic layer colorless. No phase-transfer agents or additional cosolvent was required to carry out the reduction since the weak solubility of the substrate in water (around 50 g/L at 25 °C) seemed to be enough to ensure a fast reaction.

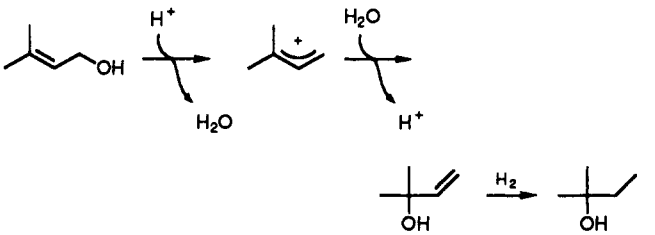
The gas chromatography analysis confirmed the absence of the saturated aldehyde (3-methylbutanal) and the only detected byproducts were the following: 3-methyl-3-buten-1-ol (isoprenol ≈ 1%) resulting from the 3-methyl-2-buten-1-ol isomerization and 2-methylbutan-2-ol (*tert*-amyl alcohol), which could be attributed to the aqueous-phase acidity.

Table IV. "Ru–TPPTS" Recycling

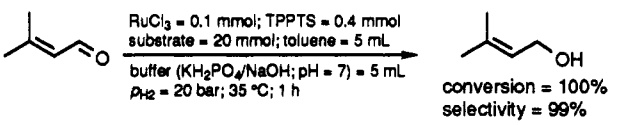
run[a]	time, h	conversion, %	selectivity,[b] %
1	1	100	96
2	0.5	99	97
3	0.5	99	97

[a] Conditions: $RuCl_3$ = 0.1 mmol; TPPTS = 0.5 mmol; 20 bar; 35 °C; 3-methyl-2-butenal = 20 mmol; water = 5 mL; toluene = 5 mL. [b] Selectivity in 3-methyl-2-buten-1-ol.

The 3-methyl-2-buten-1-ol acid-catalyzed reaction should yield the unsaturated intermediate, which would be easily hydrogenated.

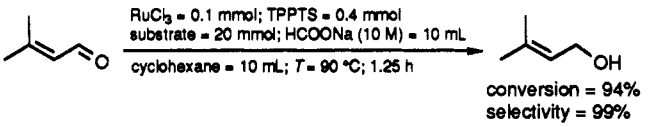


This hypothesis proved to be reasonable since working in a pH = 7 aqueous buffer completely suppressed the *tert*-amyl alcohol formation. Only traces of 3-methylbutan-1-ol (isoamyl alcohol) were found under these improved experimental conditions.



Interestingly, the reduction appeared very selective to the aldehyde moiety, and we were unable to achieve the 3-methyl-2-buten-1-ol hydrogenation to 3-methylbutan-1-ol even under prolonged reaction times.

This reduction could be also carried out by using aqueous sodium formate as described by F. Joo et al.,[7] with high selectivity in 3-methyl-2-buten-1-ol, but under more forceful temperature conditions (90 °C), likely to promote formate decomposition.



Catalyst Recycling. The biphasic reaction mixture offered advantages in product isolation and catalyst recycling. Indeed, the aqueous catalytic phase could be recycled for another run after a simple decantation under inert atmosphere. The organic layer was discarded and a fresh 3-methyl-2-butenal solution in toluene added in the glass ampule. Table IV displays the results obtained for three consecutive runs with the same aqueous phase. Interestingly, the two recycles proceeded faster than the former owing to the absence of an induction period due to the formation of the active catalyst. This phenomenon will be discussed further. As can be shown from the data, the selectivity in the unsaturated alcohol remained unaffected throughout the experiments.

Determination of the ruthenium, phosphorus, and sulfur concentrations in both phases proved there was no leak of metal and TPPTS in the organic phase.

