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Heteropolyacids enhanced the catalytic activity of $Rh_6(CO)_{16}$ in the hydroformylation of alkenes

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Active homogeneous catalytic systems based on $Rh_6(CO)_{16}$-heteropolyacids for the regioselective hydroformylation of styrene and 1-octene and their derivatives have been developed. The effects of the amount and the type of the heteropolyacid have been studied and showed a significant improvement of the conversion of styrene and the selectivity towards branched aldehydes. Other rhodium complexes were also considered in the study and the results showed the advantages of the rhodium cluster $Rh_6(CO)_{16}$ associated with the heteropolyacid $H_3PW_{12}O_{40}$,$25H_2O$ (HPA-W_{12}). The effects of temperature, type of solvent and CO/H_2 pressure have also been considered in order to optimize the reaction conditions. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: hydroformylation; rhodium cluster; heteropolyacids; styrene; 1-octene; alkenes; triphenyl phosphite; syngas

INTRODUCTION

Oxo syntheses are mainly catalyzed by cobalt (Co) and rhodium (Rh) complexes. While the industrially relevant product range of hydroformylation has remained more or less unchanged over the past 20 years, research work has continued actively in this area.[1–11] The complex catalysts for hydroformylation and carbonylation reactions profited considerably from advanced knowledge of the correlation between central atoms and ligands on the one hand and their activity and selectivity relationships on the other. For example, hydroformylation of vinylarenes, alkenes and cyclic olefins has been investigated using (1,5-cyclooctadiene)salicyladoximatorhodium, [Rh(SOX)(COD)], as catalyst precursor at 1 bar and 60 °C in toluene. The combination of Rh(SOX)(COD) with diphosphine ligands is more active in the hydroformylation of vinylarenes, but those with monophosphine ligands are favored in the hydroformylation of alkenes.[12] The hydroformylation reaction of cyclopentene, cyclohexene, 4-vinylcyclohexene, and some cyclic dienes catalyzed with a Rh(acac){$P(OPh)_3$}$_2$/$P(OH)_3$ system at 80 °C and 10 bar CO : H_2 = 1 : 1 was studied. The main reaction products of 1,3- and 1,4-cyclohexadienes and 1,3-cyclopentadiene were unsaturated monoaldehydes. In the hydroformylation of 1,5-cyclooctadiene the main product was formylcyclooctene.[13] The selectivity in the hydroformylation of 1-decene by homogeneous catalysis with $RhH(CO)(PPh_3)_3$ was studied. Aromatic solvents (benzene, toluene) gave total selectivity to aldehyde products, but alcoholic solvents gave higher *n/iso* ratios. The presence of an excess of phosphine also led to improved *n/iso* ratios.[14]

Mixed bidentate (P–N) ligands, e.g. $Ph_2P(CH_2)_2Py$ (Py = 2-pyridyl) and $Ph_2P(CH_2)_2N(CH_3)_2$, were found to enhance the rate of the rhodium-catalyzed hydroformylation of olefins.[15] Mixed amino phosphine oxide ligands, e.g. $Ph_2P(O)CH_2NMe_2$, combined with $[RhCl(COD)]_2$ show high reactivity and selectivity for the formation of the branched aldehyde in styrene hydroformylation.[16] A batch process for the hydroformylation of isobutene was developed for the production of isovaleraldehyde using a non-phosphine $Rh(CO)_2(acac)$ system at extremely low levels of rhodium.[17] Hydroformylation of 2,4,4-trimethyl-1-pentene was studied between 30–130 °C at 20–120 bar CO/H_2 = 1 using $Na_2[Rh_{12}(CO)_{30}]$ as the catalyst precursor. In the highly chemoselective reaction 3,5,5-trimethylhexanal formation approaches 100%.[18] The influence of the temperature on the regioselectivity in the hydroformylation of the vinylpyrroles has been investigated in the range of 20–100 °C at 120 bar CO/H_2 = 1 : 1 using $Rh_4(CO)_{12}$ as the catalyst precursor.[19] The combination of $P(OPh)_3$ and $Rh(acac)(CO)_2$ shows very high catalytic activity but poor regioselectivity. The catalytic activity strongly depends on the P/Rh ratio, but the regioselectivity is not markedly

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affected by the P/Rh ratio.[20] Other rhodium-based catalyst systems, including $(OC)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, $(OC)_2RhMo(CO)_3(C_5H_4PPh_2)_2$, $(OC)_2RhW(CO)_3(C_5H_4PPh_2)_3$ and $[Rh(OAc)_2]_2/PPh_3$, have been used in the hydroformylation of 1-hexene, styrene and some phosphino-, amino- and amido-alkenes. In general the catalysts showed very similar activity and selectivity.[21]

The homogeneous catalytic hydroformylation of cyclohexene to cyclohexanecarboxaldehyde was studied, starting with $Rh_4(CO)_{12}$ as catalyst precursor in *n*-hexane as solvent.[22] The hydroformylation of 1,1-diarylethenes, 1,1-diarylallylalcohols and aryl vinyl ethers was carried out in a biphasic system water/toluene (cyclohexane) in the presence of rhodium carbonyl complexes with the water-soluble ligand, sulfonated triphenylphosphine $P(C_6H_4\text{-m-}SO_3Na)_3$ (TPPTS), under standard reaction conditions.[23] Hydroformylation reactions of a series of alkenes and alkynes have been carried out using the heteronuclear rhodium–tungsten catalyst, $(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$. The results of these reactions have been compared with corresponding reactions using $[Rh(OAc)_2]_2$ as the catalyst precursor. Catalytic hydroformylation of styrene using a rhodium-tungsten catalyst gave a very high yield of the branched chain aldehyde containing only a trace of the straight chain isomer.[24]

