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Nitrile hydroboration reactions catalysed by simple nickel salts, bis(acetylacetonato)nickel(II) and its derivatives

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Go Nakamura, Yumiko Nakajima,* Kazuhiro Matsumoto, Venu Srinivas and Shigeru Shimada*

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Simple nickel salts, bis(acetylacetonato)nickel(II) and its derivatives, catalysed hydroboration reactions of aryl and alkyl nitiles with catechol borane. The reaction smoothly proceeded for nitriles with various substituents to form the corresponding bis(boryl)amines in good to excellent yields.

Introduction

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Efficient and versatile synthesis of primary amines has been intensively studied due to the significant importance of the amines as key intermediates in the chemical industry.¹ Reduction of nitriles is one of the most powerful methods for the production of primary amines and has been efficiently achieved using stoichiometric amounts of metal hydrides.² However, these methods suffer from several drawbacks, such as high temperatures, low functional group tolerance, low reaction selectivity, etc. Hydrosilylation^{3,4} and hydrogenation⁵ of nitriles have also been reported as alternative routes for the production of amines in the last few decades. In the former examples, transition metal complexes as well as a non-metallic Lewis acid are revealed to efficiently catalyse the reactions under ambient conditions. More recently, hydroboration catalysed by metal complexes has emerged as a new approach for the nitrile reductions.⁶⁻⁸ For example, the reactions are reported to be catalysed by metal complexes supported by a unique ligand system, such as imido-hydrido complex $(ArN)Mo(H)(CI)(PMe_3)_3$, ⁶ β -diketiminato *n*-butylmagnesium complex⁷ and bis(2'-hydroxy-6'-iminopyridyl)isoindoline Ru(II) complex⁸ at a catalyst loading of 5-10 mol%. Mechanistic studies supported that all these reactions proceed via agostic borylamino and/or borylimino intermediates. It is to be noted that the utility of commercial available [RuCl₂(p-cymene)]₂ was reported as the most efficient catalyst in 2016.⁹ Thus, hydroboration of various nitriles proceeds at 60 °C in the presence of 1 mol% of $[RuCl_2(p-cymene)]_2$. On the other hand, nitrile hydroboration reactions using unactivated boranes, such as HBcat (cat = catecholato) and HBpin (pin = pinacolato) are still rare, although the catalytic hydroboration reactions of a wide range of substrates bearing multiple C-C, C-O, or C-N bonds have been intensively developed.¹⁰⁻¹⁴

We have thus far engaged in the development of various nickel hydrosilylation catalysts.^{15,16} Among these studies, it that was revealed simple nickel salts. bis(acetylacetonato)nickel(II) Ni(acac)₂ (1) and its derivatives bis(hexafluoroacetylacetonato)nickel(II) (2) and bis(2,2,6,6tetramethyl-3,5-heptanedionato)nickel(II) (3) acted as selective hydrosilylation catalysts of olefins with various functional groups in the presence of NaEt₃BH.¹⁵ Since **1-3** are cheap and readily available from commercial sources and thus are expected to be a good candidate as precious metal surrogates, we became interested in the further reactivity investigation of 1-3. In this study, it was revealed that 1-3 serve as good hydroboration catalysts of various nitriles. Different from the hydrosilylation reactions, the hydroboration reactions were successufully catalysed by 1-3 without any additives such as metal hydride reagents.