Generalization to Other Unsaturated Aldehydes. The hydrogenation of other α,β-unsaturated aldehydes was

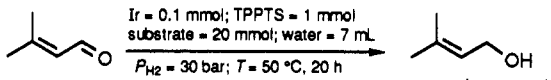
Table V. Hydrogenation of α,β-Unsaturated Aldehydes with "Ru–TPPTS"[a]

substrate	P_{H_2}, bar	T, °C	time, h	conversion, %	selectivity in unsaturated alcohols, %
3-phenyl-2-propenal	20	35	3	99	98
2-butenal	20	35	4	95	99
3-methyl-2-butenal	20	35	1	100	97
3,7-dimethyl-2,6-octenal	50	50	15	96	98

[a] Conditions: $RuCl_3$ = 0.1 mmol; TPPTS = 0.5 mmol; substrate = 20 mmol; water/toluene = 5/5 mL.

attempted under similar but nonoptimized conditions. The results in Table V show that in all cases the selectivity with respect to the unsaturated alcohol is high. It is worth mentioning the good selectivity in 2-buten-1-ol, which is to our knowledge the best so far reported. The low activity observed with 3,7-dimethyl-2,6-octadienal stemmed from its lack of solubility in water, preventing contact between the catalyst and the substrate. An additional cosolvent like methanol should enhance the reaction rate.

Extension to Other Metal/TPPTS Catalysts. Iridium/TPPTS System. In the Introduction, we mentioned that iridium compounds were known from earlier studies to promote the selective carbonyl reduction of unsaturated aldehydes.[11] Likewise, the analogous Ir/TPPTS complexes were capable of hydrogenating selectively 3-methyl-2-butenal into 3-methyl-2-buten-1-ol but with a very low activity as compared to ruthenium.



	3-methylbutanal	3-methylbutan-1-ol	3-methyl-2-buten-1-ol
yield, %	2.5	0.5	59

The complex was prepared by adding an excess of ligand to a suspension of the dimer $[IrCl(COD)]_2$ in water. Bubbling hydrogen through the orange mixture afforded a homogeneous colorless solution, presumably polyhydride iridium complex, which was neither analyzed nor characterized. At the end of the reaction, the reaction medium was biphasic and the aqueous layer still colorless.

Rhodium/TPPTS System. The synthesis of coordination compounds between rhodium and the water-soluble phosphine is well documented. Most of the Rh(I)/TPPTS adducts can be simply prepared by mixing the dimer $[RhCl(COD)]_2$ and the sulfonated phosphine in water.[24] The analogous Wilkinson–Osborn complex $RhCl(TPPTS)_3$ reacts smoothly with hydrogen to yield the oxidation product $H_2RhCl(TPPTS)_3$.

$$[RhCl(COD)]_2 + 2TPPTS \rightarrow 2(COD)RhCl(TPPTS) \xrightarrow{2TPPTS} RhCl(TPPTS)_3 \xrightarrow{H_2} H_2RhCl(TPPTS)_3$$

Organometallic rhodium complexes are well-known to achieve easily the carbon–carbon double bond hydrogenation though they also have some tendency for the decarbonylation of aldehydes.

Surprisingly, we found that the Rh(I)/TPPTS complex, prepared in situ from TPPTS and the dimer precursor, could cleanly reduce α,β-unsaturated aldehydes into *saturated aldehydes* without decarbonylation.

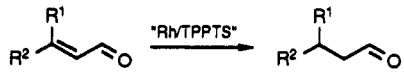


Table VI. Hydrogenation of α,β-Unsaturated Aldehydes with "Rh–TPPTS"[a]

substrate	P_{H_2}, bar	T, °C	time, h	conversion, %	selectivity in saturated aldehydes, %
3-phenyl-2-propenal	20	80	1.5	93	95.7
3-methyl-2-butenal	20	80	0.3	90	95
3,7-dimethyl-2,6-octenal	40	60	3	19	95
2-buten-al	20	30	0.3	89	96.6
1st recycle	20	30	0.3	94	98.9
2nd recycle	20	30	0.3	94	98.9

[a] Conditions: $[RhCl(COD)]_2$ = 0.05 mmol; TPPTS = 0.5 mmol; substrate = 20 mmol; water/toluene = 5/5 mL.