Keggin-type heteropolyanions containing molybdenum (Mo) or Vandium (V) as addenda atoms show an appreciable promoting effect on $PdCl_2$ catalyzed reductive carbonylation of nitrobenzene to form methyl-*N*-phenyl carbamate in the presence of methanol in a moderately polar solvent such as 1,2-dimethoxyethane at 130–170 °C under an initial CO pressure of 10–40 atm.[25–27] $PdCl_2$ has been confirmed to be the best palladium precursor but the addition of pyridine hinders the reaction.[25–27] The carbonylation of alcohols, ethers and ether alcohols to esters and/or to carboxylic acids has been discovered.[28,29] The reaction is carried out in the vapor state over a solid catalyst comprising a polyoxometallate anion in which a group VIII metal such as rhodium, iridium, palladium, cobalt or nickel was used at 225 °C and 1 atm (1.01 bar).

The use of heteropolyacids in conjunction with rhodium catalysts has not yet been fully investigated in hydroformylation reactions. Heteropolyacids may protonate and stabilize the rhodium carbonyl intermediate species and also form active Rh–W intermediates for the carbonylation reactions.

EXPERIMENTAL SECTION

General

Styrene derivatives, alkyl alkenes, anisole and all solvents were highly pure (>99%) and were purchased from Sigma-Aldrich Company. The solvents used in the experiments, such as THF, hexane, CH_2Cl_2, benzene, 1,2-dimethoxyethane, 1,4-dioxane, methyl ethyl ketone, acetone, methanol, ethanol and other solvents, were all HPLC-grade and were stored under nitrogen over activated 3 Å molecular sieves and also purchased from Sigma-Aldrich. $RhCl_3$, $3H_2O$, $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, $RhHCO(PPh_3)_3$, $RhCl(PPh_3)_3$, $Rh_6(CO)_{16}$, Rh/C (5% Rh) and other catalysts were purchased from Strem, stored under nitrogen and used without purification. The heteropolyacids $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_3SiMo_{12}O_{40}$, were purchased from Sigma-Aldrich and used as received. The heteropolyacids of general formula $H_{3+n}PMo_{12-n}V_nO_{40}$, xH_2O (HPA-*n*; $n = 1–5$) were prepared according to procedures described in the literature.[30–34]

The carbonylation reactions were carried out in 45 ml high-pressure Parr autoclaves. The products of the reaction of hydroformylation were characterized using NMR, GC and GC-MS techniques. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Joel 1500 NMR machine. Chemical shifts were reported in ppm (δ) relative to tetramethyl silane (TMS) using $CDCl_3$. Gas chromatography analyses were achieved on an HP 6890 equipped with capillary column HP-5 in the presence of anisole as internal standard. The products were identified on a bench GC-MS spectrometer (Varian 3800 coupled with mass spectrometer Saturn 2000). A Varian 3800 gas chromatograph equipped with a capillary column HP was also used. The pure mixtures of aldehydes were isolated by thin-layer chromatography (TLC) performed on silica gel Merck 60 F254 plates (250 μm layer thickness).

General procedure for the hydroformylation of aryl and alkyl alkenes

A mixture of styrene or 1-octene (5.0 mmol), rhodium catalyst (0.005 mmol) and heteropolyacid (0.010 mmol) dissolved in 5.0 ml of dry solvent was placed in the liner of a 45 ml high-pressure Parr autoclave. The autoclave was flushed thoroughly three times with carbon monoxide, subsequently pressurized with carbon monoxide followed by hydrogen. The autoclaves were placed in oil baths heated on hotplates controlled by temperature sensor to maintain the temperature constant (±0.5 °C). The rate of stirring was maintained at 750 rpm. After the reaction time elapsed, the autoclave was cooled down to room temperature and the gas was carefully released (carbon monoxide is a very poisonous gas) and the autoclave was opened. The reaction mixture was filtered through celite to remove the catalyst. Anisole, 100 μg, as internal standard was added to the mixture to determine the conversion of styrene. The products were identified using GC-MS, ^1H and ^{13}C NMR techniques. The data were compared with authentic products or to the literature data.[14,18,21,36] The ratio of branched to linear aldehydes was determined by GC and ^1H NMR.

RESULTS AND DISCUSSION

The homogeneous hydroformylation reaction of styrene derivatives and alkyl alkenes produces a wide range of aldehydes that have interesting applications in industry, such as anti-inflammatory products from branched aldehydes and alcohols from linear isomers. Reaction optimization was carried out using styrene as a model substrate of aromatic alkenes and 1-octene as a model substrate of alkyl alkenes.

Hydroformylation of Aryl Alkenes

The rhodium complex $Rh_6(CO)_{16}$ showed the highest catalytic activity in the presence of the heteropolyacid $H_3PW_{12}O_{40}$ (HPA-W_{12}) in THF as a solvent at 40 °C and in the absence of any phosphine ligand. The ratio of syngas CO/H_2 was fixed as 1/1 with 600 psi (41.4 bar) of a total pressure of the syngas at room temperature. The effects of the amount of HPA-W_{12}, the temperature, the type of solvent, the CO/H_2 ratio, and the type of rhodium catalyst and the type of the heteropolyacids have been carefully studied in order to determine the most suitable conditions for hydroformylation prior to studying the hydroformylation of other aryl alkenes. The hydroformylation of styrene usually leads to the branched aldehyde, 2-phenylpropanal (**B**), and the linear aldehyde, 3-phenylpropanal (**L**) [equation (1)]. However, other by-products such as alcohols or hydrogenated products may also be formed.

