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Direct Formation of Alcohols in Homogeneous Hydroformylation catalysed by Rhodium Complexes

Joanna K. MacDougall and David J. Cole-Hamilton*

Chemistry Department, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

Hydroformylation of hex-1-ene catalysed by $[RhH(PEt_3)_3]$ or $[Rh_2(OAc)_4]/PR_3$, R = Me, Et, or Bu, produces a mixture of aldehydes and alcohols in toluene or tetrahydrofuran but exclusively alcohols in ethanol; $[Rh_2(OAc)_4]$ or $[RhH(CO)(PPh_3)_3]$ produce mainly aldehydes or acetals when ethanol is used as the solvent.

Hydroformylation is a major industrial process and systems based on $Co_2(CO)_8$ with or without added tertiary phosphines and on $[RhH(CO)(PPh_3)_3]$ have been commercialised.[1] The rhodium based systems operate under considerably milder conditions than those based on cobalt, although the products are exclusively aldehydes. The cobalt based catalysts, particularly when promoted by tertiary phosphines, give alcohol products. Short chain aldehydes (*e.g.*, butanal) are desirable for condensation reactions, but the longer chain products are normally required as alcohols for *e.g.*, saponification. In view of the milder reaction conditions and higher selectivities that are obtainable with rhodium catalysis, it would be of considerable interest to develop rhodium catalysts that give direct conversion to alcohols.

The rhodium containing catalyst most studied[2] is $[RhH(CO)(PPh_3)_3]$ and replacement of the PPh_3 groups with *e.g.*, PBu_3 has generally led to increased alkene isomerisation and reduced hydroformylation.[3] Alcohols have been reported[4] as products in a series of patents using rhodium carbonyl complexes in the presence of amine promoters and there has been a single patent[5] on the formation of alcohols using $[\eta^5\text{-}(C_5H_5)Rh(CO)(PBu_3)]$. Hydroformylation of propenyl

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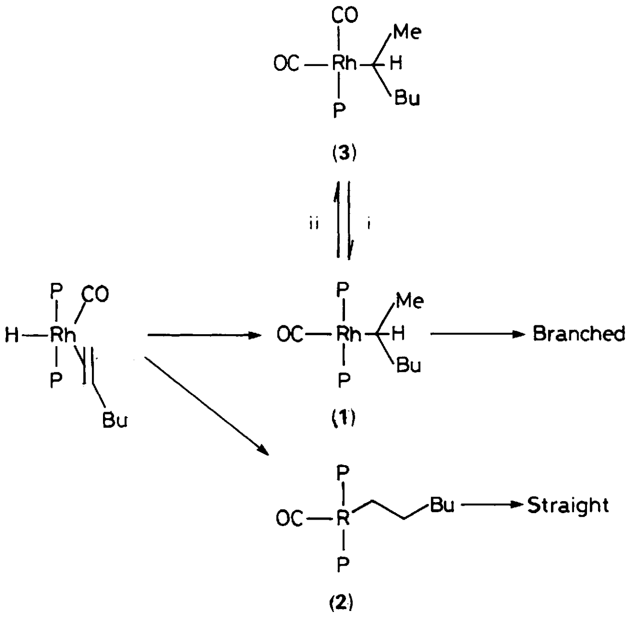
Table 1. Hydroformylation of hex-1-ene using $[RhH(PEt_3)_3]$ as catalyst.[a]

Solvent	$[Rh]/10^{-3}$ mol dm^{-3}	p/atm	$[PEt_3]/10^{-2}$ mol dm^{-3}	t/h	Yield of C_7 alcohols/%	$n:i$ ratio	Yield of C_7 aldehydes/%	$n:i$ ratio	Yield of isomerised hexenes/%
Toluene	7.6	80	—	16	13.4	3.32	74.7[b]	1.41	1.6[c]
THF	8.0	73	—	16	30.9	4.15	83.5	1.47	1.6
	8.0	55	8.9	16	27.0	5.08	80.0	1.58	3.5
	8.0[d]	0	—	336	—	—	—	—	100
	8.0[e]	29	—	16	10.1	0.88	96.0	0.6	2.1
	8.0[e]	68	8.0	16	7.0	0.37	75.4	0.13	18.7
Ethanol	7.7	80	—	4	75.4	2.02	1.0	0.3	7.3
	8.0	65	—	16	103.0	2.07	—	—	1.7
	8.0	30	—	16	97.0	1.93	—	—	1.3
	8.0	30	8.0	16	93.9	2.22	—	—	5.5
	8.0	30	8.0	5	63.3	2.6	0.7	0.38	16.1
	8.0[f]	59	2.4	16.5	102.7	2.23	—	—	1.6
	8.0[f]	52	2.4[g]	16	19.3	2.3	78.8	1.07	0.9
	8.0[f]	48	2.4[h]	16	99.1	2.54	—	—	1.4
	8.0[f]	44	2.4[i]	16	99.4	2.45	—	—	0.5
	8.0[f]	49	—	17	—	—	40	0.36	2.3[j]
	0.58[k]	37	—	16	—	—	36.5	1.20	3.3[l]