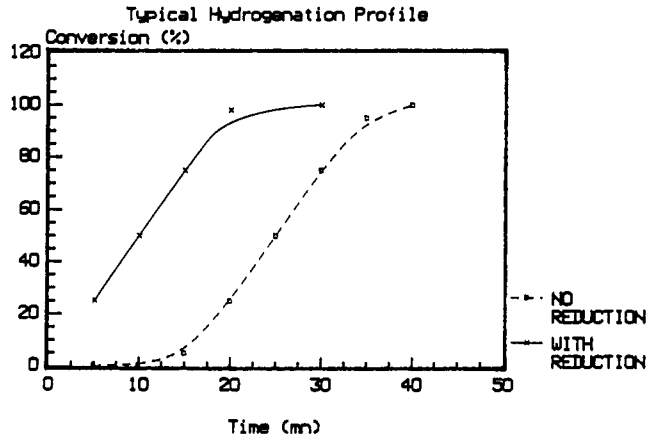


Figure 1.

As can be seen in Table VI, the selectivities under nonoptimized conditions are higher than 95%. Again, recycling the catalyst gave no problem, the selectivity and the activity being almost constant throughout the three runs. ^{31}P NMR experiments after hydrogenation afforded rather complicated spectra (mixture of Rh(I)- and Rh(III)/TPPTS complexes) but established unambigously that the oxidation of the phosphine did not occur.

Kinetics of 3-Methyl-2-butenal Hydrogenation. From a kinetic standpoint, the study of such a polyphasic system is complex, since the various physical and chemical phenomena encountered may interfere in the rate of the reaction.

We must consider (i) the gas–liquid hydrogen transfer, (ii) the substrate diffusion between the two phases, and (iii) the chemical reaction itself.

The importance of the second point was difficult to estimate, but owing to the relative solubility of prenal in the aqueous phase, we assumed this step was not rate determining.

A typical hydrogenation profile of 3-methyl-2-butenal is shown in Figure 1. The dotted line stands for a reaction conducted without prior reduction of the "Ru/TPPTS" system. Thus, before occurring, the reaction required a 10-min initiation period, during which no hydrogen uptake was observed. In contrast, when the buffered mixture of $RuCl_3$/TPPTS was subjected to reduction (20 bar; 50 °C; 1 h) before adding the substrate, hydrogen consumption started immediately (continuous line). We did not study this prereduction period in detail, and we only made sure the conditions were well chosen in order to obtain reproducible results. Consequently, all the following experiments have been done systematically with prior prereduction.

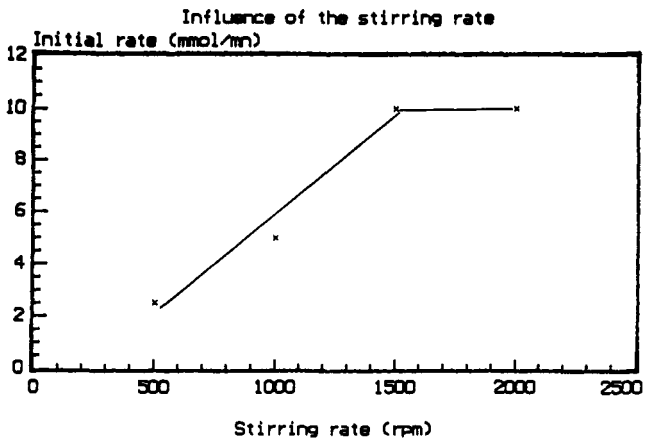


Figure 2.