Hydroformylation of styrene. Effect of the amount of $H_3PW_{12}O_{40}$, xH_2O

The effect of the amount of the heteropolyacid $H_3PW_{12}O_{40}$, xH_2O (HPA-W_{12}) as a cocatalyst in the hydroformylation of styrene was studied in the presence of the rhodium catalyst $Rh_6(CO)_{16}$ at 600 psi of syngas ($CO/H_2 = 1/1$) and 40 °C in THF as a solvent. The results of the study on the effects of the amounts of the heteropolyacid HPA-W_{12} are summarized in Fig. 1. The conversion of styrene was 61% in the absence of HPA-W_{12} and selectivity toward the branched aldehyde **B** was high (92%). The conversion of styrene into aldehydes increased from 61 to 74% with the addition of 0.0025 mmol of the co-catalyst HPA-W_{12}. The increase in the amount of the co-catalyst to 0.010 mmol improved the conversion to 97%. The selectivity toward the branched aldehyde was maintained as extremely high (92–94%). Surprisingly, the further addition of the heteropolyacid HPA-W_{12} inhibited the reaction of hydroformylation of styrene; the conversion of styrene dropped to 75% using 0.030 mmol of HPA-W_{12}. The role of the heteropolyacid HPA-W_{12} in the hydroformylation of styrene-catalyzed by rhodium (I) was most probably to protonate some possible intermediate species such as $Rh_5(CO)_{15}^{2-}$ and also in the formation of an active intermediate [W-Rh].

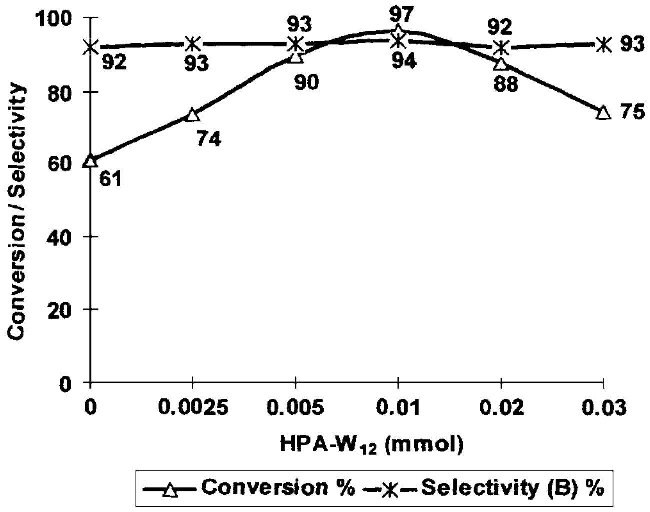

Figure 1. Hydroformylation of Styrene by $Rh_6(CO)_{16}$. Effect of the amount of HPA-W_{12}. Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol), styrene (0.5208 g = 5.0 mmol). THF (5 ml), 600 psi ($CO–H_2 = 1:1$), 40 °C, 16 h.

Hydroformylation of styrene. Effect of the type of the heteropolyacids

Other Keggin heteropolyacids such as $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$, used instead of HPA-W_{12}, also gave high conversions of styrene (90%) (Table 1, entries 1, 3). However, the ammonium salts $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$ (Table 1, entries 4, 5), and the presence of vanadium in the structure of HPA-*n*, such as $H_5PMo_{10}V_2O_{40}$ and $H_7PMo_8V_4O_{40}$ (Table 1, entries 6, 7) decreased the conversions of styrene to 74–78%. The selectivity toward the branched aldehyde **B** was high (>90%). It seems clear that these later polyoxometallates had no effect on the occurrence of the reactions and most probably do not form complexes with $Rh_6(CO)_{16}$ under the experimental conditions.

Hydroformylation of styrene. Effect of the temperature with $Rh_6(CO)_{16}$

The catalyst systems combining $Rh_6(CO)_{16}$ or $RhCl_3$, $3H_2O$ and HPA-W_{12} were carefully studied at different temperatures (Table 2). We were surprised to observe that the hydroformylation of styrene occurred with the system $Rh_6(CO)_{16}$–HPA-W_{12} even at room temperature (approximately 25 °C) with 42% conversion of styrene after

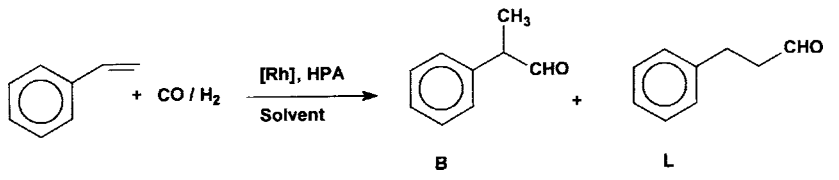

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Table 1. Hydroformylation of styrene. Effect of varying the type of the heteropolyacids and polyoxometallate.[a]

Run	Cocatalyst	Conversion,[b] %	Product distribution,[c] % B/L
1	$H_3PMo_{12}O_{40}$	90	93/7
2	$H_3PW_{12}O_{40}$	97	94/6
3	$H_4SiMo_{12}O_{40}$	90	91/9
4	$(NH_4)_3PMo_{12}O_{40}$	70	90/10
5	$(NH_4)_3PW_{12}O_{40}$	76	92/8
6	$H_5PMo_{10}V_2O_{40}$	74	94/6
7	$H_7PMo_8V_4O_{40}$	78	91/9

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.010 mmol), HPA (0.010 mmol), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi ($CO-H_2 = 1:1$), 40 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.
B = branched. L = linear.

