Hydrogenation of nitriles with iridium–triphenylphosphine complexes

Chong Shik Chin and Byeongno Lee

Department of Chemistry, Sogang University, CPO Box 1142, Seoul 100-611, Korea

Received 3 October 1991; accepted 16 March 1992

Reactions of cationic iridium(I)-COD (COD = 1,5-cyclooctadiene) complexes, $[Ir(COD)(PhCN)(PPh_3)]ClO_4$ (**1**), $[Ir(COD)(PPh_3)_2]ClO_4$ (**2**) and $[Ir(COD)(PhCN)_2]ClO_4$ (**3**) with nitriles under H_2 catalytically produce primary, secondary and tertiary amines. Hydrogenation of nitriles (RCN) gives HCl salts of amines ($RCH_2NH_2 \cdot HCl$, $(RCH_2)_2NH \cdot HCl$) in CH_2Cl_2. Secondary and tertiary amines seem to be produced by the reactions of RCN with primary and secondary amines, respectively under H_2 in the presence of catalysts. The hydrogenation in the presence of **1** and **2** is homogeneously catalyzed by soluble iridium–PPh_3 complexes formed in the reactions of **1** and **2** with H_2 and RCN whereas the hydrogenation in the presence of **3** is heterogeneous by metallic iridium powders produced in the reduction of **3** by H_2.

Keywords: Hydrogenation of nitriles; hydrogenation by iridium complexes; iridium–triphenylphosphine catalyst

1. Introduction

Catalytic hydrogenation of nitriles (–C≡N group) to give amines has been studied mostly with metallic powder (unsupported and supported) under forced conditions [1] whereas some reports have been made on the hydrogenation with BH_4^- in the presence of metal ions [2]. On the other hand, the hydrogenation of nitriles to amines with metal complexes in homogeneous solutions has been rarely reported [3,4] probably because (i) the interaction between a transition metal and nitrile mostly occurs through the nitrogen atom (but not through the π-system) of the nitrile group [5] and (ii) the products, amines, may strongly coordinate to the catalyst metal and inhibit the continuous production of amines. This inhibition effect may be negligible for metal powder catalysts [1]. Continuous production of amines in the hydrogenation of nitriles with a transition metal catalyst may be accelerated if the products, amines, are continuously converted into non-coordinating amine salts such as $RCH_2NH_2 \cdot HCl$.

We now report catalytic hydrogenation of nitriles (RC≡N) with iridium–PPh_3 complexes in CH_2Cl_2 which provides HCl to the hydrogenation products, RCH_2NH_2 and $(RCH_2)_2NH$ to produce $RCH_2NH_2 \cdot HCl$ and $(RCH_2)_2NH \cdot HCl$ and in other solvents.

2. Experimental

Catalysts, $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (**1**), $[Ir(COD)(PPh_3)_2]ClO_4$ (**2**) and $[Ir(COD)(PhCN)_2]ClO_4$ (**3**) were prepared by methods similar to those in the literature [6,7].

All the experiments for catalytic hydrogenation were carried out in the same manner as described below. A 0.02 mmol of an iridium complex was dissolved in a solution of a solvent (5 ml) and a nitrile (2.0 mmol) in a bomb reactor (Parr 1341, volume 360 ml) and H_2 was introduced up to 5 atm. The reactor was then put in an oven maintained at 100°C for certain period of time and cooled down to room temperature for product analysis.

Hydrogenation products were analyzed mostly by ^1H NMR and IR measurements, and GC and elemental analysis if necessary. Benzylamines present in the product mixtures were analyzed by $-CH_2-$ signals of ^1H NMR in $CDCl_3$ at δ 3.88 (singlet) and 7.29 for $C_6H_5CH_2NH_2$, at δ 3.82 (singlet) and 7.27 for $(C_6H_5CH_2)_2NH_2$ and at δ 3.59 (singlet) and 7.1–7.5 for $(C_6H_5CH_2)_3N$. The HCl salts of amines were separated from the product mixtures in CH_2Cl_2 before spectral (^1H NMR and IR) analysis. Ammonium chloride (much less soluble than other products) was obtained by washing off the product mixtures with a small amount of methanol. Monobenzylamine salt, $C_6H_5CH_2NH_2 \cdot HCl$, was separated from dibenzylamine salt, $(C_6H_5CH_2)_2NH \cdot HCl$, by subliming the mixture at 50°C under vacuum. Tribenzylamine, $(C_6H_5CH_2)_3N$, could be extracted from the product mixture with CH_3OH/hexane and recrystallized in hexane. $C_6H_5CH_2NH_2 \cdot HCl$ and $(C_6H_5CH_2)_2NH \cdot HCl$ were also confirmed by elemental analysis and infrared spectrum measurements with comparing spectra of authentic samples. (Amines and amine salts are not well distinguished by ^1H NMR spectra.) Other amines and their HCl salts were separated and analyzed in the same manner as described above. Ammonia was trapped in acetone-d_6 in a NMR tube and confirmed by ^1H NMR (by comparing the spectra of the samples NH_3 added).

