The Regioselective Hydroformylation of Allyl Acetate Catalysed by Cationic and Zwitterionic Rhodium Complexes

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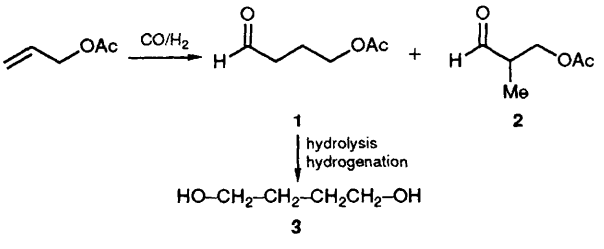
Cationic and zwitterionic rhodium complexes, with added 1,4-bis(diphenylphosphino)butane (dppb), are efficient catalysts for the highly regioselective hydroformylation of allyl acetate and related esters to yield the linear aldehyde (up to 95%) under mild conditions.

The selective hydroformylation of allyl acetate is an attractive way to synthesize difunctional compounds including, on hydrolysis and hydrogenation, butane-1,4-diol, **3**, an important industrial material.[1,2] Isomeric mixtures of 4-acetoxybutanal, **1**, and 3-acetoxy-2-methylpropanal, **2**, are obtained with low selectivity from allyl acetate. For example, selectivity for the linear product was approximately 70% using cobalt carbonyl as the catalyst at 125 °C and 200 atm (1 atm = 101 325 Pa). The presence of a weakly coordinating ligand as a promoter enabled reaction to take place under milder conditions (90 °C, 55 atm), but selectivity for **1** was not high.[4]

Recently we reported the use of the zwitterionic rhodium complex [Rh(cod)(η^6-PhBPh$_3$)] **4** (cod = cycloocta-1,5-diene), as catalyst for the hydroformylation and reductive carbonylation of alkenes[5,6] to produce aldehydes and alcohols regioselectively. Another direct route from alkenes to alcohols utilizes RhH(PEt$_3$)$_3$ and related catalysts.[7,8] The zwitterionic Rh complex is also effective for the synthesis of pyrrolidines and pyrrolidinones by the carbonylation of unsaturated amines,[9] and for the regioselective hydroformylation of α,β-unsaturated esters in the presence of 1,4-bis(diphenylphosphino)butane (dppb).[10]

This paper describes the hydroformylation of allyl acetate and related compounds, catalysed by ionic rhodium complexes, in the presence of dppb, to form linear aldehydes in high selectivity. When the zwitterionic complex [Rh(cod)(η^6-PhBPH$_3$)] **4**, or the cationic rhodium complex, [Rh(Ph$_3$P)$_2$(cod)]$^+$BPh$_4^-$, **5**, are used as catalysts for this reaction, the branched aldehyde is the major product, the ratio of linear to branched product being 36 : 64 and 20 : 80, respectively.

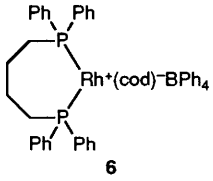


When dppb (dppb : Rh = 2 : 1) is added as a ligand to modify the zwitterionic catalyst **4** in the hydroformylation of allyl acetate, the regioselectivity of the reaction is very different with the ratio of linear to branched chain aldehydes being 95 : 5 (total yield of 56%). The same result is observed using the cationic complex **5** and dppb. In this reaction, poor regioselectivity is observed when an equimolar amount of dppb and **4** is used compared with twice the amount of dppb. The data are listed in Table 1.

Table 1 Hydroformylation of allyl acetate by Rh–phosphine[a]

Catalyst	Phosphine	Ratio of catalyst : phosphine	Yield (%)[b]	**1** : **2**[c]
4	—	—	71	36 : 64
4	dppb	1 : 1	76	40 : 60
4	dppb	1 : 2	56	95 : 5
4	dppb	1 : 4	53	91 : 9
5	—	—	68	20 : 80
5	dppb	1 : 2	55	94 : 6
4	PPh_3	1 : 1	67	56 : 44
4	PPh_3	1 : 4	74	42 : 58
4	$P(C_6H_4NMe_2\text{-}p)_3$	1 : 4	63	37 : 63

[a] *General procedure*: A mixture of 4.0 mmol of substrate and 1 mol% Rh catalyst in 10 ml of methylene chloride was stirred at 80 °C, under 40 atm of CO/H$_2$ for 12 h. The reaction was worked up by removal of the solvent and silica gel chromatography, using hexane–ethyl acetate (95 : 5) as the eluent. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy.