Table 2. Hydroformylation of Styrene by $Rh_6(CO)_{16}$-HPA-W_{12}. Effect of the temperature[a]

Run	T, °C	Conversion,[b] %	Product distribution,[c] % B/L
1	25	5	98/2
2	40	20	92/8
3[d]	40	97	94/6
4	50	47	92/8
5[e]	50	35	95/5
6	60	94	88/12
7[f]	60	69	89/11
8[e]	60	58	90/10
9[f]	80	98	73/27
10	80	100	75/25
11[g]	60	96	93/7

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol, 0.001 g), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi ($CO-H_2 = 1:1$), 6 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.
[d] Reaction time = 16 h.
[e] No HPA-W_{12} was used.
[f] Reaction time = 3 h.
[g] $P(OPh)_3$ (0.020 mmol) in place of HPA-W_{12}.

16 h of reaction with excellent selectivity (98%) to branched aldehydes **B**.

The hydroformulation of styrene by $Rh_6(CO)_{16}$–HPA-W_{12} at 40 °C suffers from the relatively prolonged time for completion of the reaction. The reaction time was improved significantly by increasing the reaction temperature to 60 °C; however, the selectivity was affected by the change. We have studied the effect of the temperature and the addition of a ligand with the objective of improving the reaction time while maintaining the selectivity and the conversion of the reaction relatively high.

The effect of the reaction temperature on the reaction time was studied carefully by considering a wide range of temperatures (25–80 °C) for the catalyst system $Rh_6(CO)_{16}$–HPA-W_{12} in tetrahydrafuran (THF) (Table 2). The results of the reaction after 6 h showed very low conversion (5–20%) at 25–40 °C (Table 2, entries 1–2). The conversion increased to 47% and further to 94% at 50 and 60 °C, respectively (Table 2, entries 3, 6). In the absence of HPA-W_{12}, conversions of styrene were lower (35 and 58%) at 50 and 60 °C, respectively (Table 2, entries 5, 8). The conversion after 3 h using $Rh_6(CO)_{16}$–HPA-W_{12} as catalytic system dropped to 69% at 60 °C (Table 2, entry 7). At 80 °C almost total conversion (98%) of styrene after 3 h was observed but the selectivity toward the branched aldehyde **B** dropped to 73% (Table 2, entry 8). The most interesting result was observed when HPA-W_{12} was replaced by the phosphite ligand $P(OPh)_3$ (Table 2, entry 11). The conversion was still excellent (96%) and the selectivity toward the branched aldehyde was also extremely high (93%) after 6 h of reaction.

Hydroformylation of styrene. Effect of the type of solvent

The study of the effect of changing the type of solvent on the hydroformylation of styrene by the catalytic system $Rh_6(CO)_{16}$–HPA-W_{12} is shown in Table 3. Among the tested solvents, THF, 1,2-dimethoxyethane (DME), 1,4-dioxane and dichloromethane (CH_2Cl_2), gave conversions of 97, 92, 88 and 84%, respectively (Table 3, entries 1–4). 2-Butanone and toluene gave lower conversions of styrene (45 and 46%). The catalytic system with other solvents such as acetonitrile and hexane gave traces or no reaction at 40 °C for 16 h. It seems that the catalytic system shows higher catalytic activity in polar (except acetonitrile) rather than in non-polar solvents. This can be explained by the stability of the catalytic active intermediate species in THF and other polar solvents. No major change was observed in terms of conversions with the same catalyst system $Rh_6(CO)_{16}$–HPA-W_{12}–THF used at 60 °C for 6 h.

Hydroformylation of styrene. Effect of the ratio of $CO–H_2$

The effect of the ratio of $CO–H_2$ at constant total pressure of 600 psi was also studied with the catalytic system $Rh_6(CO)_{16}$–HPA-W_{12} (Table 4). An increase in the ratio of $CO–H_2$ from 1 : 1 to 4 : 2 and 5 : 1 decreased the conversions of styrene from 97 to 75 and 28%, respectively (Table 4, entries 1–3). However, the decrease in the $CO–H_2$ ratio to 2 : 4 and 1 : 5 gave relatively high conversions (92 and 88%) with a slight drop in selectivity to the branched aldehyde **B** (Table 4, entries 4, 5). No products were obtained in the absence of hydrogen (Table 4, entry 6).

Hydroformylation of styrene. Effect of the reaction time at 40 °C

The study of the conversions of the reaction of the hydroformylation of styrene at different times with the

Table 3. Hydroformylation of styrene. Effect of solvent[a]

Run	Solvent	Conversion,[b] %	Product distribution,[c] % B/L
1	THF	97	94/6
2	DME	92	93/7
3	1,4-Dioxane	88	95/5
4	CH_2Cl_2	84	92/8
5	2-Butanone	45	94/6
6	Toluene	46	94/6
7	Acetonitrile	0	—
8	Hexane	3	99/1

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), solvent (5 ml), 600 psi ($CO-H_2$ = 1 : 1), 40 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.

