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A general and expedient amination of alcohols catalysed by a single-site (NN)Co(II)-bidentate complex under solventless conditions†

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Here we designed and synthesized a NN–Co^{II} bidentate complex and efficiently used it for general and expedient amination of alcohols under benign, *solventless* conditions. Both primary (including unactivated aliphatic) alcohols and sterically hindered secondary alcohols exhibited very good reactivity and provided diverse amines with good substrate scope (88 examples; up to 95% yields) and excellent functional group tolerance (methoxy, thiomethoxy, phenoxy, trifluoromethyl, amino, alcoholic and halides including bromo and iodo groups). Furthermore, a sequential bis-*N*-alkylation of diamines was also demonstrated. It was observed that the pyrazole moiety in the ligand backbone plays a crucial role in the amination reaction. Very interestingly, the reusability of the present homogeneous cobalt catalyst was successfully demonstrated.

Introduction

Amines are fundamentally important compounds and play a vital role in the chemical and biological sciences.[1,2] They are industrially significant commodity chemicals, as well as versatile building blocks to produce fine and specialty chemicals. In particular, *N*-alkylated amine derivatives have widespread applications in agrochemicals, pharmaceuticals, lubricants, organic dyes, corrosion inhibitors, surfactants, and polymer industries.[3–5] In view of this, numerous synthetic routes have been developed for C–N bond formation reactions to *N*-alkylated amines.[6–12] Conventionally, this process involves nucleophilic substitution with organic halides,[13] hydroamination,[12,14,15] and reductive amination of aldehydes or carboxylic acids.[16–19] However, these methods have been curtailed due to the need for harsh reaction conditions, utilization of toxic and harmful reagents, and preactivated starting materials, leading to the generation of a large amount of inorganic waste, resulting in poor selectivity and low yield, thereby limiting their applicability. Thus, the development of new catalytic systems for the sustainable and affordable benign synthesis of *N*-alkylated amines is highly demanding and challenging.

The borrowing hydrogen (BH) and the hydrogen auto transfer (HA) amination strategies are powerful approaches to access *N*-alkylated amine derivatives, starting from simple and abundantly available alcohols as alkylating agents.[20–25] The C–N bond formation reactions *via* the BH/HA approach are superior from the step- and atom-economic point of view, as they integrate transfer hydrogenation by circumventing the direct use of hydrogen gas with other (*in situ*) intermediate reactions to selectively yield the desired compounds. Thus, BH/HA catalysis offers several advantages over traditional methods, as this tandem process replaces the use of hazardous and mutagenic alkylating agents by activating the alcohol moiety, resulting in expedient production of *N*-alkylated amines with water as the sole by-product. There are seminal reports on *N*-alkylation amines or amination of alcohols *via* the BH/HA strategy, mostly catalysed by rare noble-metals.[26–38] Of late, the development of sustainable, earth-abundant, and non-precious transition-metal-based catalytic systems (Cu, Ni, Co, Fe, and Mn) are becoming more appealing for the replacement of rare element-based catalytic chemical production.[39–41]

In recent years, there is considerable growing evidence that molecular cobalt complexes can be potential catalysts for (de)hydrogenation and related reactions.[40,42,43] However, there are very limited reports on cobalt-catalysed selective amine alkylation reactions[44–54] and BH C–C and C–N bond forming reactions.[55–59] Most of the molecular Co-complexes employed for catalytic *N*-alkylation of amines with alcohols

