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Very Important Publication

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Selective Synthesis of Secondary Amines from Nitriles by a User-Friendly Cobalt Catalyst

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Abstract. Selective hydrogenation/reductive amination of nitriles to secondary amines catalyzed by an inexpensive and user-friendly cobalt complex, (Xantphos)CoCl₂, is reported. The use of (Xantphos)CoCl₂ and ammonia borane (NH₃-BH₃) combination affords the selective reduction of nitriles to symmetrical secondary amines, whereas the employment of (Xantphos)CoCl₂ and dimethylamine borane (Me₂NH-BH₃) along with external amines produce unsymmetrical secondary amines and tertiary amines. The general applicability of this methodology is demonstrated by the synthesis of 43 symmetrical and unsymmetrical secondary and tertiary amines bearing diverse functionalities.

Keywords: Cobalt; Hydrogenation; Nitriles; Reductive amination; Secondary amines

Amines are the privileged organic compounds extensively used as starting materials in the pharmaceuticals, agrochemicals, fungicides, fragrances, plastics, and dyes.^[1] Thus, efficient and cost-effective synthesis of amines using a simple catalyst system is very crucial. Among the various methods developed, the synthesis of amines by the catalytic reduction of nitriles is the most common route and is among the active field of research significance.^[1c,d,2] However, the catalytic reduction of nitriles suffers from critical selectivity problem leading to the formation of various amines, like primary amines, secondary amines, and tertiary amines, as well as imines (Scheme 1). Nevertheless, notable methods are known for the selective synthesis of amines or imines from nitriles via direct hydrogenation using 4d noble metal catalysts, such as ruthenium,^[4] molybdenum,^[3] rhodium,^[5] palladium,^[5c,6] iridium,^[5b,7] platinum.^[8] Considering the sustainability and environmental benefits, recently, diverse 3d transition metal-based catalysts have been employed for the reduction of nitriles to amines and imines. For example, the groups of Beller, Milstein, and others have extensively reported on the

hydrogenation of nitriles using pincer ligated manganese,^[9] iron,^[10] and cobalt^[11] catalysts (Scheme 2A).^[12] Guan has demonstrated the reduction of nitriles to primary amines in the absence of ^{iPr}PNP-ligand, whereas the reaction led to aldimines employing ^{iPr}PNP/CoX₂ catalyst.^[11e] Notably, all the reported direct hydrogenation of nitriles uses a very high hydrogen pressure, which needed special reaction set-up and expertise, and could be hazardous.



Scheme 1. General scheme for the hydrogenation of nitrile.

The transfer hydrogenation is an alternative protocol to the direct hydrogenation of nitriles,^[13] wherein sacrificial hydrogen source is used in place of hydrogenation pressure, and simple reaction set-up is needed. In that direction, the hydrogenation of nitriles to primary- and tertiary amines has been reported by palladium catalysis using HCOOH/base as the hydrogen source.^[14] Similarly, the ruthenium-catalyzed reduction of nitriles to primary and secondary amines has been demonstrated.^[15] Considering the importance and sustainability of base metal catalysis, Li and Garcia independently demonstrated the cobalt^[16] and nickel^[17] catalyzed transfer hydrogenation of nitriles to primary amines and imines, wherein the selectivity remained a challenging task. Although, the selective direct hydrogenation or transfer hydrogenation of nitriles to

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primary amines and aldimines is significantly progressed (Scheme 2A), the report on the selective synthesis of secondary amines *via* reductive amination of nitriles is scarce, with one example of the (PNN)-pincer cobalt catalyzed hydrogenation of nitriles to secondary amines using ammonia-borane is demonstrated by Zhou and Liu (Scheme 2B).^[18]



Scheme 2. Examples of base-metal catalyzed reductions of nitriles to primary and secondary amines.