Table 4. Hydroformylation of styrene. Effect of $CO-H_2$ initial pressure[a]

Run	Pressure $CO-H_2$ psi	Conversion,[b] %	Product distribution,[c] % B/L
1	300/300	97	94/6
2	400/200	75	92/8
3	500/100	28	93/7
4	200/400	92	89/11
5	100/500	88	86/14
6	600/0	—	—

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 40 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.

catalytic system $Rh_6(CO)_{16}$–HPA-W_{12} is summarized in Table 5. Low conversions after 3–6 h (28–34%) and good conversions after 9–12 h (70–82%) were obtained. The results indicate clearly that the kinetics of the reaction are slow with this catalytic system. It seems clear that the advantage of the slower reaction is to maintain high conversions and high selectivity of products.

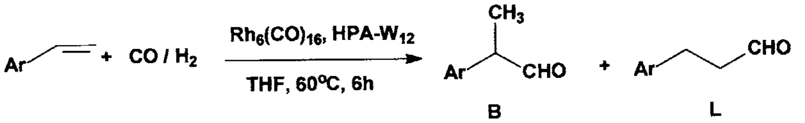
Hydroformylation of styrene. Effect of the type of rhodium catalyst

Different rhodium complexes have been used as catalysts in the presence HPA-W_{12} as a cocatalyst in THF at 40 °C for 16 h (Table 6). Low conversions (25 and 48%) of styrene were observed with the rhodium (I) complexes $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ (Table 6, entries 2 and 3). The heterogeneous catalyst Rh/C gave higher conversion (80%) of styrene (Table 6, entry 4). In all previous experiments, the selectivities were high (92–94%). No products or only traces of products were detected with the complexes $RhCl_3, 3H_2O$, $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ (Table 6, entries 5–7). The high catalytic activity of the cluster $Rh_6(CO)_{16}$ compared with other rhodium complexes is probably due to, as mentioned earlier, the protonation of the rhodium carbonyl intermediates and stabilization of the active catalytic intermediate Rh-W. Attempts to isolate this intermediate were not yet successful.

Hydroformylation of various aryl alkenes by $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2–THF

The hydroformylation of different styrene derivatives was achieved with high conversions and selectivities with the catalytic system $Rh_6(CO)_{16}$–HPA-W_{12}–CO/H_2–40 °C–16 h in THF as a solvent [equation (2)] (Table 7). The presence of a methyl group, two methyl groups, three methyl groups or *p*-tert-butyl substituted on the benzene ring did not affect the reactivity of styrene derivatives in terms of conversions and selectivities of branched aldehydes **B** (Table 7, entries 2–5). However, the *p*-methoxystyrene gave excellent conversion and selectivity in the presence of $H_3PMo_{12}O_{40}$ (HPA-Mo_{12}; Table 7, entry 6) in place of HPA-W_{12}, because we have observed that 50% of *p*-methoxystyrene was polymerized with HPA-W_{12} but not with HPA-Mo_{12}. 2-Chloro, 4-chlorostyrene and 2-vinylnaphthalene were also very reactive substrates and led to excellent conversions and selectivities of the reactions (Table 7, entries 7–8, 10). 3-Nitrostyrene also undergoes hydroformylation with relatively good conversion (64%) and selectivity toward the corresponding branched aldehyde **B** (86%) (Table 7, entry 9).

β-Methylstyrene reacted under the conditions of the catalytic system including $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2–40 °C–16 h and gave a good conversion (65%), forming two branched aldehydes, $\mathbf{B_1}$ and $\mathbf{B_2}$, with a ratio of 84 : 16 [equation (3)].



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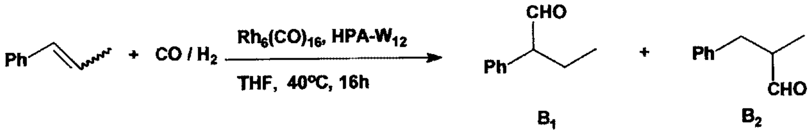

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Table 5. Hydroformylation of styrene. Effect of the reaction time[a]

Run	Time, h	Conversion,[b] %	Product distribution,[c] % B/L
1	3	28	94/6
2	6	34	93/7
3	9	70	92/8
4	12	82	93/7
5	16	97	94/6

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), THF 5 ml), 40 °C.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^{1}H NMR.

Table 6. Hydroformylation of styrene. Effect of the type of rhodium catalyst.[a]

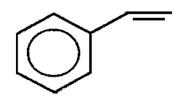
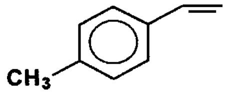
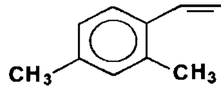
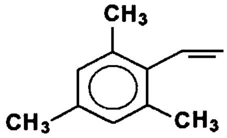
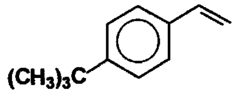
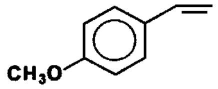
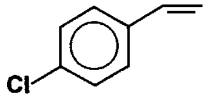
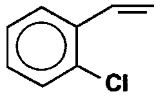
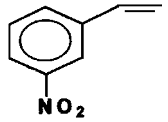
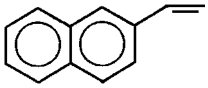
Entry	Rhodium catalyst (mmol)	Conversion,[b] %	Product distribution,[c] % B/L
1	$Rh_6(CO)_{16}$ (0.001)	97	94/6
2	$[Rh(COD)Cl]_2$ (0.0050)	25	94/6
3	$[Rh(CO)_2Cl]_2$ (0.005)	48	93/7
4	Rh/C (5%) 0.005 mmol of Rh	80	92/8
5	$RhCl_3$, $3H_2O$ (0.005)	—	—
6	$RhCl(PPh_3)_3$ (0.005)	Traces	—
7	$RhH(CO)(PPh_3)_3$ (0.005)	Traces	—

[a] Reaction conditions: HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO–H_2 = 1 : 1), 40 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^{1}H NMR.