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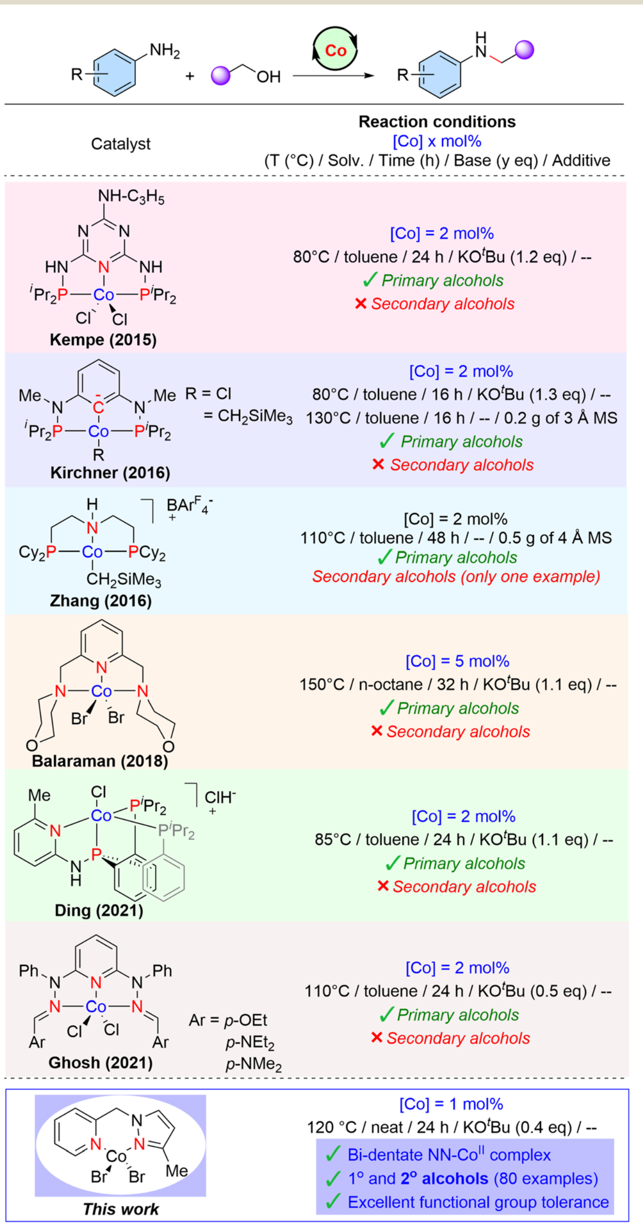
are based on tridentate PNP or PNN ligand systems (Scheme 1). In 2015, Kempe and co-workers reported a PN_5P ligand with triazine backbone stabilized Co(II)–PNP pincer complex employed for the efficient *N*-alkylation of both aromatic and aliphatic amines with alcohols.[54] Kirchner[46] developed a molecular cobalt(II) complex stabilized by an anionic PCP ligand based on the 1,3-diaminobenzene scaffold for the alkylation of amines by primary alcohols. A base-free *N*-alkylation of anilines catalysed by aliphatic PNP–Co(II) complex was reported by Zhang and co-workers.[47]

Recently, the research groups of Ding[48] and Ghosh[50] independently reported cobalt-catalysed *N*-alkylation of amines based on tridentate PNP and NNN systems, respectively. Özdemir described the alkylation of anilines by activated benzyl alcohols catalysed by an alkyl



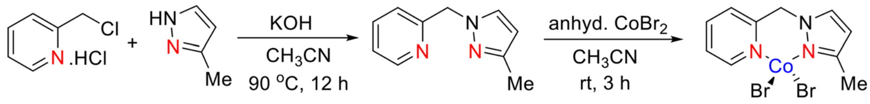
Scheme 1 Molecular Co(II)-complexes for amine alkylation.

benzimidazole–cobalt(II) complex.[52] However, this reaction is unselective and produced a mixture of *N*-alkylated amines and imines. Our group also developed a NNN–Co(II) complex for the *N*-alkylation of amines using primary alcohols.[51] The prior examples of molecular cobalt(II) complexes employed for the *N*-alkylation reaction are mainly based on tridentate-supported ligand systems, and applicable only to primary alcohols. Indeed, the application of a secondary alcohol for the *N*-alkylation reaction is scarcely explored due to their lower reactivity compared to the primary ones. Here, we have established a bench-stable, phosphine-free Co-complex supported by an NN^{PyMe} (L_1) bidentate ligand, which has been proven to be an efficient and versatile precatalyst for the expedient *N*-alkylation of amines under benign conditions. Both primary (including unactivated aliphatic) alcohols and sterically hindered secondary alcohols exhibited excellent reactivity with broad substrate scope under the present Co-catalysed conditions.