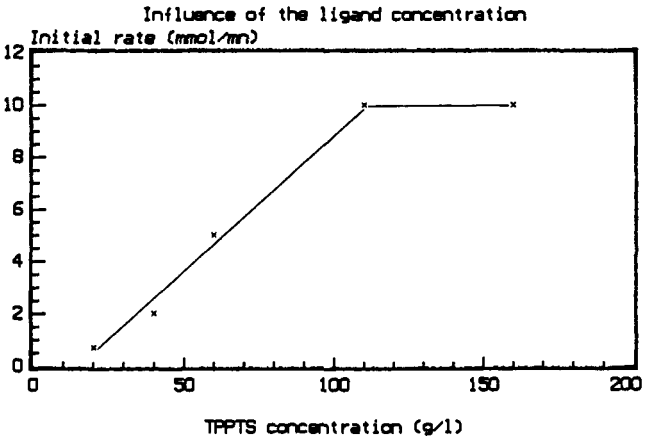
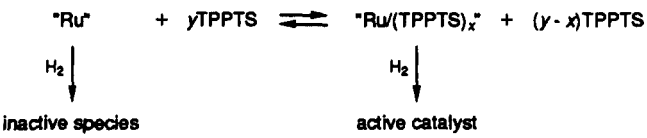


Figure 3.

Effect of Agitation Speed. Figure 2 shows the initial rate of the reaction vs the stirring rate at 50 °C. Beyond 1500 rpm, the reaction rate was independant of the stirring ensuring that the gas–liquid mass transfer was not rate determining. Therefore, in all experiments, the agitation speed was set at 2000 rpm.

Effect of Substrate Concentration. From the profile displayed in Figure 1, the linear variation of the 3-methyl-2-butenal consumption during the course of the reaction suggest a zero-order dependence with respect to substrate concentration. Comparative experiments at different concentrations afforded in all cases the same initial rate.

Influence of Ligand Concentration. The initial rate as a function of ligand concentration deserves comments. As illustrated in Figure 3, an increase in TPPTS concentration results in a spectacular improvement of the rate, up to a limit beyond which a constant rate was observed. The correlation activity/phosphine concentration can be discussed on the basis of an equilibrium between ruthenium and the phosphorus ligand. The coordination of the TPPTS being likely indispensable for the molecular hydrogen activation, its concentration should play a key role for the "Ru/TPPTS" complex formation, high concentration reflecting a right-shifted equilibrium.



One should also keep in mind that trisulfonate groups confer tensioactive properties to the water-soluble phosphine and might explain a more rapid migration of the

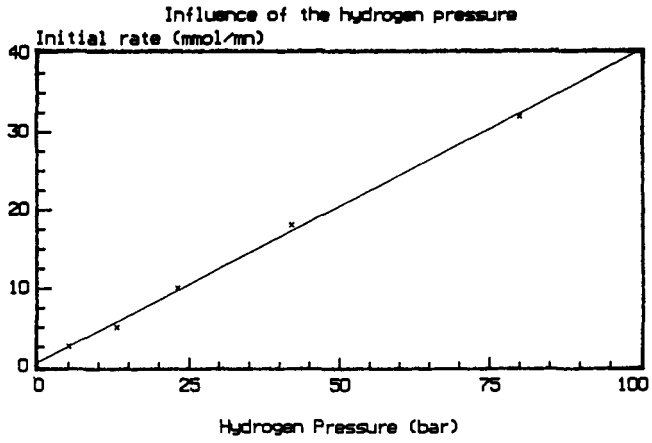


Figure 4.

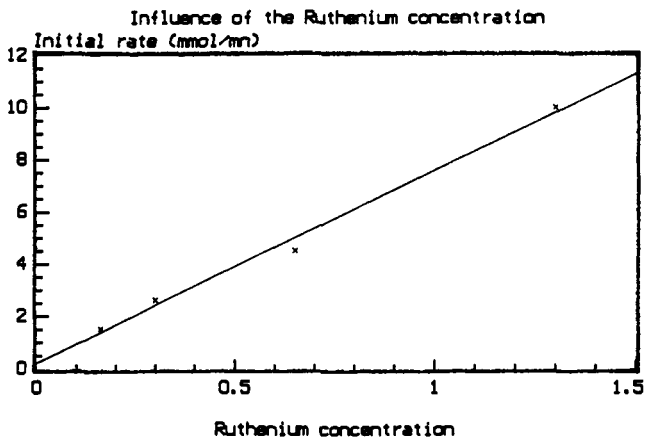
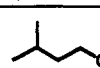


Figure 5.