Furthermore, the developed protocols for the synthesis of amines from nitriles have certain limitations. For example, most of the approaches employ a tridentate pincer-ligated catalyst system,^[2,19] wherein the synthesis of pincer ligands and corresponding catalysts involves multiple steps. Besides, most of the employed ligand systems are based on the expensive and sensitive alkyl phosphines, and hence, requires specialized expertise on the ligand synthesis. Thus, a generalized protocol for the synthesis of secondary amines by using a commercially available ligand with inexpensive cobalt salt under mild hydrogen source is highly desirable. To address these limitations associated with

the existing amination/reductive amination protocols, and within our interest on base-metal catalysis,^[20] herein, we report a user-friendly (Xantphos)CoCl₂ catalyst system for the selective reductive amination of nitriles to symmetrical and unsymmetrical secondary amines under mild conditions (Scheme 2B). Thus, the cobalt catalyst selectively reduces the aromatic nitriles to symmetrical secondary amines using ammonia-borane (H₃N-BH₃) as a hydrogen source, whereas the use of external amines and dimethylamine borane (Me₂NH-BH₃) afforded unsymmetrical secondary and tertiary amines.

We have initiated the optimization studies for the reductive amination of benzonitrile (1a) to afford secondary amine 2a employing CoCl₂ and various commercially available nitrogen- and phosphine ligands (Table 1). Based on the literature precedents, we could quickly rationalize that the alcoholic solvents are suitable for the reductive amination. Thus, the reductive amination of benzonitrile (0.3 mmol) as a model substrate using simple CoCl₂ (5 mol%) as a catalyst and inexpensive dimethylamine borane (2.0 equiv) as the hydrogen source in methanol afforded dibenzylamine (2a) in addition to the trace formation of benzyl amine (A) at 60 °C (entry 1). The reaction in ethanol or *iso*-propanol solvents did not lead to any significant improvement, and overall conversion was in the range of 15-25%. Notably, the reaction in the solvent HFIP was improved and gave 56% overall conversion with 27% of reductively aminated product 2a (entry 4). The employment of nitrogen ligands bpy or phen has little influence on the overall amination reaction (entries 5,6). To our surprise, the use of phosphine ligands along with CoCl₂ gave quantitative conversion and good selectivity for the reductive amination product 2a (entries 7-9). Particularly, the employment of Xantphos/CoCl₂ system provided 73% of dibenzylamine 2a and 24% of aminated product A using Me₂NH-BH₃ as the hydrogen source. Upon performing the same reaction using H₃N-BH₃ as hydrogen source under Xantphos/CoCl₂ catalyst system, the reaction afforded 87% of product 2a (entry 10). The reaction led to the quantitative formation of product 2a even at room temperature (27 °C) (entry 11). Notably, the employment of 1.0 mol% of Xantphos/CoCl₂ or (Xantphos)CoCl₂ (isolated complex)^[21] as catalyst, the reaction selectively gave reductive amination product 2a in around 89% isolated yield (entries 12,13). When the Me₂HN-BH₂ was employed as a hydrogen source under the optimized conditions, the reaction was slightly less effective (entry 14). Without a cobalt catalyst, the reaction failed to deliver the reductive amination or simple amination products (entry 15). The use of other cobalt precursors, such as CoBr₂, Co(OAc)₂, $Co(OAc)_3$ along with Xantphos are slightly less effective. The catalytic reaction using *n*-hexane as solvent (Zhou and Liu conditions) afforded 8% of primary amine (A) and 3% of amine 2a.

		CoCl ₂ (5 mol%) ligand (6 mol%)	N [*] N*	\sim				
	«CN —	solvent	+	+				
	(1a)	60 °C, 16 h (A)	(2	!a)	(4	A')		
entry	[H ₂]-source	ligand [or cat]	solvent GC			GC yield (%) ^[c]		
				conv (%) ^[b]	Α	2a	А'	
1	Me ₂ NH-BH ₃	-	MeOH	25	4	15	-	
2	Me ₂ NH-BH ₃	-	EtOH	24	7	14	-	
3	Me ₂ NH-BH ₃	-	ⁱ PrOH	15	9	3	-	
4	Me ₂ NH-BH ₃	-	HFIP	56	2	27	3	
5	Me ₂ NH-BH ₃	bpy	HFIP	25	14	7	-	
6	Me ₂ NH-BH ₃	phen	HFIP	30	17	8	-	
7 ^[d]	Me ₂ NH-BH ₃	PPh ₃	HFIP	100	-	56	16	
8	Me ₂ NH-BH ₃	dppe	HFIP	99	3	61	34	
9	Me ₂ NH-BH ₃	Xantphos	HFIP	100	24	73	3	
10	NH ₃ -BH ₃	Xantphos	HFIP	100	5	87	2	
11 ^[e]	NH ₃ -BH ₃	Xantphos	HFIP	100	4	90	1	
12 ^[e,f]	NH3-BH3	Xantphos	HFIP	100	6	94 (88)	-	
13 ^[e,f]	NH3-BH3	(Xantphos)CoCl ₂	HFIP	100	6	94 (89)	-	
14 ^[e]	Me ₂ NH-BH ₃	Xantphos	HFIP	75	8	51	12	
15 ^[e]	NH ₃ -BH ₃	-	HFIP	-	-	-	-	
16 ^[e]	NH ₃ -BH ₃	[Co]/Xantphos	HFIP	80	4	68	2	
17	NH ₃ -BH ₃	(Xantphos)CoCl ₂	<i>n</i> -hexane	15	8	3	-	