The NN^{PyMe}–Co(II) bi-dentate complex is easy to synthesize and simple to activate. This can be synthesized quantitatively on a gram scale and is an air-stable crystalline material for several months (both in solid and solution states). The reaction of a phosphine-free NN^{PyMe} bi-dentate ligand (L_1) with anhydrous $CoBr_2$ in acetonitrile solvent at room temperature under ambient conditions resulted in the corresponding Co-complex in 90% isolated yield (Scheme 2). In a similar manner, the $(NN)^{Mor}$–$CoBr_2$ complex was also synthesized (see the ESI†).

The NN^{PyMe}–$CoBr_2$ complex was fully characterized using various analytical (elemental analysis, high-resolution mass spectrometry) and spectroscopic techniques such as IR, UV-vis, and ^1H NMR. The magnetic behavior of $(NN)^{PyMe}CoBr_2$ was confirmed using the Evans method, suggesting a magnetic moment of 1.88 BM at the Co^{II}-center ($S = 1/2$) (see the ESI†). The complex crystallized in the triclinic space group $P\bar{1}$. The molecular structure of complex **I** was confirmed by a single-crystal X-ray diffraction study, as shown in Fig. 1. The X-ray diffraction analysis reveals that the Co(II) center in Co_L_1 displayed a four coordinated, distorted tetrahedral structure with two nitrogen donor atoms of the ligand (L_1) and two bromide ions. The bond angle of N(1)–Co(1)–N(2), N(2)–Co(1)–Br(2), N(1)–Co(1)–Br(2), N(2)–Co(1)–Br(1) and N(1)–Co(1)–Br(1) are found to be 92.28(17)°, 110.72(13)°, 113.33(12), 116.66(12) and 115.51(12), respectively.

Intrigued by literature precedents, we commenced to explore the potential catalytic activity of the newly synthesized phosphine ligand-free NN–Co(II) bidentate complex as a precatalyst for the selective amine alkylation reaction using alcohols as alkylating agents. For our initial studies, unsubstituted aniline (**1a**) and benzyl alcohol (**1b**) were chosen as the benchmark substrates. Several reaction parameters, including solvent, reaction temperature, and base were examined systematically by using these substrates (Table 1 and see the ESI,† for optimization studies). Thus, in a typical experiment, the reaction of aniline (**1a**), benzyl alcohol (**1b**), a catalytic amount of $(NN)^{PyMe}$ cobalt complex



(NN)^{PyMe} (91% yield) **(NN)^{PyMe}CoBr$_2$** (90% yield)

Scheme 2 Synthesis of the bi-dentate (NN)^{PyMe}CoBr$_2$ bidentate complex.

(**I**; 1 mol%) and KO^{t}Bu (40 mol%) in toluene at 140 °C (silicon oil-bath temperature) after 12 h afforded the corresponding amine alkylated product *N*-benzylaniline (**2**) in 55% yield. Indeed, continuing the reaction for 24 h at the same temperature didn't improve the yield of the product. Under similar reaction conditions, *n*-octane and THF gave 58% and 28% yields, respectively. Interestingly, the effective *N*-alkylation of **1a** with **1b** proceeded in 73% yield under *solventless* (neat) conditions at 120 °C after 6 h. Encouraged by this result, we performed the same reaction for 12 h and yielded product **2** in an 89% isolated yield. Screening of bases such as Cs_2CO_3, NaOMe, and KOH under *solvent-free* conditions gave unsatisfactory results. Notably, in the absence of catalyst or base, no formation of product was observed. Employing a low catalytic amount of a Co-complex (0.05 mol%), the *N*-alkylation reaction also worked efficiently, and product **2** was isolated in 76% yield (see the ESI†). Notably, under similar reaction conditions, a (NN)^{Mor}–CoBr$_2$ complex (**II**) derived from the 4-(5yridine-2-ylmethyl) morpholine as the ligand did not perform better than the (NN)^{PyMe} cobalt complex (**I**). It was observed that the pyrazole moiety in the ligand backbone plays a crucial role in the amination reactions. Indeed, the pyrazole ligand is an excellent π-acceptor, which stabilizes low-valent cobalt species and also provides extra stability to the Co(II)-complex due to its kinetically inert nature.