Table VII. Influence of the Temperature[a]

T, °C	time, min	conversion, %	yield, %		selectivity, %
					
35	100	97	96		99
50	50	100	99		99
80	25	98	93	4	95
100	25	100	92	6	92

[a] Conditions: $RuCl_3$ = 0.5 mmol; TPPTS = 18 mmol; buffer (pH = 7) = 100 mL; 3-methyl-2-butenal = 0.5 mol; P_{H_2} = 20 bar; prereduction = 20 bar; 50 °C; 1 h.

3-methyl-2-butenal into the catalytic phase. The 3-methyl-2-buten-1-ol selectivity was unaffected by variations of this parameter and remained at 99%.

Influence of the Hydrogen Pressure. The effect of the hydrogen pressure was examined at 50 °C and at high concentrations of phosphorus ligand. The initial rate was found to vary linearly with respect to hydrogen pressure (see Figure 4). The first-order dependence suggests that oxidative addition of H_2 to the ruthenium phosphine complex is likely to be rate determining. No variation of the 3-methyl-2-buten-1-ol selectivity was noticed by varying the hydrogen pressure.

Influence of Ruthenium Concentration. Figure 5 shows also a first-order relationship relative to the metal concentration, as expected.

Influence of the Temperature. Although raising the temperature could be beneficial for the catalyst activity, the selectivity in 3-methyl-2-buten-1-ol slightly decreased above 50 °C to the advantage of the totally hydrogenated product 3-methylbutan-1-ol (Table VII). An Arrhenius

plot yielded a formal activation energy of 7 kcal/mol. This unusual low value does not reflect the correct temperature effect and must be due to inaccurate initial rate determinations at temperatures above 50 °C, where the kinetic control is no longer governed by the chemical reaction but by physical factors.

The influence of the parameters on the selectivity and the catalytic activity have been summarized. As far as the selectivity is concerned, temperatures below or equal to 50 °C are strongly recommended in order to obtain the best yield of 3-methyl-2-buten-1-ol. On the other hand, ligand concentration plays a crucial role with respect to the activity. A large excess of phosphine is likely required to maximize the "Ru/TPPTS" concentration, a key factor of the catalyst activity. Under optimized conditions, the kinetics can be summarized by the simple equation $R = k(T)[\mathrm{Ru}][\mathrm{H_2}]$.

Mechanistic Considerations. A few mechanistic reports have been devoted to ruthenium-catalyzed hydrogenation,[25-29] and it turns out that the mechanism pathways with this metal should be considered much more complicated than the corresponding rhodium ones. Two publications describing crotonic and pyruvic acid catalyzed hydrogenation with "Ru/TPPMS" and cyclohexene reduction with "Ru/EDTA" are the only studies carried out with aqueous-phase systems.[22,30] We wish to describe in this contribution some detailed NMR studies, which should help eventually in understanding the reduction processes better.

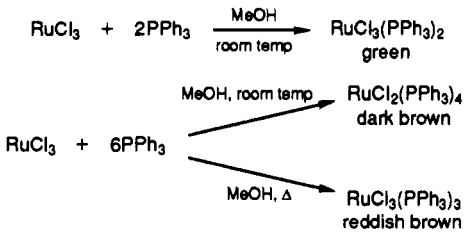
As stated by Seddon et al.,[31] commercial hydrated ruthenium chloride is an ill-defined material and a mixture of hydroxo, oxochloro, monomeric, and polymeric ruthenium complexes. One easily understands that the chemistry of the so-called ruthenium chloride in water has not been greatly investigated and is of an extreme complexity. For instance, evidence for the following pH-dependent equilibria has been reported:[32]

$$\mathrm{RuCl_2(H_2O)_5^{2+} + Cl^- \rightleftarrows RuCl_2(H_2O)_4^+ + H_2O}$$

$$\mathrm{RuCl_2(H_2O)_4^+ + Cl^- \rightleftarrows RuCl_3(H_2O)_3 + H_2O}$$

$$\mathrm{RuCl_3(H_2O)_3 + Cl^- \rightleftarrows RuCl_4(H_2O)_2^- + H_2O}$$

The synthesis of high-valent triphenylphosphine ruthenium derivatives is well-known from $RuCl_3$[33,34] to yield either $RuCl_2(PPh_3)_{3or4}$ or $RuCl_3(PPh_3)_2$, depending on the experimental conditions.