Results and Discussion

Catalytic activities of various metal salts including 1-3 were initially investigated for the hydroboration of benzonitrile (PhCN) with HBcat at room temperature. As shown in Table 1, it was revealed that 1-3 exhibited excellent performance in benzene to quantitatively give 1,1-bis(boryl)amine, PhCH₂N(Bcat)₂ (Table 1, entries 1-3). The use of polar solvents such as tetrahydrofuran and 1,2-dichloroethane resulted in the drastic decrease in the product yields (trace amounts). The reaction also proceeded at 1 mol% catalyst loading of 1-3 at slower rate, yielding PhCH₂N(Bcat)₂ in 49, 19, and 78% yields, respectively. Thus, the highest activity of 3 among three was confirmed. NiCl₂ did not catalyse the reaction, whereas $Ni(cod)_2$ (cod = cyclooctadiene) exhibited good catalytic activity (vide infra) (Table 1, entries 4 and 5). Among other metal

^a National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

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Table 1. Hydroboration of PhCN with HBcat catalysed by metal salts^[a]

Ph—≡N	+ 2 HBcat	catalyst (5 mol%) C ₆ H ₆ , RT, 12 h	Ph N Bcat Bcat
entry	catalyst		yield ^[b]
	(mol%)		(%)
1	1		>99 (49) ^[c]
2	2		>99 (19) ^[c]
3	3		>99 (78) ^[c]
4	NiCl ₂		ND
5	Ni(cod)₂		87
6	Co(acac) ₂	!	37
7	Cu(acac) ₂	!	ND
8	Mn(acac)	2	ND
9	Pd(acac) ₂		ND

[a] Catalyst (0.01 mmol), PhCN (0.20 mmol), HBcat (0.44 mmol) in C_6H_6 5 mL at room temperature for 12 h. [b] NMR yield based on an internal standard (PhSiMe₃). [c] The values in parenthesis represent the yields at a 1 mol% catalyst loading.

acetylacetonates, only $Co(acac)_2$ showed moderate catalytic activity (Table 1, entries 6-9).

Next, the scope of the reaction was investigated using the most active catalyst 3. The results are summarized in Table 2. Hydroboration of benzonitrile was achieved at lower catalyst loading, 0.5 mol% of 3, resulting in the quantitative formation of PhCH₂N(Bcat)₂ (Table 2, entry 1). Similarly, those of mtolunitrile and p-tolunitrile smoothly proceeded to quantitatively form ArCH₂N(Bcat)₂ (Ar = m-CH₃C₆H₄, p-CH₃C₆H₄) under the same reaction conditions (Table 2, entries 3, 4). In contrast, hydroboration of o-tolunitrile resulted in the formation of $(o-CH_3C_6H_4)CH_2N(Bcat)_2$ in 40% yield even at 5 mol% catalyst loading of 3, indicating the induced steric hindrance by the o-methyl group (Table 2, entry 2). It is to be mentioned that the reactions of benzonitriles with both electron-donating OMe and -withdrawing CF₃ groups smoothly proceeded at 0.5 mol% catalyst loading (Table 2, entries 5, 6). Hydroborations of *m*- and *p*-chlorobenzonitriles required a higher catalyst loading, 5 mol%, to attain good yields, 81% and 78%, respectively (Table 2, entries 7, 8). It was revealed that p- XC_6H_4CN (X = Br, I) did not undergo hydroboration under the same reaction conditions, probably due to the occurrence of C–X bond cleavage.¹⁷ A heteroaromatic nitrile, 2furancarbonitrile, was successfully hydroborated (Table 2, entry 9), whereas the reaction of 2-thiophenecarbonitrile slowly proceeded to give the corresponding hydroborated product in 47% yield (Table 2, entry 10). Hydroborations of various alkyl nitriles were also achieved at a catalyst loading of 3-5 mol% giving the products quantitatively. (Table 2, entries 11-16).

To obtain information on the reaction mechanism, reactions of **3** with PhCN or HBcat in C_6D_6 were monitored by ¹H NMR spectroscopy. The addition of PhCN (2 equiv) to **3** resulted in no observable spectroscopic change. It is likely that there is a fast coordination equilibrium between **3** and PhCN, as previously reported by Henneike et al.¹⁸ In contrast, **3** was

completely consumed on the treatment with 4 equiv of HBcat after 15 min

 Table 2. Hydroboration of various nitriles with HBcat catalysed by 3^[a]