Having identified the optimized reaction conditions (1 mol% of complex **I**, 40 mol% of KO^{t}Bu under *solventless* conditions), we investigated the *N*-alkylation of anilines with various benzyl alcohols catalysed by the NN^{PyMe}–cobalt bidentate complex for the generality of this reaction as well as to extend the substrate scope. It is interesting to see that the NMR, GC, and GC–MS analyses of the crude reaction mixture showed no formation of *N*,*N*′-dialkylated products under our standard conditions.

Initially, we explored the selective *N*-alkylation of benzyl alcohols **1b** with various substituted aniline derivatives (Table 2). Regardless of the positions (*para* and *meta*) of the electron-releasing and the electron-withdrawing substituents on anilines, the reaction proceeded smoothly under the present cobalt-catalysis and yielded the corresponding *N*-alkylated products in good to excellent yields. Thus, electron-donating groups (–SMe, –OMe and –benzyl) at the *para* position of aniline afforded the corresponding *N*-alkylated products (**9**, **11**, and **33**) in good yields up to 82%. Similarly, the electron-withdrawing substituents (–F and –CF_3) on aniline also yielded the desired *N*-alkylated products in very good yields (products **22–28**; up to 72% yields). Interestingly, anilines possessing

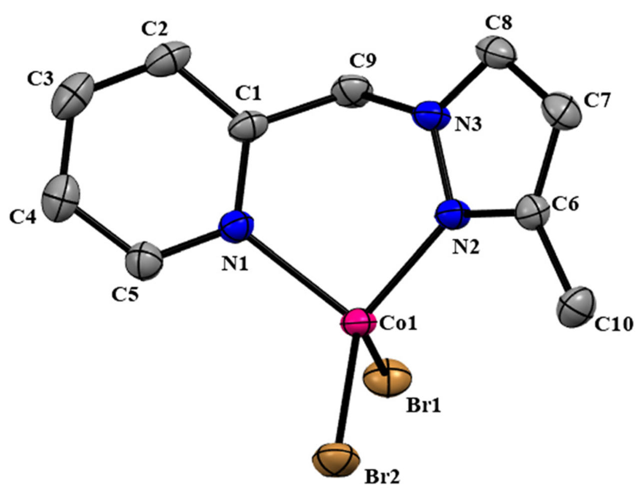
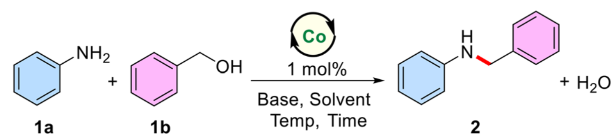
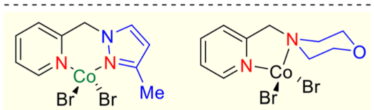


Fig. 1 ORTEP diagram of the (NN)^{PyMe}CoBr$_2$ complex with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. CCDC no: 2264033.

Table 1 Screening of catalytic conditions[a,b]