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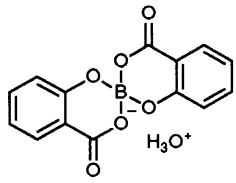

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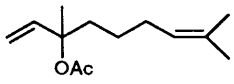
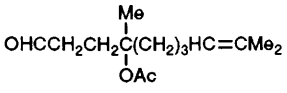
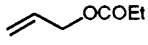
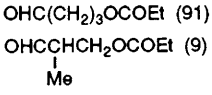
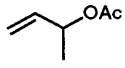
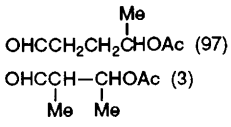
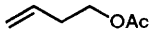
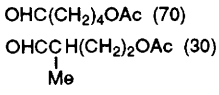
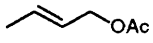
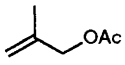
Table 2 Hydroformylation of unsaturated esters catalysed by **4** and dppb[a]

Substrate	Yield of aldehydes (%)[b]	Product ratio
	29	
	67	
	69	
	87	
	0	
	0	

[a] See footnote *a* of Table 1 for procedure. [b] Isolated yield.

When triphenylphosphine and tris(4-dimethylaminophenyl)phosphine are employed with **4**, a mixture of aldehydes was obtained in low selectivity from allyl acetate. The hydroformylation of allyl acetate occurs in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) and *cis*-1,2-diphenylphosphinoethane catalysed by **4** to form a trace amount of benzaldehyde as the unexpected product. It is conceivable that one of the phenyl groups on the phosphine experiences migration to the central rhodium atom, and then undergoes carbonylation and hydrogenation to give benzaldehyde.[11]

The key structural difference of **4** and **5** is that the zwitterionic complex has π-coordination of one of the benzene rings of the BPh_4 unit to rhodium, while in **5**, the BPh_4^- is an anion not complexed to the metal. It is interesting to consider why the same result can be obtained by using the two catalysts in the presence of dppb. Based on the results in Table 1, it is possible that the pre-catalysts **4** and **5** may be converted to an active species, **6**, which carries out the regioselective hydroformylation, with the cod ligand likely replaced by carbonyl, hydride, and olefin ligands in subsequent steps.

To test this hypothesis, the related complex [Rh+(dppb)(cod)] BF_4^-, **7**, which has a similar structure to **6**, can be used to catalyse the hydroformylation of allyl acetate. The expected result was not obtained as the selectivity of **1**:**2** was 30:70. When an excess amount of $NaBPh_4$ (four times the amount of **7**) was added in an attempt to replace the BF_4^- anion of **7**, 80% linear aldehyde was obtained. This experiment supports the postulate that complex **6** is possibly an active species, and also that the bulky borate anion plays an important role in this hydroformylation reaction. Further support for the participation of **6** as the active species comes from the following experiments.

A mixture of $[Rh(cod)Cl]_2$, **8** (0.02 mmol), dppb (0.08 mmol) and $NaBPh_4$ (0.08 mmol) catalyses the hydroformylation of allyl acetate (4 mmol) to give **1** and **2** in a 96:4 ratio, in 70% yield. When this reaction was performed in the absence of $NaBPh_4$, a mixture of **1** and **2** was obtained in 78% yield with a selectivity of 56:44. Upon substitution of hydronium bis[2-hydroxybenzoato(2−)-O^1,O^2]borate(1−), **9**, for $NaBPh_4$ in the above reaction, the linear aldehyde is formed as the major product in 59% yield with **1**:**2** in 93:7 selectivity.

The products of the hydroformylation of other unsaturated acetates using **4**–dppb are shown in Table 2. Use of linalyl acetate resulted in regiospecific formation of the linear aldehyde in 29% yield, and allylpropionate produced 67% of aldehydes in a 96:4 ratio of linear:branched products. 1-Methylprop-2-enyl acetate can be transformed into the linear aldehyde as the predominant product in 69% yield. The linear aldehyde is an intermediate in the synthesis of (+)-sulcatol, an insect pheromone.[12]

It should be mentioned that the **4**–dppb system did not catalyse the hydroformylation of allyl acetates having a disubstituted double bond. The homoallylic acetate, CH_2=$CHCH_2CH_2OAc$, does undergo hydroformylation in fair regioselectivity.

In summary, the rhodium catalysts **4**, **5** and **8** with dppb–$NaBPh_4$, are highly regioselective for the hydroformylation of allyl acetates.

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