3. Results and discussion

Table 1 summarizes the hydrogenation of nitriles with iridium complexes, $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (**1**, COD = 1,5-cyclooctadiene), $[Ir(COD)(PPh_3)_2]ClO_4$ (**2**) and $[Ir(COD)(PhCN)_2]ClO_4$ (**3**). Complex **1**, is known to be catalytically

Table 1
Hydrogenation of RCN (2.0 mmol) with [Ir(COD)(PPh$_3$)(PhCN)]ClO$_4$ (**1**, 0.02 mmol), [Ir(COD)(PPh$_3$)$_2$]ClO$_4$ (**2**, 0.02 mmol) and [Ir(COD)(PhCN)$_2$]ClO$_4$ (**3**, 0.02 mmol) at 100°C under 5 atm pressure of H_2 for 72 h

Catalyst	RCN	Solvent	Product (%)
1	R=C_6H_5	CH_2Cl_2	$(RCH_2)_3N$ (80), $(RCH_2)_2NH \cdot HCl$ (trace), NH_4Cl
			$(RCH_2NH_2 + RCH_2NH_2 \cdot HCl)$ (20), $(RCH_2)_2NH \cdot HCl$ (trace) [a]
		CH_3OH	$(RCH_2NH_2 + (RCH_2)_2NH)$ (25), NH_3
		C_6H_6	$(RCH_2NH_2 + (RCH_2)_2NH)$ (10), NH_3
	$C_6H_5CH{=}CH$	CH_2Cl_2	$C_6H_5CH_2CH_2CN$ (60), $(C_6H_5CH_2CH_2CH_2)_2NH \cdot HCl$ (40), NH_4Cl
	CH_3 [b]	CH_2Cl_2	$(RCH_2NH_2 + (RCH_2)_2NH)$ (50) [c], NH_4Cl
	$CH_3CH_2CH_2$	CH_2Cl_2	$(RCH_2NH_2 + (RCH_2)_2NH)$ (40), NH_4Cl
2	C_6H_5	CH_2Cl_2	no hydrogenation observed
		CH_3OH	$(RCH_2)_3N$ (90), $(RCH_2)_2NH$ (10), NH_3
		C_6H_6	$(RCH_2)_2NH$ (trace)
3	C_6H_5	CH_2Cl_2	$(C_6H_{11}CH_2)_2NH \cdot HCl$ (95) [d], NH_4Cl
			$RCH_2NH_2 \cdot HCl$ (90) [e]
		CH_3OH [d]	$(RCH_2)_2NH$ (90), $(C_6H_{11}CH_2)_2NH$ (5), NH_3
		C_6H_6 [d,f]	$(RCH_2)_2NH$ (70), $(C_6H_{11}CH_2)_2NH$ (25), NH_3

[a] At 25°C under 5 atm of H_2 for 120 h.

[b] Reaction was carried out at 50°C since b.p. of CH_3CN is low (82°C).

[c] A part of $C_2H_5NH_2$ could be lost during the analysis due to the low b.p. (16.7°C).

[d] For 15 h (note hydrogenation of aromatic rings by metallic iridium powders, see text).

[e] At 25°C for 15 h (relatively rapid even at low temperature). Hydrogenation is catalyzed by metallic iridium powder (see text).