It appears that the catalytic systems $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2–40°C–16 h in THF are efficient homogeneous systems for the hydroformylation of styrene derivatives at low temperature leading to excellent conversions of alkenes and excellent selectivities toward branched aldehydes.

Hydroformylation of Alkyl Alkenes

Table 7. Hydroformylation of various aryl alkenes by $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2–THF[a]

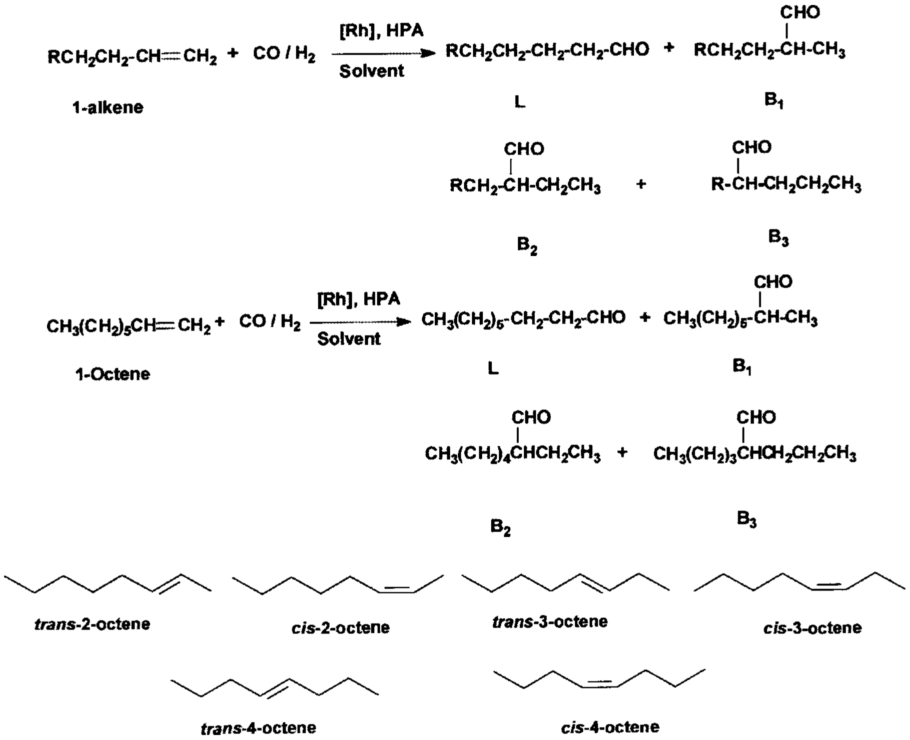
Entry	Substrate	Conversion,[b] %	Product distribution,[c] % B/L
1		97	94/6
2		96	93/7
3		95	92/8
4		95	92/8
5		97	93/7
6[d]		96	93/7
7		98	95/5
8		96	93/7
9		64	86/14
10		98	93/7

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.010 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (5.0 mmol), THF (5 ml), 600 psi (CO–H_2 = 1 : 1), 40 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^{1}H NMR.
[d] $H_3PMo_{12}O_{40}$ (HPA-Mo_{12}) was used in place of HPA-W_{12}.

In general, the alkyl alkenes are not very reactive in this hydroformylation reaction and lead to complex mixtures of products. During our study we have also explored the reaction of hydroformylation of 1-octene and other terminal alkyl alkenes using the catalytic system applied for styrene derivatives and also other rhodium catalysts. The reaction gave a mixture of aldehydes (four to six isomers) with the terminal **L** and the branched **B** aldehydes as predominant isomers [equation (4)]. We would like to report in this section the study of the hydroformylation of 1-octene and also other alkyl alkenes.

Hydroformylation of 1-octene. Effect of the temperature with $Rh_6(CO)_{16}$ and $[Rh(COD)Cl]_2$

The hydroformylation of 1-octene was carried out in the presence of the catalytic system Rh(I)–HPA-W_{12}–CO–H_2 in



(4)

(5)

Scheme 1.

THF as a solvent [equation (5)]. The preliminary results with 1-octene showed again that the heteropolyacid HPA-W_{12} was the most active heteropolyacid and THF was the most suitable solvent among the other solvents considered in this reaction. We have studied the effects of the temperature with the two rhodium (I) catalysts $Rh_6(CO)_{16}$ and $[Rh(COD)Cl]_2$ (Tables 8 and 9). The conversion of 1-octene was 10% at room temperature (Table 8, entry 1) and 49, 75 and 94% at 40, 45, 50 °C, respectively (Table 8, entries 2–4). In contrast with styrene, the selectivity with 1-octene was less affected by temperature and was maintained almost the same with ratios 43–48 : 52–57%. The low selectivity with 1-octene is common for many homogeneous and heterogeneous catalytic systems due to electronic effects. The presence of the alkyl group, as a weak electron-donating group on the double bond, facilitates almost equally the coordination of rhodium complex on the terminal carbon as well as the internal carbon of the double bond. The two carbon atoms are equally reactive toward rhodium coordination, especially in the absence of a bulky phosphine ligand that favored the access to the terminal carbon of the double bond leading to the linear aldehyde as the major product. In addition, the use of $P(OPh)_3$ in place of HPA-W_{12} did not improve significantly the conversion of 1-octene and the selectivity of the reaction (Table 8, entry 8). After 6 h of reaction the conversion was 70% and the selectivity toward branched aldehyde **B** increased slightly to 52%. Therefore, $P(OPh)_3$ was not considered for the hydroformylation of 1-octene as no real improvement in the conversion and the selectivity has been shown at different experimental conditions of temperature and reaction time. In addition, the unreacted 1-octene was isomerized to different internal octenes (Scheme 1).