P		>	Bcat
		C ₆ H ₆ , RT, 18 h	R N Bcat
entry	R	3 (mol%)	Product yields% ^[b]
1	Ph	0.5	>99 (93)
2	$o-CH_3C_6H_4$	5	40 (36)
3	m-CH ₃ C ₆ H ₄	0.5	>99 (92)
4	p-CH ₃ C ₆ H ₄	0.5	>99 (92)
5	<i>p</i> -MeOC ₆ H ₄	0.5	>99 (95)
6	$p-CF_3C_6H_4$	0.5	>99 (85)
7	$m-CIC_6H_4$	5	81 (64)
8	$p-CIC_6H_4$	5	78 (62)
9	2-furyl	5	>99 (95)
10	2-thienyl	5	47 (29)
11	PhCH₂	3	>99 (88)
12	Me	3	>99 (84)
13	Et	3	>99 (90)
14	<i>i</i> Pr	3	>99 (94)
15	<i>t</i> Bu	5	>99 (90)
16	Су	5	>99 (90)

[a] Nitriles (0.20 mmol), HBcat (0.44 mmol) and catalyst (0.5-5 mol% vs nitriles) in C_6H_6 5 mL at room temperature for 18 h. [b] NMR yield (isolated yield).

to form black precipitates, which was confirmed to be catalytically inactive. In this reaction, dissociation of the ligand was evidenced by the formation of [*t*BuCOCHC(*t*Bu)O- κ O, κ O']Bcat (4), which was confirmed by ¹H and ¹¹B NMR as well as by a single crystal X-ray diffraction analysis. No signal assignable to the NiH group was observed in the hydride region (δ 0 to -30 ppm) of the ¹H NMR spectra. Based on these experiments, it is presumable that **3** is reduced on the treatment with HBcat to form catalytically active Ni(0) species, which could be easily converted to black precipitate.¹⁹

There are several potential mechanisms for hydroboration catalysed by 1-3. One possible mechanism is postulated, following the previously reported Ni-catalyzed hydroborations (Scheme 1).^{13,20} The reaction starts with the reduction of **3** by HBcat to form an active Ni(0) species A accompanied by the formation of 4. The Ni(0) species A undergoes oxidative addition of HBcat, leading to the formation of boryl hydride intermediate B. Complex B undergoes insertion of a nitrile into the Ni-H bond to give C.²¹ After the occurrence of reductive elimination, borylimine RCH2=NBcat is formed as the monohydroborylated product and reproduce A. RCH₂=NBcat further reacts with HBcat to give the final product RCH₂N(Bcat)₂. It was confirmed that the reaction of Nbenzylidenebenzylamine with HBcat resulted in the quantitative formation of (PhCH₂)₂NBcat at room temperature without a catalyst. This result strongly supports the occurrence of the non-catalysed final hydroboration step.



The proposed mechanism including the active Ni(0) species is consistent with the comparable activity of $Ni(cod)_2$ as 1-3. On the other hand, it was also confirmed that the product yield significantly decreased to 38% when the hydroboration of PhCN was performed in the presence of excess Hg with vigorous stirring.²² The result supports the *in situ* formation of metallic nickel(0) particles as an active catalyst.²³ Thus, it is possible that the reaction is catalysed by both homogeneous and heterogeneous Ni(0) species.

Conclusion

In this study, we have shown one of rare examples of hydroboration reactions of various nitriles using commercially available simple nickel salts 1-3. It is to be noted that the catalysts 1-3 are completely free from the complexity in the preparations, which are often troublesome in the previously reported systems. In addition, the catalyst loading could be reduced to 0.5 mol% in the hydroboration of benzonitriles. Studies to elucidate the mechanistic details and further applications of 1-3 as catalysts are to be performed.

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hydroboration of nitriles catalyzed by simple Ni salts



Simple Nickel salts, bis(acethylacetonato)nickel(II) abd its derivatives, catalyzed hydroboration reactions of aryl and alkyl nitriles with catechol borane.