[f] A significant amount of C_6H_{12} (hydrogenation product of solvent C_6H_6) was also observed.

active for the hydrogenation of carbonyl groups of aldehydes [6]. Related compounds, [Ir(COD)(PR$_3$)(PhCN)]ClO$_4$ (PR$_3$ = various tertiary phosphines) are also known to catalyze the hydrogenation of olefinic groups in enamides and dehydroamino acid derivatives [7]. Bis(tertiary phosphine) complexes, [Ir(COD)(PR$_3$)$_2$]$^+$ are known to be good catalysts for hydrogenation of olefins [8] and carbonyl groups [9]. While no catalytic reaction has been reported with bis(nitrile) complexes, [Ir(COD)(CH$_3$CN)$_2$]$^+$ was used to prepare polyoxoanion-supported Ir(I) complex, [Ir(COD)-polyoxoanion]$^{8-}$ which shows catalytic activities for hydrogenation of olefins [10]. To our knowledge, there has been no report on the hydrogenation of nitriles with an iridium complex in solution.

It is noticed in table 1 that the hydrogenation in the presence of **1** is considerably higher in CH_2Cl_2 than in either polar or non-polar solvents. This may be understood by the formation of non-coordinating amine–HCl salts in CH_2Cl_2 which cannot be formed both in methanol and benzene.

It was found during the hydrogenation of C_6H_5CN (**4**) in CH_2Cl_2 with **1** that a large amount of dibenzylamine · HCl salt, $(C_6H_5CH_2)_2NH \cdot HCl$ (**5**) was initially observed and tribenzylamine, $(C_6H_5CH_2)_3N$ (**6**) gradually increases at the expense of **4** and **5** while a very small amount of monobenzylamine · HCl salt, $C_6H_5CN_2NH_2 \cdot HCl$ (**7**) was measured. Separate experiments have been carried out in order to find the way of forming **5** and **6**. Under the same experimental conditions (100°C, 5 atm of H_2, CH_2Cl_2), the reaction of $C_6H_5CH_2NH_2$ (**7a**) with **1** in the absence of **4** produced only **7** but neither **5** nor **6** has been observed whereas the reaction of **7a** with **1** in the presence of **4** produced **5** and **6**. Similarily tribenzylamine, **6** has been produced from the reactions of **5** and **7** with **1** only in the presence of **4** and has not been produced in the absence of **4**. These observations suggest the following reaction pathway:

$$\begin{aligned}
&\underset{\mathbf{4}}{C_6H_5CN} \xrightarrow{2H_2} \underset{\mathbf{7a}}{C_6H_5CH_2NH_2} \quad \left(\text{or } \underset{\mathbf{7}}{C_6H_5CH_2NH_2 \cdot HCl} \text{ in } CH_2Cl_2\right),\\
&\mathbf{7a}\ (\mathbf{7}) + \mathbf{4} \xrightarrow{2H_2} \underset{\mathbf{5a}}{(C_6H_5CH_2)_2NH} + NH_3\\
&\qquad\qquad\qquad \left(\text{or } \underset{\mathbf{5}}{(C_6H_5CH_2)_2NH \cdot HCL} + NH_4Cl \text{ in } CH_2Cl_2\right),\\
&\mathbf{5a}\ (\mathbf{5}) + \mathbf{4} \xrightarrow{2H_2} \underset{\mathbf{6}}{(C_6H_5CH_2)_3N} + NH_3 \quad (NH_4Cl \text{ from } \mathbf{5}).
\end{aligned} \tag{1}$$

Holy obtained similar results in the benzonitrile hydrogenation with polymer-supported rhodium(I) complex [3]: C_6H_5CN is hydrogenated to give $C_6H_5CH_2NH_2$ which then reacts with another mole of C_6H_5CN and H_2 to produce $C_6H_5CH_2NHCH(NH_2)C_6H_5$ which finally loses NH_3 to yield $C_6H_5CH_2N{=}CHC_6H_5$. Hydrogenation of **4** in the presence of **2** is faster than that in the presence of **1** in CH_3OH. On the other hand, hydrogenation does not even occur in CH_2Cl_2 in the presence of **2** while the hydrogenation with **1** is significantly faster in CH_2Cl_2 than in CH_3OH (see table 1). These differences may not be clearly understood until the nature of the actual catalysts (iridium–PPh_3 complexes) present in the solution under the catalytic conditions is known.