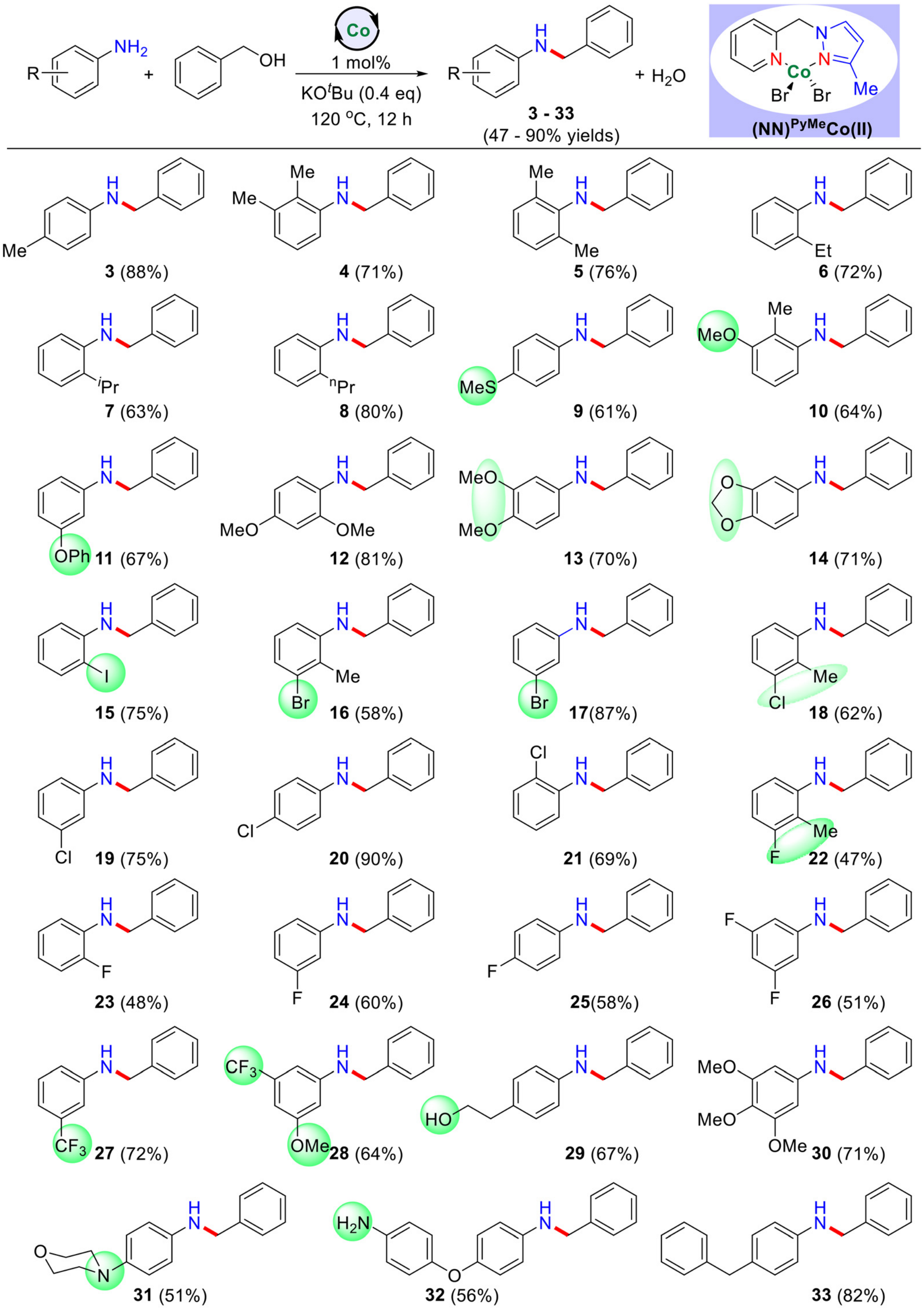
Entry	Complex	Solvent	Base	Time (h)	Temp (°C)	Yield (%)[b]
1	I	Toluene	KO^{t}Bu	12	140	55
2	I	n-Octane	KO^{t}Bu	12	140	58
3	I	THF	KO^{t}Bu	12	120	28
4	I	Neat	KO^{t}Bu	6	120	73
5	**I**	**Neat**	**KO^{t}Bu**	**12**	**120**	**89**
6	I	Neat	Cs_2CO_3	12	140	62 (41)[c]
7	I	Neat	NaOMe	12	140	55 (38)[c]
8	I	Neat	KOH	12	120	34
9	II	n-Octane	KO^{t}Bu	12	140	47
10	II	Neat	KO^{t}Bu	12	120	52



(NN)^{PyMe}CoBr$_2$ (I) **(NN)^{Mor}CoBr$_2$ (II)**

[a] Reaction conditions: aniline **1a** (0.5 mmol), benzyl alcohol **1b** (0.55 mmol), catalyst (0.005 mmol), base (0.2 mmol), and solvent (1 mL) heated at a given temperature (silicon oil-bath temp) and time. [b] Isolated yield of **2**. [c] At 120 °C.

