$[NiCl_2(PPh_3)_2]$ catalysed Transfer Hydrogenation of Ketones and Aldehydes by Propan-2-ol†

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In the presence of the cocatalyst NaOH, $[NiCl_2(PPh_3)_2]$ 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 H_2 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 $[RuCl_2(PPh_3)_3]$ 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 $[NiCl_2(PPh_3)_2]$ 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 $[NiCl_2(PPh_3)_2]$ as catalyst for the reduction of ketones and aldehydes.

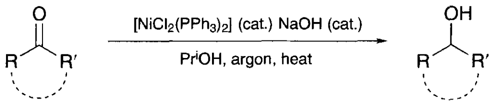
A solution of acetophenone (3 mmol) in Pr^iOH, containing $[NiCl_2(PPh_3)_2]$ (15 mol%) and NaOH (0.04 g, 1 mmol) when refluxed for 30 h, produced phenethyl alcohol in high yield (82%). The reaction did not proceed in the absence of NaOH.

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

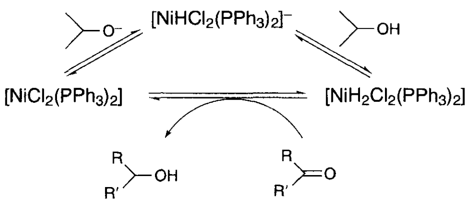
The reduction of aldehydes proceeded at a faster rate and was complete in 12 h. Aliphatic ketones such as cyclohexanone and 4-*tert*-butylcyclohexanone were reduced in 24 h. The reactions were also dependent on the concentration of NaOH used.

We also studied the effect of other ligands on the reaction. When $Ph_2PCH_2CH_2PPh_2$ was used instead of PPh_3 there was no reaction at all. PBu_3 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 $[NiCl_2(PPh_3)_2]$, (*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.



R = alkyl, aryl, vinyl
R′ = H, alkyl



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, $[NiCl_2(PPh_3)_2]$ in conjunction with NaOH serves as an excellent catalyst for transfer hydrogenation of ketones and aldehydes.

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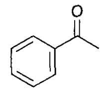
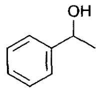
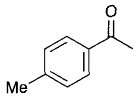
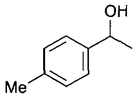
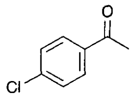
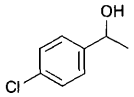
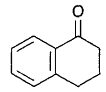
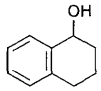
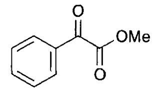
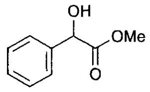
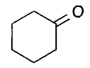
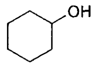
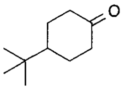
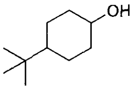
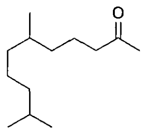
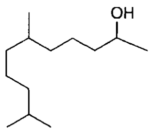
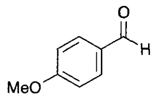
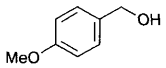
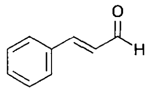
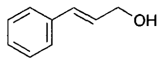
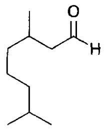
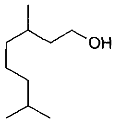
Table 1 $[NiCl_2(PPh_3)_2]$ catalysed transfer hydrogenation of ketones and aldehydes

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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