Adding 4 equiv of TPPTS to a rigorously deaerated aqueous solution of ruthenium chloride afforded a dark reddish homogeneous mixture. The ^{31}P NMR spectra were recorded at different time intervals under ambient conditions to determine the evolution of the different species in the solution (see Figure 6). Three compounds have been detected: (i) TPPTS (δ = −5.8 ppm), (ii) TPPTS oxide (δ = +34 ppm), and (iii) a "Ru(II)/TPPTS" complex (δ = +57 ppm).

About 7 h was necessary to reach a plateau corresponding to the following composition: TPPTS = 56%; OTPPTS = 28%; "Ru/TPPTS" = 16% (OTTPTS stands for TPPTS oxide).

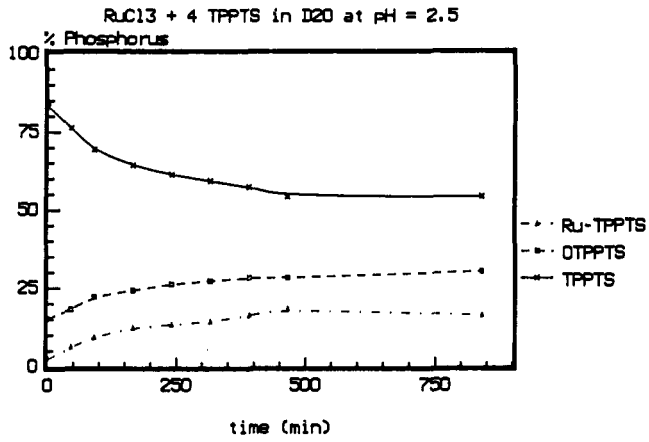


Figure 6.

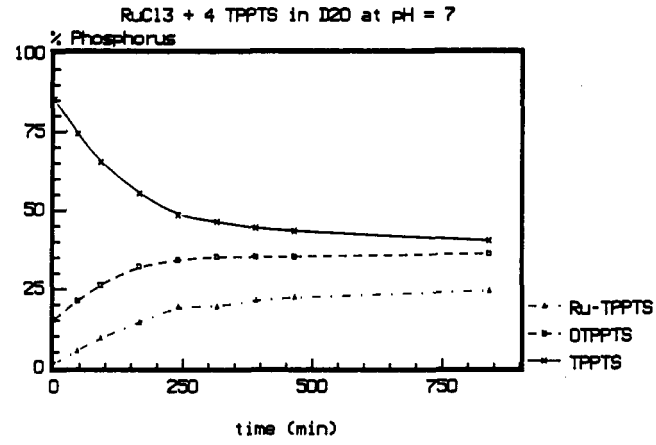
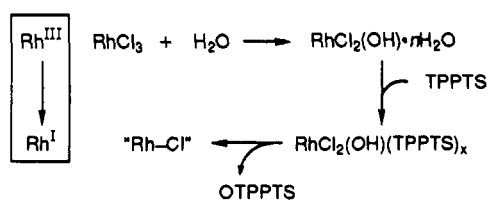


Figure 7.

As illustrated in Figure 7, the same behavior was observed in the buffered (pH = 7) medium but with a slight difference in the composition: TPPTS = 40%; OTPPTS = 36%; "Ru/TPPTS" = 24%.

Whatever the pH was, the complexation of the water-soluble phosphine and the ruthenium did not occur immediately and appeared to be an unfavorable step. Moreover, we observed another phenomenon, namely the phosphine oxidation, suspected to occur prior to the coordination.