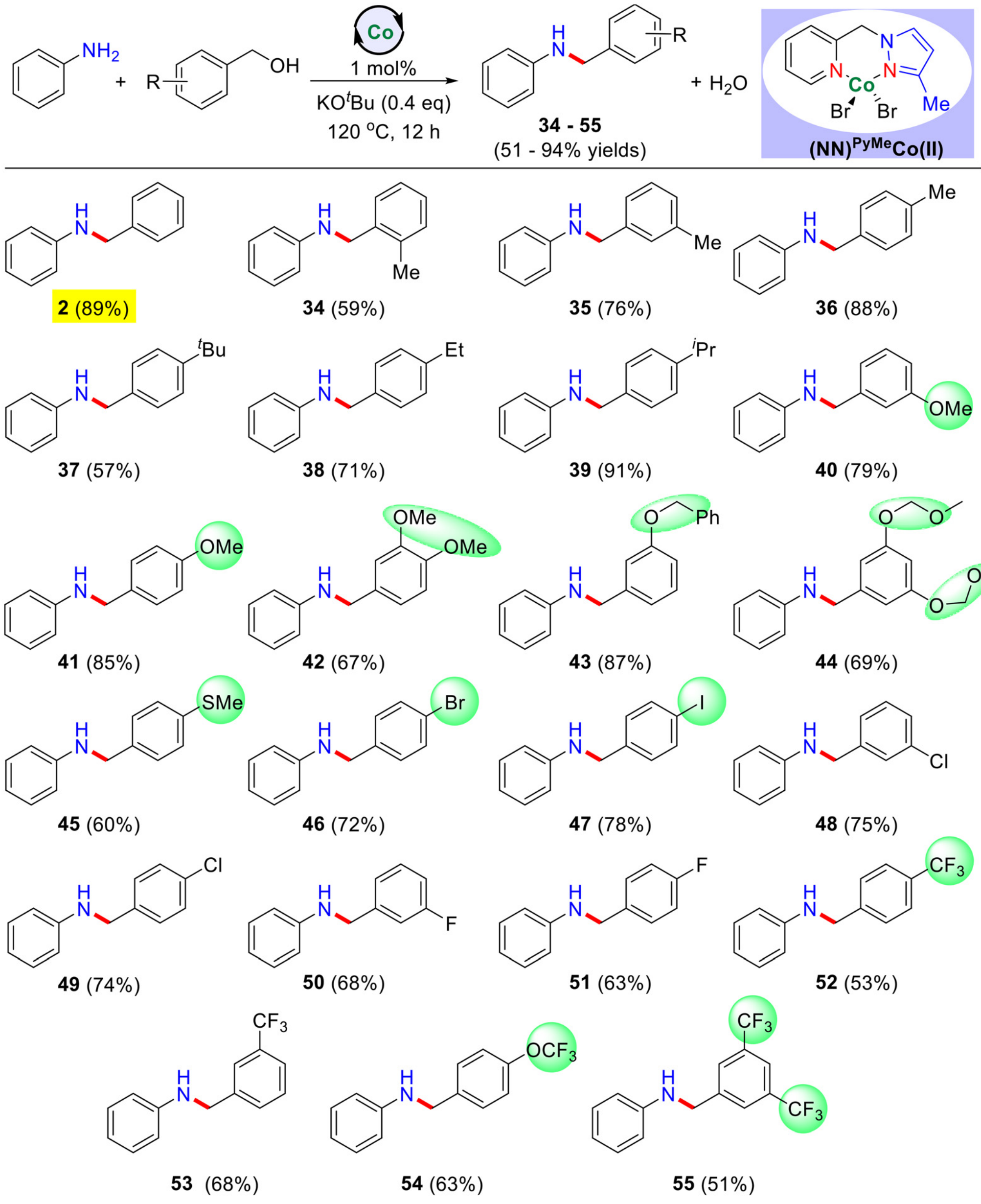
Table 2 (NN)^{PyMe}Co(II)-catalysed amination of alcohols: scope of anilines[a]



[a] Reaction conditions: aniline derivatives (0.55 mmol), benzyl alcohol (0.5 mmol), catalyst **I** (1 mol%), and KO^{t}Bu (0.2 mmol) heated at 120 °C (silicon oil-bath temperature) for 12 h under an argon atmosphere. The yields of isolated products is in parentheses.

