



Efficient nickel-catalyzed hydrocyanation of alkenes using acetone cyanohydrin as a safer cyano source



Koji Nemoto^{a,*}, Tsuyoshi Nagafuchi^a, Ken-ichi Tominaga^{a,b}, Kazuhiko Sato^{a,b}

^a Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
^b Catalysis Research Center, Hokkaido University, Kita21, Nishi10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

ARTICLE INFO

Article history:

Received 1 April 2016

Revised 4 June 2016

Accepted 9 June 2016

Available online 11 June 2016

Keywords:

Nickel catalyst
 Hydrocyanation
 Cyanohydrin
 Alkene

ABSTRACT

An active nickel catalyst prepared in situ from a Ni(II) compound, phosphine ligand, and zinc powder was found to be an efficient catalyst system for the hydrocyanation of various alkenes using acetone cyanohydrin as a safer cyano source. The combination of NiCl₂·6H₂O and 1,3-bis(diphenylphosphino)propane was the most efficient catalyst precursor in DMF. Under the optimized conditions, various styrenes, heterocyclic alkenes, and aliphatic alkenes were converted to their corresponding nitriles in excellent yields.

© 2016 Elsevier Ltd. All rights reserved.

Introduction

The nitrile functional group is particularly useful in organic synthesis as it can be converted into a range of other functional groups. For example, amine, amide, carboxylic acid, ester, aldehyde, and ketone moieties can be obtained from nitriles.¹ In addition to being versatile compounds in chemical transformations, nitriles are also important building blocks in the preparation of pharmaceuticals, pesticides, and other functional materials widely used in daily life.² To date, various methods have been reported for the preparation of nitriles.³ Pioneering examples of alkene hydrocyanation using homogeneous Co(0) have been reported,⁴ and Pd(0)⁵ and Ni(0)⁶ catalyst systems have also been proposed, with Ni(0)-promoted hydrocyanation being developed recently.⁷ In particular, the DuPont adiponitrile synthesis is one of the most studied processes.⁸ This hydrocyanation process requires an expensive Ni(0) catalyst and an excess amount of hydrogen cyanide as the cyano source. However, the Ni(0) catalyst is difficult to handle due to its sensitivity to moisture and oxygen, while hydrogen cyanide is extremely toxic. Therefore, an alternative, more environmentally benign method is required.

We considered that the preparation of an active catalyst species and the choice of cyano source were key to developing such a strategy. Thus, we focused on the in situ preparation of an active species from a metal precatalyst and a phosphine ligand.

Alternative cyano sources to hydrogen cyanide were also considered, with acetone cyanohydrin being selected as a safer cyano source. This reagent is liquid at room temperature, and so is considered easier to handle than cyanide compounds. The combination of these approaches yielded an efficient hydrocyanation system, the details of which are disclosed and discussed below.

Results and discussion

The hydrocyanation of 2-norbornene was attempted using various Ni(II) precatalysts in *N*-methyl-2-pyrrolidone (NMP), which is known to be a suitable solvent for catalytic C–C bond forming reactions.⁹ The results of the various experiments are summarized in Table 1. Initially, Ni(acac)₂·4H₂O was selected, as it is a good precursor to Ni(0) species.¹⁰ Hydrocyanation proceeded to give 2-norbornanecarbonitrile as the major product, as determined by GC-FID (gas chromatography–flame ionization detection). However, a poor yield of only 4% was obtained. Nickel halide hydrates were also screened (entries 2–4), with NiCl₂·6H₂O giving relatively good product yields and selectivities. No improvement in yield was obtained even upon employing anhydrous precatalysts. Poor results were also obtained for Ni(OAc)₂·4H₂O (entry 5). In an attempt to improve conversion, a range of solvents were screened for use with NiCl₂·6H₂O. Slightly polar solvents such as THF, MeOH, and acetonitrile were not effective in this reaction (entries 6–8) due to the poor solubility of NiCl₂·6H₂O, indicating that precatalyst solubility is important in this reaction. Strongly polar solvents such as DMSO and DMF gave similar results to NMP, but as with DMAc, selectivity

* Corresponding author. Tel.: +81 29 861 3553; fax: +81 29 861 4872.