Table 1. Optimization of reaction parameters for the reductive amination of benzonitrile to dibenzylamine.^[a]

[H₂]-source

[a] Reaction conditions: Benzonitrile (0.031 g, 0.30 mmol), [H₂]-source (0.60 mmol), CoCl₂ (0.0019 g, 0.015 mmol, 5 mol%), ligand (0.018 mmol, 6 mol%), solvent (1.0 mL). [b] GC conversion based on substrate benzonitrile. [c] Yield determined using *n*-tetradecane as internal standard, isolated yield is in parenthesis. [d] 12 mol% of PPh₃ was used, 25% tribenzyl amine (tertiary amine) was observed. [e] Reaction carried out at 27 °C. [f] Employing 1.0 mol% of CoCl₂/Xantphos or 1.0 mol% of (Xantphos)CoCl₂ complex. HFIP = Hexafluoroisopropanol, bpy = 2,2'-Bipyridine, phen = 1,10-Phenanthroline, dppe = 1,2-Bis(diphenylphosphino)ethane, Xantphos = 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene. [Co] = CoBr₂, Co(OAc)₂, or Co(OAc)₃.

With the optimized reaction conditions in hand, we started substrate scope for the synthesis of symmetrical secondary amines using 1.0 mol% of catalyst (Xantphos)CoCl₂ and ammonia-borane (2.0 equiv) at room temperature (Scheme 3). Thus, the para-substituted benzonitrile bearing various functionalities, such as alkyl, alkoxy, -F, -Cl, -Br, -CF₃ smoothly underwent reductive amination to secondary benzylamines (2a-2h) in good to excellent yields. Both the electron-donating and electronwithdrawing functionalities favoured the reaction, thus leading to quantitative conversion. Similarly, the *meta-* and *ortho-substituted* benzonitriles participated in the reaction with excellent activity and good functional group tolerability delivering the products 2i-2m. The tolerability of halide functionalities in the synthesis of secondary benzylamines is very crucial as these compounds can further be employed in the

The fluoro-substituted cross-coupling reactions. 3,5-difluorobenzonitrile benzonitriles, and 3,5bis(trifluoromethyl)benzonitrile underwent reductive amination under the cobalt catalysis to produce bis(3,5-difluorobenzyl)amine (2n)and bis(3,5bis(trifluoromethyl)benzyl)amine (20) in 77% and 64% yields, respectively. These kinds of fluoro containing amines have extensive usage in pharmaceuticals as they significantly enhance the lipophilicity and metabolic stability of the desired drug molecule. The reductive amination reaction condition was well tolerated by aromatic nitrile with a heteroatom, *i.e.*, 3-cyano thiophene by yielding 75% product of isolated 2p. Furthermore, the chemoselectivity of the methodology has been checked by using methyl-4-cyanobenzoate, wherein only the nitrile part was reduced to amine keeping the ester functionality intact (2q). When the 4cyanobenzaldehyde was subjected for the reductive

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amination under the optimized conditions, both the carbonyl and nitrile groups were reduced to give secondary amine 2r in 65% yield. In all the reductive amination reactions, we have selectively observed the formation of secondary amines, whereas the imines or *tert*iary amines were not detected. However, only traces of primary amine products were observed during the reductive amination reactions.



