Catalytic Hydrogenation of Nitriles and Dehydrogenation of Amines with the Rhodium(I) Hydrido Compounds $[RhH(PPr^i_3)_3]$ and $[Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4]$

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Summary $[RhH(PPr^i_3)_3]$ and $[Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4]$ 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.

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.

$[RhH(PPr^i_3)_3]$
(**1**)

$[Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4]$
(**2**)

Hydrogenation of phenylacetonitrile (5 mmol) with (**1**) (0·05 mmol) at 20 °C (under 1 atm of H_2) 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 catalysts[5] 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 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.

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

R	% Yield of amine RCH_2NH_2[b]	
	with (**1**)	with (**2**)
$Me[CH_2]_4$	100	
Pr^i	100	78
Bu^t	67	
$PhCH_2$	96	69
$CH_2{=}CHCH_2$	70[a]	8[c]
MeCH=CH (*trans*)	72[d]	5[d]
Ph	45	0
α-Naphthyl	44	

[a] (**1**) (0·05 mmol) or (**2**) (0·025 mmol)–nitrile (5·0 mmol) in THF at 20 °C under H_2 (1 atm) for 20 h. [b] Analysed by g.l.c. [c] $R = MeCH_2CH_2$·$MeCH_2CH_2C{\equiv}N$ also formed [30% with (**1**) and 92% with (**2**)]. [d] $R = MeCH_2CH_2$·$MeCH_2CH_2C{\equiv}N$ also formed [28% with (**1**) and 95% with (**2**)].

Compound (**2**), a precursor of the three-co-ordinate rhodium(I) hydride $[RhH\{P(cyclohexyl)_3\}_2]$,[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(N_2)-(PPhBu$^t_2$)$_2$],[7] which gives stable nitrile complexes *trans*-[RhH(NCR)(PPhBu$^t_2$)$_2$] (R=Me, PhCH$_2$, or Ph) involving end-on co-ordination, shows no activity. It should be noted that [RhCl(PPh$_3$)$_3$], an active catalyst for hydrogenation of olefins, was totally inactive for hydrogenation of nitriles (20 °C, 1 atm of H_2, 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 N_2, 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%).

We thank Toray Science Foundation for partial financial support.

(*Received, 11th June* 1979; *Com.* 608.)

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