E-mail address: k-nemoto@aist.go.jp (K. Nemoto).

Table 1
Hydrocyanation of 2-norbornene using various Ni(II) precatalysts, solvents, and reductants^a

Entry	Precatalyst	Solvent	Reductant	Ligand	Product yield ^b (%)	Substrate remaining ^b (%)	Selectivity ^b (%)
1	Ni(acac) ₂ ·2H ₂ O	NMP	Zn	PPh ₃	4	91	44
2	NiCl ₂ ·6H ₂ O	NMP	Zn	PPh ₃	31	61	79
3	NiBr ₂ ·3H ₂ O	NMP	Zn	PPh ₃	24	56	55
4	NiI ₂ ·6H ₂ O	NMP	Zn	PPh ₃	33	36	52
5	Ni(OAc) ₂ ·4H ₂ O	NMP	Zn	PPh ₃	7	73	26
6	NiCl ₂ ·6H ₂ O	THF	Zn	PPh ₃	3	87	23
7	NiCl ₂ ·6H ₂ O	MeOH	Zn	PPh ₃	3	63	8
8	NiCl ₂ ·6H ₂ O	Acetonitrile	Zn	PPh ₃	2	89	18
9	NiCl ₂ ·6H ₂ O	DMF	Zn	PPh ₃	48	34	73
10	NiCl ₂ ·6H ₂ O	DMAc	Zn	PPh ₃	16	59	39
11	NiCl ₂ ·6H ₂ O	DMSO	Zn	PPh ₃	44	40	73
12	NiCl ₂ ·6H ₂ O	CH ₂ Cl ₂	Zn	PPh ₃	1	96	25
13	NiCl ₂ ·6H ₂ O	Toluene	Zn	PPh ₃	1	94	17
14	NiCl ₂ ·6H ₂ O	Hexane	Zn	PPh ₃	3	78	14
15	NiCl ₂ ·6H ₂ O	DMF	Mg	PPh ₃	Trace	92	–
16	NiCl ₂ ·6H ₂ O	DMF	Al	PPh ₃	Trace	94	–
17	NiCl ₂ ·6H ₂ O	DMF	Mn	PPh ₃	21	60	53

^a Reaction conditions: 2-norbornene, 16.0 mmol; acetone cyanohydrin; 16.0 mmol, catalyst, 3 mol %; ligand, 6 mol %; reductant, 30 mol %; solvent, 5 mL, under N₂ (0.5 MPa), 90 °C, 15 h.

^b Determined by GC-FID analysis.

was poor (entries 9–11). Weakly polar solvents such as CH₂Cl₂, toluene, and hexane were not suitable, yields of 1–3% being obtained (entries 12–14). Subsequently, Mg, Al, and Mn were also screened as reductants combined with NiCl₂·6H₂O, but no improvement in yield was observed (entries 15–17), thus indicating that the choice of reductant was also important. Adequate generation of the Ni(0) species is therefore expected to be key in this reaction.

Initially, NiCl₂·6H₂O reacts with triphenylphosphine to give NiCl₂(PPh₃)₂ complexes, which are readily reduced to the Ni(0) species by Zn via transmetalation. The active species in this reaction system appears to be the Ni(0)-phosphine complex, as reported by Miyaura et al.¹¹ As this Ni(0) complex is unstable and short-lived at room temperature,^{11b} spectroscopic confirmation is problematic, even at low temperatures. Identification of the Ni(0) species by NMR spectroscopy was unfortunately not successful. We hypothesized that the Ni(0) species was stabilized by the coordination of a 2-norbornene-like Ni(cod)₂ complex, and that hydrocyanation was triggered by this stabilization. We therefore attempted to synthesize the nickel bis(triphenylphosphine)-bis(2-norbornene) complex, but all attempts were unsuccessful. Instead of the desired Ni(0) complex, a norbornene dimer was observed by mass spectrometry.¹² Examination of the literature revealed that such dimerizations were likely induced by an Ni(0) species coordinated to two norbornene molecules.¹³ Indeed, this dimerization itself confirms our hypothesis, and so we expect that our hydrocyanation proceeded in a similar manner.