Scheme 3. Scope of reductive amination of nitriles to symmetrical secondary amines. Substrate 1 = 0.5 mmol, NH₃-BH₃ = 0.031 g, 1.0 mmol. [a] 2.0 mmol of NH₃-BH₃ used.

The user-friendly and inexpensive cobalt catalysis further extended to the synthesis was of unsymmetrical secondary amines and tertiary amines using diverse external amine compounds. During the reaction optimization, we have found that the use of less expensive dimethylamine borane (Me₂NH-BH₃) instead of ammonia-borane as a hydrogen source for the synthesis of unsymmetrical amines was beneficial and resulted with high selectivity of the desired compound (Table 2). Thus, dimethylamine-borane was employed for the synthesis of unsymmetrical secondary amines, and tertiary amines. Initially, we have performed reductive amination of benzonitrile using diverse external amines. The benzonitrile underwent partial reduction and reacted smoothly with aniline derivatives to afford the desired products 4a-4c in good to excellent yields. Similarly, benzylamines participated in the reductive amination of benzonitrile to deliver products 4d-4f in attractive vields. In addition to the aromatics and benzylamines,

the aliphatic amines can be used as external amine source for the reaction yielding 4g and 4h in 69% and 78%, respectively. The amine 3i bearing -OH functionality reacted smoothly to produce the desired secondary amine (4i) in moderate yield. Additionally, the secondary amines as nucleophiles took part in the reductive amination of benzonitrile to give tertiary amines 4j and 4k in 75% and 83% yield, respectively. The secondary cyclic amines 1.2.3.4tetrahydroquinoline and morpholine upon reaction with benzonitrile under reductive amination conditions afforded tertiary amines 4l and 4m in excellent yields. The reaction tolerated pyridinylsubstituted compounds and underwent reductive amination in moderate to good yields (4n-4p). Furthermore, electronically distinct substituents, such as -OMe, -Br, -CF₃, -COOMe were well tolerated on the benzonitrile backbone and delivered the desired products (4q-4s) in good to excellent yields. In addition to the aromatic nitriles, the aliphatic nitriles 2-phenylacetonitriles and butyronitrile underwent reductive amination with aniline derivatives to give secondary amines 4t-4w in good yields. The heteroarenes nitrile, nicotinonitrile upon treatment with aniline under reductive amination conditions afforded 4x in 83% yield. Notably, the use of 1,3-dicyanobenzene upon reductive amination with aniline produced 4y in 74% yield, which can be employed as a tridentate NCN-pincer type of ligand.

Table 2. Reaction conditions for the reductive amination of benzonitrile to unsymmetrical amine.^[a]

(1a)	-CN + H ₂ N-(3a)	[H ₂]-source (Xantphos)CoCl; (1.0 mol%) HFIP (1.0 mL) 27 °C, 16 h		(2a) + (4	4a)	
entry [H ₂]-source		GC conv.	GC yield (%) ^[c]			
		(%) ^[b]	2a	4a	other	5
1	H ₃ N-BH ₃	100	27	68	< 4	
2	Me ₂ NH-BH ₃	100	7	91 (87)	< 2	

[a] Reaction conditions: Benzonitrile (0.052 g, 0.50 mmol), aniline (0.051 g, 0.55 mmol), [H₂]-source (1.0 mmol), (Xantphos)CoCl₂ (0.0035 g, 0.005 mmol, 1.0 mol%). [b] GC conversion based on substrate benzonitrile. [c] Yield determined using *n*-tetradecane as internal standard, isolated yield is in parenthesis.



Scheme 4. Scope of reductive amination of nitriles to unsymmetrical secondary amines. [a] 0.75 mmol of amine used. [b] 1.0 mmol of amine used. [c] 4.0 equiv of Me_2NH-BH_3 is used.

Considering the synthetic importance of secondary amines and taking advantage of simple cobalt catalyzed protocol, we have demonstrated the practical utility of the developed method for the synthesis of symmetrical secondary amine in gram scale. Thus, the reductive amination of 1.0 g benzonitrile with NH₃-BH₃ using (Xantphos)CoCl₂ in HFIP gave 82% yield of product **2a** (Scheme 5).