The relatively rapid hydrogenation with bis(benzonitrile) complex, **3**, even at room temperature (see table 1) seems to be a catalysis by metallic iridium powders generated in reaction of **3** with H_2. Almost quantitative amounts of ultrafine (particle diameter < 0.1 μm) metallic iridium powders could be obtained at 25°C under 5 atm of H_2 within 20 h in CH_2Cl_2 [11]. Hydrogenation of **4** with **3** at 100°C produces a significant amount of cyclohexylmethylamine · HCl whereas the hydrogenation of the aromatic ring has never been observed in the hydrogenation of **4** with **1** and **2**. No metallic iridium, however, has been observed in the hydrogenation with **1** and **2**. All the tests suggested for the detection of insoluble metallic solids * have been carried out and found to be negative. Complexes **1**, **2** and **3** rapidly react with H_2 even at room temperature to liberate cyclooctane both in the absence and presence of excess nitrile. All these observations suggest that the hydrogenation of nitriles with **1** and **2** is a homogeneous catalysis by soluble iridium–triphenylphosphine complexes containing no COD as a ligand, and the one with **3** is a heterogeneous reaction by iridium metal.

It is noticed that the heterogeneous catalysis with **3** (iridium metal powders) occurs even at 25°C under atmospheric pressure of H_2 (see table 1) whereas the homogeneous one with **1** and **2** (soluble iridium complexes) did not produce detectable amounts of amines for 5 days under the same conditions. Increasing H_2 pressure, however, significantly increases the rates of the hydrogenation with **1** and **2** to be measured (see table 1).

The catalytic activities (yields in table 1) obtained with **1** and **2** do not seem to decrease for 5 days until 200 molecules of C_6H_5CN (per molecule of iridium complex) were hydrogenated.

Finally, the fact that the hydrogenation of **4** is faster than that of other nitriles (see table 1) seems somewhat unusual. It may be worthwhile to mention that the addition of a radical initiator, AIBN did not show any effect on the rates of hydrogenation at all.

Acknowledgement

Authors are grateful for the financial supports from Korea Science and Engineering and the Daewoo Foundation (for BL).

References

[1] F.S. Wagner, in: *Applied Industrial Catalysis*, Vol. 2, ed. B.E. Leach (Academic Press, New York, 1983) pp. 27–108;
S.T. McMillan and P.K. Agrawal, Ind. Eng. Chem. Res. 27 (1988) 243.
[2] R.H. Crabtree and A.J. Pearman, J. Organomet. Chem. 157 (1978) 335;
T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji and Z. Imai, Tetrahedron Lett. (1969) 4555;
E. Diamond, B. Grant, G.M. Tom and N. Taube, Tetrahedron Lett. (1974) 5025.
[3] N. Holy, J. Org. Chem. 44 (1979) 239.
[4] T. Yoshida T. Okano and S. Otsuka, Chem. Commun. (1979) 870.
[5] S.J. Bryan, P.G. Huggett, K. Wade, J.A. Daniels and J.R. Jennings, Coord. Chem. Rev. 44 (1982) 149.
[6] C.S. Chin and B. Lee, J. Chem. Soc. Dalton Trans. (1991) 1323.

---

* Detailed characterization of the iridium powders will be reported elsewhere along with their catalytic activities.

[7] M. Green, T.A. Kuc and S.N. Taylor, J. Chem. Soc. A (1971) 2334;
R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 3089.
[8] J.A. Cabeza, C. Cativiela, M.D.D. de Villegas and L.A. Oro, J. Chem. Soc. Perkin Trans. I (1988) 1881;
L.A. Oro, J.A. Cabeza, C. Cativiela, M.D.D. de Villegas and E. Melendes, J. Chem. Soc. Chem. Commun. (1983) 1383.
[9] R.N. Crabtree, Acc. Chem. Res. (1979) 331.
[10] E. Farnetti, M. Pesce, J. Kaspar, R. Spogliarch and M. Graziani, J. Chem. Soc. Chem. Commun. (1986) 746.
[11] R.G. Finke, D.K. Lyon, K. Nomiya, S. Sur and N. Mizuno, Inorg. Chem. 29 (1990) 1784;
D.L. Lyon and R.G. Finke, Inorg. Chem. 29 (1990) 1789.
[12] D.A. Anton and R.H. Crabtree, Organometallics 2 (1983) 855;
J. Blum, Ibrahim, X.P.C. Vollhardt, H. Schwarz and G. Hohne, J. Org. Chem. 52 (1987) 2804;
J.E. Hamlin, K. Hirai, A. Millan and P.M. Maitlis, J. Mol. Catal. 7 (1980) 543.