[a] Hexene (1 cm^3), solvent (4 cm^3), 120 °C; some total yields apparently exceed 100%. In these cases small amounts of solvent are recovered from outside the glass liner of the autoclave at the end of the reaction. [b] Includes 2-ethyl pentanal. [c] Includes hexane. [d] Room temperature. [e] Using isomerised hexenes formed by standing the catalyst solution containing hex-1-ene for >24 h prior to use. [f] $[Rh_2OAc_4]$. [g] $[PPr^i_3]$. [h] $[PMe_3]$. [i] $[PBu_3]$. [j] Diethyl acetals of C_7 aldehydes are also formed (48%; $n:i$ = 2.04). [k] $[RhH(CO)(PPh_3)_3]$. [l] Diethyl acetals of C_7 aldehydes are also formed (50%; $n:i$ = 3.87).



Scheme 1. Possible reactions of intermediate (**1**) which determine the selectivity of the hydroformylation reaction, P = PPh_3 or PEt_3. i, +P; ii, +CO.

alcohol catalysed by $[Rh_6(CO)_{16}]/PEt_3$ gives[6] the diol product, butanediol. We now report on studies involving the catalyst precursor $[RhH(PEt_3)_3]$[7] in which we find that high conversions directly to alcohols are possible under mild conditions.

Table 1 presents the results of various hydroformylation reactions carried out in the presence of $[RhH(PEt_3)_3]$. In tetrahydrofuran (THF) or toluene, the major products are aldehydes, although some alcohols derived by hydrogenation of the aldehydes are also produced. The high ratio of heptanol to 2-methylhexanol and the low ratio of heptanal to 2-methylhexanal suggest that the linear aldehyde is more easily hydrogenated than the branched. Addition of PEt_3 does not greatly affect the reaction in THF, although the selectivity to straight chain alcohol is increased. Observation of 2-ethylpentanal as a product in some of these reactions shows that a species in the catalytic mixture acts as a hexene isomerisation catalyst and this is confirmed by the recovery of small amounts of isomerised alkenes at the end of the reaction, as well as by the observation that hex-1-ene is completely isomerised to a mixture of hex-2-enes and hex-3-enes on standing in a THF solution of $[RhH(PEt_3)_3]$ for several days at room temperature. Interestingly, hydroformylation of this solution containing isomerised hexenes gives almost exclusively branched products (Table 1). Hydroformylation of internal alkenes to branched chain aldehydes does occur[8] using $[RhH(CO)(PPh_3)_3]$ as catalyst although the rate of reaction is only *ca.* 3% of that obtained using terminal alkenes.

When reactions are carried out in ethanol, alcohols are almost exclusively produced. At pressures of 30 to 80 atm, the straight to branched ratio is about 2.0 and almost complete conversion of hexene is observed after 4 h. Similar product distributions to those from $[RhH(PEt_3)_3]$ are obtained if the reaction is carried out using a catalyst prepared *in situ* from $[Rh_2(OAc)_4]$ and PEt_3.

The production of alcohols from rhodium catalysed hydroformylation reactions in ethanol does not appear to be general since reactions catalysed by $[RhH(CO)(PPh_3)_3]$, $[Rh_2(OAc)_4]$, or $[Rh_2(OAc)_4]$ with added PPr^i_3 all give aldehydes as their major products or, in the case of $[RhH(CO)(PPh_3)_3]$ and $[Rh_2(OAc)_4]$, diethyl acetals which arise from reactions of the aldehydes with ethanol.

Reactions carried out using $[Rh_2(OAc)_4]$ in the presence of PMe_3 or PBu_3 do produce alcohols with a slightly higher preference for the straight chain product than when PEt_3 is employed. These results suggest that tris(primary alkyl) phosphines and ethanol are required for obtaining high yields of alcohols using rhodium based hydroformylation reactions.

Addition of excess PEt_3 to reactions catalysed by $[RhH(PEt_3)_3]$ causes a decrease in the reaction rate and a small but significant increase in straight : branched ratio of product. Similar increases in selectivity towards straight chain products have been observed on addition of excess PPh_3 to

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$[RhH(CO)(PPh_3)_3]$ catalysed reactions and have been attributed[9] to a destabilisation of the secondary alkyl intermediate (**1**) in Scheme 1, causing a preference for the formation of primary alkyl insertion product (**2**) and hence straight chain aldehyde. In the absence of added PPh_3, one PPh_3 is displaced by CO to give a much less sterically crowded intermediate (**3**) which gives much lower selectivity. Similar compounds but containing PEt_3 have been identified[7] in water-gas shift reactions catalysed by $[RhH(PEt_3)_3]$, {*i.e.*, from $[RhH(PEt_3)_3]$ under CO}. Mechanistic details of these unusual reactions are currently under active investigation.

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