The rhodium (I) catalyst $[Rh(COD)Cl]_2$ was also considered in the study of the effect of temperature in the hydroformylation of 1-octene in the presence of HPA-W_{12} as a cocatalyst in THF as a solvent (Table 9). The reaction gave traces and low conversions (5–32%) at temperatures 25–80 °C. It seems that $[Rh(COD)Cl]_2$ was probably sensitive to acidity and did not form the expected active intermediate complex with HPA-W_{12}. The selectivity of the reaction was the same (36–38 : 62–64%) with a small increase toward the linear aldehyde **L** compared to $Rh_6(CO)_{16}$.

Hydroformylation of 1-octene. Effect of the reaction time

The study of the effect of the reaction time was also achieved with the catalyst system $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2 at 50 °C in THF (Table 10). The rate of the reaction of the hydroformylation of 1-octene was comparable to the reaction of styrene; conversions of 10, 24, 34, 65 and 86% were obtained at 2–12 h (Table 10, entries 1–5). The maximum conversion was achieved after 16 h of reaction. The rate of the reaction could be improved by increasing the temperature to 80 and

Table 8. Hydroformylation of 1-octene with $Rh_6(CO)_{16}$. Effect of temperature[a]

Run	*T*, °C	Conversion,[b] %	Product distribution,[c] B_1/L %	1-Octene, %	Other octene isomers, %
1	25	10	48/52	90	10
2	40	49	47/53	86	14
3	45	75	46/54	78	22
4	50	94	45/55	72	28
5	60	94	43/57	66	34
6[d]	60	65	38/62	64	36
7[e]	60	40	39/62	68	32
8[d,f]	60	70	52/48	45	55

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (0.6111 g = 5.0 mmol), THF (5 ml), 600 psi ($CO{-}H_2 = 1:1$), 16 h.

[b] Determined by GC using anisole as internal standard.

[c] Determined by GC and ^1H NMR.

[d] Reaction time = 6 h.

[e] Reaction time = 6 h, no HPA-W_{12} was used.

[f] $P(OPh)_3$ (0.020 mmol) in place of HPA-W_{12}.

Table 9. Hydroformylation of 1-octene with $[Rh(COD)Cl]_2$. Effect of temperature[a]

Run	*T*, °C	Conversion,[b] %	Product distribution,[c] B_1/L %	1-Octene, %	Other octene isomers, %
1	25	Traces	—	99	1
2	40	Traces	—	99	1
3	45	Traces	—	99	1
4	50	5	38/62	95	5
5	60	13	37/63	92	8
6	70	21	36/64	90	10
7	80	32	34/66	88	12

[a] Reaction conditions: $[Rh(COD)Cl]_2$ (0.005 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (0.6111 g = 5.0 mmol), THF (5 ml), 600 psi ($CO{-}H_2 = 1:1$), 16 h.

[b] Determined by GC using anisole as internal standard.

[c] Determined by GC and ^1H NMR.

100 °C but the selectivities of the reactions decreased by forming the other aldehyde isomers $\mathbf{B_2}$, $\mathbf{B_3}$ and $\mathbf{B_4}$.

Hydroformylation of 1-octene. Effect of the type of rhodium catalyst

Other rhodium complexes have been also used in the reaction of the hydroformylation of 1-octene (Table 11). The rhodium (III) complex, $RhCl_3.3H_2O$, gave no products of reaction at 50 °C (Table 3, entry 1) or only traces of aldehydes at 100 °C. Other rhodium (I) complexes, such as $[Rh(CO)_2Cl]_2$ and $RhH(CO)(PPh_3)_3$, also gave very low conversion of 1-octene at 50 °C (Table 11, entries 5, 6). The results obtained showed that $Rh_6(CO)_{16}$ combined with HPA-W_{12} under syngas ($CO{-}H_2 = 1:1$) in THF at 50 °C represents the most suitable catalytic system for the hydroformylation of various terminal alkyl alkenes.

Table 10. Hydroformylation of 1-octene. Effect of the reaction time[a]

Run	Time, h	Conversion,[b] %	Product distribution,[c] B_1/L %	1-Octene, %	Other octene isomers, %
1	2	8	47/53	96	4
2	4	24	46/54	94	6
3	6	34	45/55	90	10
4	9	65	46/44	86	14
5	12	86	44/56	79	21
6	16	94	45/55	72	28

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (5.0 mmol), THF (5 ml), 50 °C.

[b] Determined by GC using anisole as internal standard.

[c] Determined by GC and ^1H NMR.

