

Catalytic Hydrogenation of Nitriles and Dehydrogenation of Amines with the Rhodium(I) Hydrido Compounds $[\text{RhH}(\text{PPr}^i)_3]$ and $[\text{Rh}_2\text{H}_2(\mu\text{-N}_2)\{\text{P}(\text{cyclohexyl})_3\}_4]$

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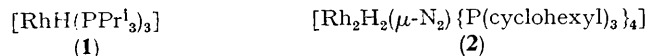
Summary $[\text{RhH}(\text{PPr}^i)_3]$ and $[\text{Rh}_2\text{H}_2(\mu\text{-N}_2)\{\text{P}(\text{cyclohexyl})_3\}_4]$ are active catalysts for the hydrogenation of nitriles under ambient conditions, producing primary amines selectively; they are also active for the dehydrogenation of amines at higher temperatures to give nitriles or imines.

unchanged at the end of the hydrogenation. The rate of reduction of pivalonitrile is much slower than that of primary or secondary aliphatic nitriles. In case of $\alpha\beta$ - and $\beta\gamma$ -unsaturated nitriles, hydrogenation of the olefinic group takes place more readily than that of the nitrile group. The catalytic activity of (1) for the hydrogenation of aromatic nitriles is not so high as for aliphatic nitriles.

WHILE a variety of active homogeneous catalysts are known for the hydrogenation of carbon-carbon multiple bonds,¹ this is not the case for the hydrogenation of nitriles and, so far, no known homogeneous catalysts are active under ambient conditions.²⁻⁵ We have found that the rhodium(I) hydrides (1) and (2)⁶ are active catalysts for homogeneous hydrogenation under ambient conditions.

TABLE. Hydrogenation of the nitriles $\text{RC}\equiv\text{N}$ catalysed by the complexes (1) and (2).^a

R	% Yield of amine $\text{RCH}_2\text{NH}_2^b$	
	with (1)	with (2)
Me $[\text{CH}_2]_4$	100	
Pr ⁱ	100	78
Bu ^t	67	
PhCH ₂	96	69
CH ₂ =CHCH ₂	70 ^a	8 ^c
MeCH=CH (<i>trans</i>)	72 ^d	5 ^d
Ph	45	0
α -Naphthyl	44	



Hydrogenation of phenylacetonitrile (5 mmol) with (1) (0.05 mmol) at 20 °C (under 1 atm of H₂) in tetrahydrofuran (THF) (10 ml) gave phenethylamine in 80% yield after 1 h and 89% yield after 2 h. The hydrogenation is highly selective, and the secondary or tertiary amines are not formed. This contrasts with other known catalysts such as metal carbonyls^{2,3} or polymer-supported Rh^I catalysts⁵ which require more drastic conditions and fail to suppress the formation of secondary and tertiary amines.

A variety of nitriles were hydrogenated with (1) under ambient conditions (Table). Primary and secondary aliphatic nitriles were converted into the corresponding amines quantitatively, and compound (1) can be recovered

^a (1) (0.05 mmol) or (2) (0.025 mmol)-nitrile (5.0 mmol) in THF at 20 °C under H₂ (1 atm) for 20 h. ^b Analysed by g.l.c. ^c R = MeCH₂CH₂·MeCH₂CH₂C≡N also formed [30% with (1) and 92% with (2)]. ^d R = MeCH₂CH₂·MeCH₂CH₂C≡N also formed [28% with (1) and 95% with (2)].

Compound (2), a precursor of the three-co-ordinate rhodium(I) hydride $[\text{RhH}\{\text{P}(\text{cyclohexyl})_3\}_2]$,⁶ also catalyses hydrogenation of nitriles (Table), but in general it is less efficient than (1). It is inactive for the hydrogenation of benzonitrile under ambient conditions. Under high pressure (20 °C, 100 atm), however, the benzonitrile is

completely converted into benzylamine. *trans*-[RhH(N₂)-(PPhBu^t₂)₂],⁷ which gives stable nitrile complexes *trans*-[RhH(NCR)(PPhBu^t₂)₂] (R=Me, PhCH₂, or Ph) involving end-on co-ordination, shows no activity. It should be noted that [RhCl(PPh₃)₃], an active catalyst for hydrogenation of olefins, was totally inactive for hydrogenation of nitriles (20 °C, 1 atm of H₂, in THF).

Compound (1) also serves as catalyst for dehydrogenation of amines. Thus, on heating benzylamine (5 mmol) with

(1) (0.05 mmol) in toluene (110 °C, 24 h) under a gentle stream of N₂, benzonitrile (27%) is obtained. Under similar conditions, *N*-phenylbenzylamine gives PhCH=NPh (6%). Dehydrogenation of benzylamine to benzonitrile is also catalysed by (2) but in poor yield (13%).

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