We then carried out ligand screening to improve product yields and selectivities. According to previous reports, phosphite ligands tend to be effective in hydrocyanation reactions. Indeed, the product yield was improved to 86% when triphenylphosphite was used (Table 2, entry 1). However, as some decomposition to phenol was observed, the phosphite ligands were unsuitable for reuse. Similarly, alkyl phosphines such as trimethylphosphine, tributylphosphine, and tri-*tert*-butylphosphine were easily decomposed, and spontaneously caught fire upon contact with air. These ligands were therefore excluded as ligand candidates. Other monodentate ligands such as tri(mesityl)phosphine, tri(1-naphthyl)phosphine, and tri(*o*-tolyl)phosphine were investigated, with no reaction being observed (entries 2–4), suggesting that steric bulkiness affected the Ni(0) species activity. Bidentate ligands with a wide bite angle were therefore expected to influence the activity of the Ni(0) species, and so various bisphosphine ligands were tested in the presence of NiCl₂·6H₂O and Zn in DMF

(entries 5–10). The use of bisphosphine ligands drastically increased both the product yield and selectivity. In particular, the reaction proceeded smoothly and almost quantitatively when 1,3-bis(diphenylphosphino)propane (dppp) was employed (entry 7). The reaction solution became a bright red-orange color when dppp was used, indicating that the NiCl₂(dppp) complex was generated in situ, which supported the above-mentioned reaction mechanism. Indeed, a stoichiometric quantity of acetone cyanohydrin was sufficient to achieve almost complete conversion. Other bidentate ligands, such as *N,N,N',N'*-tetramethylethylenediamine and ethylene glycol dimethyl ether, were not beneficial to the reaction. However, the reaction proceeded moderately when 2,2'-bipyridine was used, the product yield was 49%.

Further optimization allowed reduction in the catalyst amount to 1 mol %, ligand loading to 2 mol % and reductant amount to 10 mol % without any significant decrease in yield for the hydrocyanation of 2-norbornene (Table 3, entry 1).¹⁴ Our catalyst system was then compared to typical homogeneous catalysts for the hydrocyanation reaction, but the reaction was not successful (entries 2–8). The reaction gave only trace amounts of product in the presence of Ni(CO)₂(PPh₃)₂, Ni(PPh₃)₄, Ni[P(OPh)₃]₄, and Pd(PPh₃)₄. With the exception of entry 4 (Ni(PPh₃)₄), adequate amounts of 2-norbornene remained intact. In these reactions, the inactivated species were presumably formed through catalyst poisoning. Indeed, it has been reported that some Ni(0), Pd(0), and Co(0) catalysts were deactivated through the formation of cyanide complexes.¹⁵ However, our reaction proceeded smoothly, demonstrating that a distinguished and convenient system had been developed.

With the optimized conditions in hand, we attempted the hydrocyanation of a range of aromatic and heterocyclic alkenes (Table 4). Styrene was converted to their corresponding mononitrile mixtures in good yields (entry 1). Moreover, halogenated styrenes were also converted to their corresponding mononitrile mixtures in good yields (entries 2–4). It was interesting that aromatic carbon–bromine bond was not cleaved. Strong electron-donating group such as –OMe group accelerated the reaction, to give their corresponding mononitrile mixtures in good yields (entry 5). Indeed, our catalyst system was not affected by the coordination effect of the methoxy group. However, the reaction was disturbed by a strong electron-withdrawing group such as the –CO₂Me group. The conversion was notably decreased to give corresponding mononitrile mixture only in 19% (entry 6). We also

Download English Version:

<https://daneshyari.com/en/article/5258871>

Download Persian Version:

<https://daneshyari.com/article/5258871>

[Daneshyari.com](https://daneshyari.com)