Hydroformylation of various terminal alkyl alkenes

The hydroformylation of different terminal alkyl alkenes was carried out by the catalytic system formed of $Rh_6(CO)_{16}$–HPA-W_{12}–$CO{-}H_2$ in THF (Table 12). We have observed that alkenes with shorter alkyl chains, such as 1-heptene, were less reactive than 1-octene. At 50 °C the conversion of 1-heptene was only 46% compared with 66 and 86% at 60 and 80 °C, respectively (Table 12, entries 1–3). 1-Dodecene was as reactive as 1-octene; the conversion of 1-dodecene was 75% at 40 °C, 85% at 50 °C and 91% at 60 °C (Table 12, entries 5–7). 1-Tetradecene also undergoes the hydroformylation reaction with relatively high conversion (78%) at 60 °C (Table 12, entry 8). Interestingly, alkene isomerization was a function of temperature and the length of alkyl chain of the alkene. For example, at 50 °C the unreacted alkenes for 1-heptene, 1-octene and 1-dodecene at the end of the reaction were as follows: 83% as 1-heptene (17% other heptene isomers), 72% as 1-octene (28% other octene isomers) and 59% as 1-dodecene (41% other dodecene isomers). The effect of the temperature on the isomerization of 1-alkyl alkenes was clear with 1-heptene as a substrate, where the percentage of unreacted 1-heptene was 83% at 50 °C, 68% at 60 °C and 56% at 80 °C.

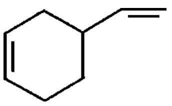
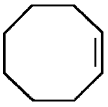
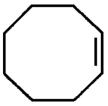
These results confirmed previous ones on the study of the effects of temperature on the hydroformylation of 1-octene (Table 8); the percentage of unreacted 1-octene dropped from 86% at 40 °C to 66% at 60 °C. The selectivity toward the linear aldehyde was increased when a bulky group was attached to the double bond. For example, the hydroformylation of 4-vinyl-1-cyclohexene was carried out at 60 °C leading to a mixture of branched and linear aldehydes with a ratio of 26 : 74 in favor of the linear product (Table 12, entry 9). Cyclooctene was less reactive than other non-aromatic alkenes. The

Table 11. Hydroformylation of 1-octene. Effect of the type of rhodium catalyst[a]

Run	Rhodium catalyst (mmol)	Conversion,[b] %	Product distribution,[c] B_1/L %	1-Octene, %	Octene isomers, %
1	$RhCl_3, 3H_2O$ (0.02)	—	—	—	—
2	$Rh_6(CO)_{16}$ (0.0010)	94	45/55	72	28
4	$[Rh(COD)Cl]_2$ (0.0050)	13	35/65	95	5
5	$[Rh(CO)_2Cl]_2$ (0.0050)	10	38/62	96	4
6	$RhH(CO)(PPh_3)_3$ (0.0050)	15	41/59	96	4

[a] Reaction conditions: HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (0.6111 g = 5.0 mmol), THF (5 ml), 600 psi ($CO{-}H_2$ = 1/1), 50 °C, 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.

Table 12. Hydroformylation of various alkyl alkenes and cycloalkenes[a]

				Product distribution,[c] %		Alkenes,[b] %	
No.	Alkene	T, °C	Conversion,[b] %	B_1/L	Other aldehyde isomers, $B_2 + B_3 + B_4$	1-Alkene	Other alkene isomers
1	1-Heptene	50	46	42/58	0	83	17
2	1-Heptene	60	66	69/61	0	68	32
3	1-Heptene	80	86	34/66	0	56	44
4	1-Octene	50	94	42/52	6	72	28
5	1-Dodecene	40	75	41/59	0	82	18
6	1-Dodecene	50	85	39/50	11	59	41
7	1-Dodecene	60	91	38/49	13	54	46
8	1-Tetradecene	60	78	38/50	12	45	55
9		60	87	26/74	—	—	—
10		60	35	100/0	—	—	—
11		80	58	100/0	—	—	—

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (5.0 mmol), THF (5 ml), 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.

conversion at 60 °C was only 35%, which improved to 58 at 80 °C (Table 11, entries 10, 11).

CONCLUSION

The results of our study show clearly that the homogeneous catalytic system $Rh_6(CO)_{16}$–HPA-W_{12}–CO–H_2–40°C–16 h in THF is active in the hydroformylation of styrene derivatives and alkyl alkenes. Excellent conversions of alkenes, in general, and excellent selectivity to aryl aldehydes were observed. The branched aryl aldehydes were the major products. Excellent conversions of alkyl alkenes were obtained at the relatively low temperature of 50–60 °C with high ratio of substrate to rhodium catalyst (1000 : 1). The hydroformylation of 1-octene led to almost equal amount of branched and linear aldehydes. Higher selectivity in linear aldehyde was observed at lower conversion. Also, the isomerization of unreacted alkenes was significant at high conversion. Attempts to improve the selectivity in linear or branched aldehydes with 1-alkenes, as well to solve the problem of isomerization of unreacted alkenes were not successful with the present catalytic system. The role of the heteropolyacid HPA-W_{12} is not yet understood and more studies are needed to clarify this issue.

We have shown in this study that the hydroformylation of styrene is sensitive to temperature, the type of the solvent, the amount and the type of the ligand or additives, and the CO–H_2 ratio. The choice of the type of rhodium complex is also very important. Among the rhodium complexes, the cluster $Rh_6(CO)_{16}$ showed the highest catalytic activity while other rhodium (I) and (III) complexes gave either low or no conversion of styrene.

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