The stoichiometric oxidation of TPPTS in water by rhodium chloride has been described previously in the literature.[35] The plausible redox mechanism assessed by NMR experiments involved hydroxo–rhodium intermediates to explain the oxygen transfer from the water to the phosphorus atom.



The same process should take place in our experiments, although we were unable to isolate any kind of hydroxo–ruthenium complex. Nevertheless, we propose a redox reaction accounting for the reduction of Ru(III) concommitant with the oxidation of the phosphine.

$$\mathrm{Ru^{III}Cl_3 + (\mathit{n} + \tfrac{1}{2})TPPTS + \tfrac{1}{2}H_2O \rightarrow Ru^{II}Cl_2(TPPTS)_\mathit{m} + \tfrac{1}{2}OTPPTS + (\mathit{n}-\mathit{m})TPPTS + HCl}$$

Again, attempts to isolate the Ru(II)/TPPTS complex starting from the mixture $RuCl_3$/TPPTS failed, but we believe the Ru(II)/TPPTS complex should correspond to the formula $[RuCl_2(TPPTS)_2]_2$. This compound has been fully characterized and synthesized by a phosphine-exchange reaction using $RuCl_2(PPh_3)_3$ and TPPTS.[36] Its ^{31}P NMR spectra display a low-field NMR shift at +57 ppm.

The effect of the ligand concentration becomes more understandable in light of these experiments. Clearly, the complexation is not facile since, under equilibrium conditions (in the case of the buffer solution for instance), we note only 24% of the total phosphorus coordinated to the ruthenium center. Assuming a molar ratio TPPTS/Ru of 3 gives 30% of the initial ruthenium bound to TPPTS. Consequently, an increase in the ligand concentration results in an increase of the "Ru/TPPTS" species.

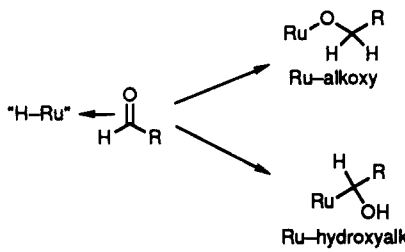
The ^{31}P NMR spectra of a hydrogenated solution of $RuCl_3$/10TPPTS show a broad peak at δ = +57 ppm. Neither proton NMR nor IR experiments allow the detection of the hydride resonance, as expected, whereas $HRuCl(TPPTS)_3$ could be prepared independently and perfectly characterized by NMR spectroscopy.[36] Since the reduction of the substrate needs the molecular hydrogen activation, we may envision the following sequence yielding a possible active catalyst.

$$[RuCl_2(TPPTS)_2]_2 \xrightarrow{+\,H_2,\ -\,TPPTS} [RuHCl(TPPTS)_2]_2 \xrightarrow{+\,TPPTS} HRuCl(TPPTS)_3$$

^{31}P NMR (D_2O) δ = 56 ppm

^{31}P NMR (D_2O) δ = 57 ppm; ^1H NMR (D_2O) δ = −18.5 ppm (q)

The mechanism of aldehyde hydrogenation with ruthenium catalysts[37] has been discussed in terms of elementary steps involving (i) coordination of an aldehyde to a low-valent coordinatively unsaturated hydrido–Ru(II) complex, (ii) hydride transfer to a coordinated aldehyde to form either a metal–alkoxy or metal–hydroxyalkyl intermediate



(iii) oxidative addition of molecular hydrogen, and (iv) reductive elimination of alcohol, which completes the cycle.

All these steps can be accommodated for $HRuCl(TPPTS)_3$, as in Scheme II.

