

A Rh Cluster which selectively reduces Aldehyde Functions using CO and H₂O as the Hydrogen Source

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The Rh₆(CO)₁₆-*N,N,N',N'*-tetramethyl-1,3-propanediamine catalyst system has high activity for the reduction of aldehydes using CO and H₂O as the hydrogen source; unsaturated aldehydes give the corresponding unsaturated alcohols in high yields.

The application of the water gas shift reaction (WGSR) to organic synthesis is potentially significant because reduction can be carried out without the direct use of molecular hydrogen. Recently we have reported that Rh₆(CO)₁₆-diamine systems show high activities for nitrobenzene reduction and for alcohol synthesis from olefins under mild WGSR conditions.¹ Reduction of carbonyl functions is an important procedure in organic synthesis. We now report that the Rh₆(CO)₁₆-*N,N,N',N'*-tetramethyl-1,3-propanediamine catalyst system can reduce various aldehydes and ketones to the corresponding alcohols

using CO and H₂O. It should be noted that this catalyst system exclusively reduces the aldehyde function in the presence of an olefinic double bond.

The reaction procedure was similar to that used for a previously described alcohol synthesis.¹ Various amines were examined as additives in the reduction of nonanal using Rh₆(CO)₁₆. *N,N,N',N'*-Tetramethyl-1,3-propanediamine was found to be the most effective. The Rh₆(CO)₁₆ cluster complex had the highest activity; Rh₆(CO)₁₆ > [Rh(CO)₂Cl]₂ > RhCl₃·3H₂O > RhCl(PPh₃)₃. Table 1 shows examples of

Table 1. Reduction of carbonyl compounds using Rh₆(CO)₁₆-diamine as the catalyst.^a

Substrates	Products	Yield ^b (%)	Reaction conditions	
			<i>t</i> /h	<i>T</i> /°C
n-C ₈ H ₁₇ CHO	n-C ₈ H ₁₇ CH ₂ OH	>99	2.5	80
Me ₂ CHCHO	Me ₂ CH ₂ OH	>99	5.0	80
PhCHO	PhCH ₂ OH	>99	2.5	80
CH ₂ [CH ₂] ₄ C(:O)	CH ₂ [CH ₂] ₄ CHOH	94	10.0	80
PhCHO + PhC(:O)Me	PhCH ₂ OH	>99	5.0	30
PhCHO + PhCH=CH ₂	PhCH ₂ OH	98	5.0	30
	+ PhCH ₂ Me	2		
Me ₂ C=CH[CH ₂] ₂ CH(Me)CH ₂ CHO ^c	Me ₂ C=CH[CH ₂] ₂ CH(Me)CH ₂ CH ₂ OH	>99	5.0	60
Me ₂ C=CH[CH ₂] ₂ C(Me)=CHCHO ^d	Me ₂ C=CH[CH ₂] ₂ C(Me)=CHCH ₂ OH	94	48.0	30
	+ Me ₂ C=CH[CH ₂] ₂ CH(Me)CH ₂ CH ₂ OH	6		
	PhCH=CHCH ₂ OH	85	48.0	30
PhCH=CHCHO ^e	+ Ph[CH ₂] ₂ CH ₂ OH	14		
	+ Ph[CH ₂] ₂ CHO	1		

^a A stainless autoclave (120 ml) was used, reaction conditions: substrate, 3.0 mmol; Rh₆(CO)₁₆, 0.05 mmol; Me₂N[CH₂]₃NMe₂, 15 mmol; H₂O, 40 mmol; *P*_{CO}, 5 atm.; 2-ethoxyethanol, 0.5 ml. ^b Determined by g.l.c. ^c *P*_{CO}, 10 atm. ^d H₂O, 10 mmol; *P*_{CO}, 10 atm. ^e Me₂N[CH₂]₃NMe₂, 30 mmol; H₂O, 10 mmol; *P*_{CO}, 20 atm.

aldehydes and ketones reduced using the $\text{Rh}_6(\text{CO})_{16}$ - N,N,N',N' -tetramethyl-1,3-propanediamine system. Aliphatic and aromatic aldehydes were smoothly reduced to the corresponding alcohols. Ketones showed lower reactivity than aldehydes for reduction; a prolonged reaction time was necessary for a high conversion of cyclohexanone. The reduction of aldehydes took place at temperatures as low as 30 °C, which is in sharp contrast with the WGSR.² The catalytic hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols is a challenging problem owing to the higher co-ordinating power of the olefins.³ Many effective catalysts for selective aldehyde reduction are inhibited by at least two additional metals. We find that the use of this rhodium catalyst system achieves selective reduction of carbonyl functions in unsaturated aldehydes. Citronellal gave citronellol as the sole product. The α,β -unsaturated aldehydes, cinnamaldehyde and citral gave cinnamyl alcohol (85% yield) and 3,7-dimethyl-2,6-octadien-1-ol (94%), respectively. The high selectivity for aldehyde functions was also proved by the competitive reaction of benzaldehyde and styrene, which afforded benzyl alcohol with only a small amount of ethylbenzene. The high activity for the reduction of carbonyl functions is due to

facile formation of the metal hydride anion⁴ which then brings about nucleophilic attack on the carbonyl groups.

α,β -Unsaturated aldehydes gave products where the olefinic double bond was reduced exclusively on using 4-dimethylaminopyridine in place of the diamine.¹ The choice of suitable amines together with the presence of the $\text{Rh}_6(\text{CO})_{16}$ complex allows selective reduction of the carbonyl or olefinic function of unsaturated aldehydes under WGSR conditions.

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