Scheme 5. Gram scale synthesis.

In summary, we have developed a simple, inexpensive and user-friendly cobalt-catalyzed method for the selective and practical synthesis of symmetrical and unsymmetrical secondary amines via reductive amination of nitriles. The employment of (Xantphos)CoCl₂ and ammonia borane (NH₃-BH₃) led to the selective reduction of the nitriles to symmetrical secondary amines, whereas the use of dimethylamine borane (Me₂NH-BH₃) along with external amines selectively afforded unsymmetrical secondary amines, and tertiary amines. The reaction tolerated diverse functionalities, such as alkyl, alkyl ether, halides (-F, -Cl, -Br), -CF₃, -COOMe and heteroarenes. Both the aromatic and aliphatic nitriles, as well as primary and secondary amines, efficiently took part in the reaction to afford the secondary amines and tertiary amines in excellent yields. The developed user-friendly method is expected to be beneficial for the practical use in the synthesis of symmetrical and unsymmetrical secondary amines.

Experimental Section

Representative procedure for the synthesis of symmetrical secondary amines: Dibenzylamine. A Teflon screw-cap tube was introduced with (Xantphos)CoCl₂ (0.0035 g, 0.005 mmol), ammonia borane (0.031 g, 1.0 mmol) and benzonitrile (0.052 g, 0.50 mmol) inside the glove box. The solvent HFIP (1.0 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 °C) for 16 h. At ambient temperature, the reaction mixture was quenched with MeOH (5.0 mL), and the resulting solution was concentrated under vacuum. The crude reaction mixture was then purified by flash chromatography usin petroleum ether/EtOAc: 5/1 as eluent to obtain dibenzylamine (**2a**; 0.044 g, 89%).

Representative procedure for the synthesis of unsymmetrical secondary amines: *N-Benzylaniline*. A Teflon tube introduced with screw-cap was (Xantphos)CoCl₂ (0.0035 g, 0.005 mmol), dimethylamine borane (0.059 g, 1.0 mmol), benzonitrile (0.052 g, 0.50mmol) and aniline (0.051 g, 0.55 mmol) inside the glove box. The solvent HFIP (1.0 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 °C) for 16 h. At ambient temperature, the reaction mixture was quenched with MeOH (5.0 mL), and the resulting solution was concentrated under vacuum. The crude reaction mixture concentrated under vacuum. was then purified by flash chromatography using petroleum ether/EtOAc: 10/1 as eluent to obtain N-benzylaniline (4a; 0.080 g, 87%).

Procedure for gram scale synthesis of dibenzylamine (2a). A Teflon screw-cap thick-walled pressure tube (4 mL) was introduced with (Xantphos)CoCl₂ (0.069 g, 0.097 mmol), ammonia borane (0.60 g, 19.41 mmol) and benzonitrile (1.0 g, 9.7 mmol) inside the glove box. The solvent HFIP (20.0 mL) was added to the reaction vessel under the argon atmosphere. The reaction mixture was then stirred at room temperature (27 °C) for 20 h. At ambient temperature, the reaction mixture was quenched with MeOH (30.0 mL), and the resulting solution was concentrated under vacuum. The crude reaction mixture was then purified by flash chromatography using petroleum ether/EtOAc: 5/1 as eluent to obtain dibenzylamine (2a; 0.78 g, 82%). *Precaution:* Reaction develops excess of ammonia pressure during the reaction, thus, the reaction vessel should be designed to hold the pressure.

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COMMUNICATION

Nitriles by a User-Friendly Cobalt Catalyst	(Xantphos)CoCl ₂ H ₃ N-BH ₃ R N R H 18 examples up to 92% yield				
Adv. Synth. Catal. Year, Volume, Page – Page	$R-C\equiv N$ + H ₂ N-R' (Xantphos)CoCl ₂ Me ₂ NH-BH ₃ R N H 25 examples up to 94% yield				
Dipesh M. Sharma, Benudhar Punji*	 Efficient and practical synthesis of secondary amines User-friendly catalyst system Excellent functional group tolerance Less expensive dimethylamine-borane used 				