

[NiCl₂(PPh₃)₂] catalysed Transfer Hydrogenation of Ketones and Aldehydes by Propan-2-ol†

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In the presence of the cocatalyst NaOH, [NiCl₂(PPh₃)₂] catalyses efficiently the transfer hydrogenation of aliphatic and aromatic ketones and aldehydes in high yields.

Metal catalysed transfer hydrogenation is convenient in large-scale synthesis since there is no need to employ a high H₂ pressure or to use hazardous reducing agents. The use of propan-2-ol in the presence of a transition metal catalyst for transfer hydrogenation has been extensively studied.¹ Cationic rhodium complexes with KOH as cocatalyst, catalyse the transfer hydrogenation of ketones with propan-2-ol.² More recently the influence of NaOH as a cocatalyst in the [RuCl₂(PPh₃)₃] catalysed transfer hydrogenation of ketones and imines has been reported.³ Although these methods are facile, they involve the use of precious noble metal catalysts.

An earlier report mentions the use of [NiCl₂(PPh₃)₂] as catalyst for the hydrogenation of an olefin.⁴ Raney-Ni in conjunction with propan-2-ol has also been used for the transfer hydrogenation of ketones.⁵ In the light of these studies we decided to investigate the use of [NiCl₂(PPh₃)₂] as catalyst for the reduction of ketones and aldehydes.

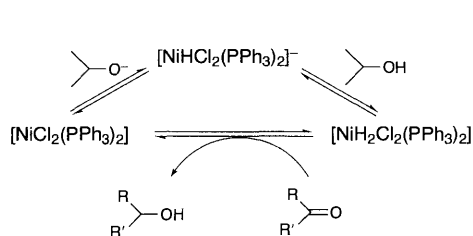
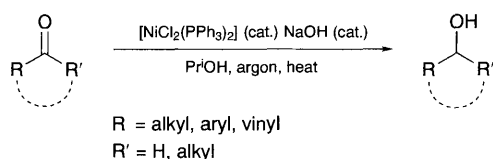
A solution of acetophenone (3 mmol) in PrⁱOH, containing [NiCl₂(PPh₃)₂] (15 mol%) and NaOH (0.04 g, 1 mmol) when refluxed for 30 h, produced phenethyl alcohol in high yield (82%). The reaction did not proceed in the absence of NaOH.

Table 1 summarises a selection of ketones and aldehydes which could be efficiently reduced in refluxing PrⁱOH. Aliphatic, alicyclic and aromatic ketones undergo reduction readily under these conditions. Aromatic and aliphatic aldehydes also undergo reduction, albeit in slightly lower yields.

The reduction of aldehydes proceeded at a faster rate and was complete in 12 h. Aliphatic ketones such as cyclohexanone and 4-*tert*-butylcyclohexanone were reduced in 24 h. The reactions were also dependent on the concentration of NaOH used.

We also studied the effect of other ligands on the reaction. When Ph₂PCH₂CH₂PPh₂ was used instead of PPh₃ there was no reaction at all. PBU₃ and P(OMe)₃ similarly showed less activity for the transfer hydrogenation.

The reaction probably proceeds *via* the following sequence of events (i) attack of isopropoxide on [NiCl₂(PPh₃)₂], (ii) β-hydride elimination leading to acetone and a nickel hydride species, (iii) rapid protonation of the anionic species giving a nickel dihydride, (iv) reduction of the ketone or aldehyde by the nickel dihydride.



We are currently exploring the utility of this process in the transfer hydrogenation of other functionalities such as imines, oximes *etc.* and also in enantioselective hydrogen transfer reactions using chiral nickel complexes.

In conclusion, [NiCl₂(PPh₃)₂] in conjunction with NaOH serves as an excellent catalyst for transfer hydrogenation of ketones and aldehydes.

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Table 1 [NiCl₂(PPh₃)₂] catalysed transfer hydrogenation of ketones and aldehydes

Entry	Substrate	t / h	Product	Yield (%)
1		30		82
2		36		80
3		24		77
4		36		65
5		36		65
6		24		56
7		20		56
8		24		72
9		12		76
10		30		51
11		24		57

Footnote

† NCL Communication No. 6119

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