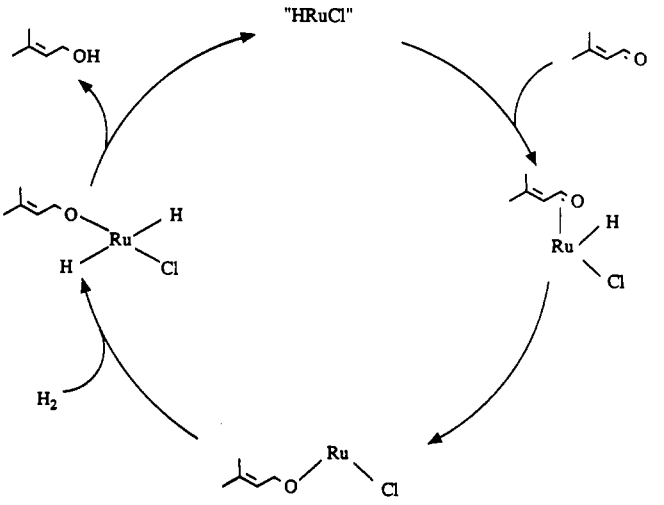
From our kinetics data, the coordination step is fast and the oxidative addition of hydrogen appears to be rate determining. At high TPPTS concentration, the rate nondependence on the ligand concentration shows that dissociation of TPPTS is not an important feature of the reaction.

In the absence of conclusive spectroscopic evidence, we cannot rule out a zero-valent ruthenium catalyst. NMR studies of the complex $HRuCl(TPPTS)_3$ in the presence of hydrogen have demonstrated the existence of an equilibrium between mono- and dihydrido species.[36]

$$HRuCl(TPPTS)_3 + H_2 + TPPTS \rightleftarrows H_2Ru(TPPTS)_4 + HCl$$

This pathway might involve the dihydrido complex (or its tautomeric η^2-H_2 complex[38,39]) as a potential catalytic intermediate. In this case, oxidative addition of H_2 to an electron-rich Ru(0)/TPPTS complex should take place prior aldehyde coordination. These mechanisms remain speculative, and much work has to be done in order to elucidate the nature of the intermediates.

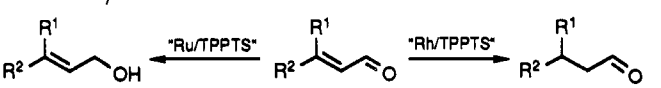
Scheme II. Plausible Mechanism for the Ruthenium-Catalyzed Hydrogenation of 3-Methyl-2-butenal[a]



[a] Ligands are omitted for the sake of clarity.

Conclusions

The work presented in this paper has demonstrated again the potentiality of catalysis in water through a new application. High regioselectivity and easy recycling of the aqueous catalytic phase are the important features described here. We have shown it was possible to direct the hydrogenation by carefully choosing the nature of the metal so that α,β-unsaturated aldehydes could be reduced either into the corresponding allylic alcohols with the "Ru/TPPTS"[40] system or into the saturated aldehydes with "Rh/TPPTS".[41]



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Registry No. TPPTS, 63995-70-0; $(CH_3)_2C{=}CHCHO$, 107-86-8; $(CH_3)_2C{=}CHCH_2OH$, 556-82-1; $H_2Ru(PPh_3)_4$, 19529-00-1; $RuCl_2(PPh_3)_3$, 15555-77-8; $HRuCl(CO)(PPh_3)_3$, 16971-33-8; $HRu(OAc)(PPh_3)_3$, 25620-80-8; $RuCl_3{\cdot}3H_2O$, 13815-94-6; PPh_3, 603-35-0; $PhCH{=}CHCHO$, 104-55-2; $OHCCH{=}CHCH_3$, 4170-30-3; $(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO$, 5392-40-5; $PhCH{=}CHCH_2OH$, 104-54-1; $H_3CCH{=}CHCH_2OH$, 6117-91-5; $(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OH$, 624-15-7; $[IrCl(COD)]_2$, 12112-67-3; $[RhCl(COD)]_2$, 12092-47-6; $Ph(CH_2)_2CHO$, 104-53-0; $(CH_3)_2CHCH_2CHO$, 590-86-3; $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CHO$, 5988-91-0; $H_3CCH_2CH_2CHO$, 123-72-8; sodium formate, 141-53-7.

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