the *ortho* substituents, such as alkyl (methyl, ethyl, *iso*propyl, *n*-propyl), methoxy and halide (–F, –Cl, –I) substituents were very well tolerated, and gave the corresponding products in moderate to good yields (products **3–8**, **10**, **12**, **16**, and **21–23**; 47–81% isolated yields). These reaction conditions were also compatible with methyl ether and methylene dioxy groups and afforded the corresponding products in good yields (products **13** in 70%

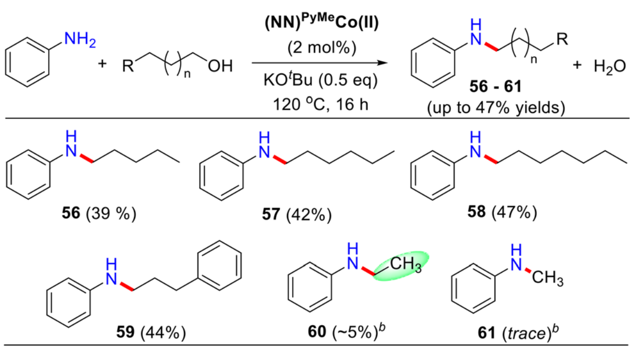
Table 3 $(NN)^{PyMe}Co(II)$-catalysed amination of alcohols: scope of benzyl alcohols[a]



[a] Reaction conditions: aniline (0.5 mmol), benzyl alcohol derivatives (0.55 mmol), catalyst **I** (1 mol%), and KO^{t}Bu (0.2 mmol) heated at 120 °C (silicon oil-bath temperature) for 12 h under an argon atmosphere. Yield of isolated products are in parentheses.

and **14** in 71% yields). Challenging substituents such as bromide and iodides also worked very well under the optimized reaction conditions and gave the expected *N*-alkylated products with hydrodehalogenation (products **15** in 75%, **16** in 58%, and **17** in 87% yields). Next, we investigated the effect of the withdrawing groups like –F, $–CF_3$, $–OCF_3$ and observed a moderate yield of the product. Notably, a trace amount of product was only observed in the case of the $–NO_2$ and –COOH groups. It may be due to the formation of other side reactions like hydrogenation of nitro compounds and esterification of carboxylic acid, respectively. It was also observed that highly electron-rich substrates showed excellent reactivity with good product yield, while electron-withdrawing groups had lower catalytic activity. Importantly, substrates bearing an amino group (Table 2, products **31–32**) were well-tolerated with this method and provided 51–56% yields. The reaction of aniline with benzyl alcohols containing an alcoholic group under standard reaction conditions led to the *N*-alkylated product (**29**) in 67% isolated yield (product). Notably, the alcoholic motif in **29** remains intact and indeed, there was no formation of self-coupled product. This is evidence that

Table 4 $(NN)^{PyMe}Co(II)$-catalysed amination of alcohols: scope of aliphatic alcohols[a]



[a] Reaction conditions: aniline **1** (0.5 mmol), aliphatic alcohols (0.55 mmol), catalyst **I** (2 mol%), and KO^tBu (0.25 mmol) were heated at 120 °C (silicon oil-bath temperature) under argon for 16 h. Yields of isolated products are in parentheses. [b] GC and GCMS analyses.

activated benzyl alcohols showed excellent reactivity compared to unactivated alcohols.

Next, we have investigated a variety of substituted benzyl alcohols for the *N*-alkylation reaction using unsubstituted aniline as the benchmark substrate (Table 3). Notably, electron-donating substituents (–Me, –OMe, –SMe, $-^i$Pr, $-^t$Bu, –Et, and others) at the *meta* and *para* positions of the benzyl alcohol substrate gave the corresponding *N*-alkylated products in good to excellent yields ranging from 57–91% (Table 3, products **34–45**). Additionally, *meta*-substituted dimethoxy, phenoxy, and 3,5-bismethoxymethoxy groups also yielded the desired products in good yield (Table 3, products **42–44**). Similarly, electron-withdrawing groups such as –F, –Cl, $-CF_3$, and $-OCF_3$ were well-tolerated and resulted in the corresponding *N*-alkylated products in moderate yields ranging from 51–68% (Table 3, products **50–55**). Furthermore, *para*-substituted benzyl alcohols bearing –I and –Br were also successfully employed, yielding the desired *N*-alkylated products in good yield (Table 3, products **46–47**).

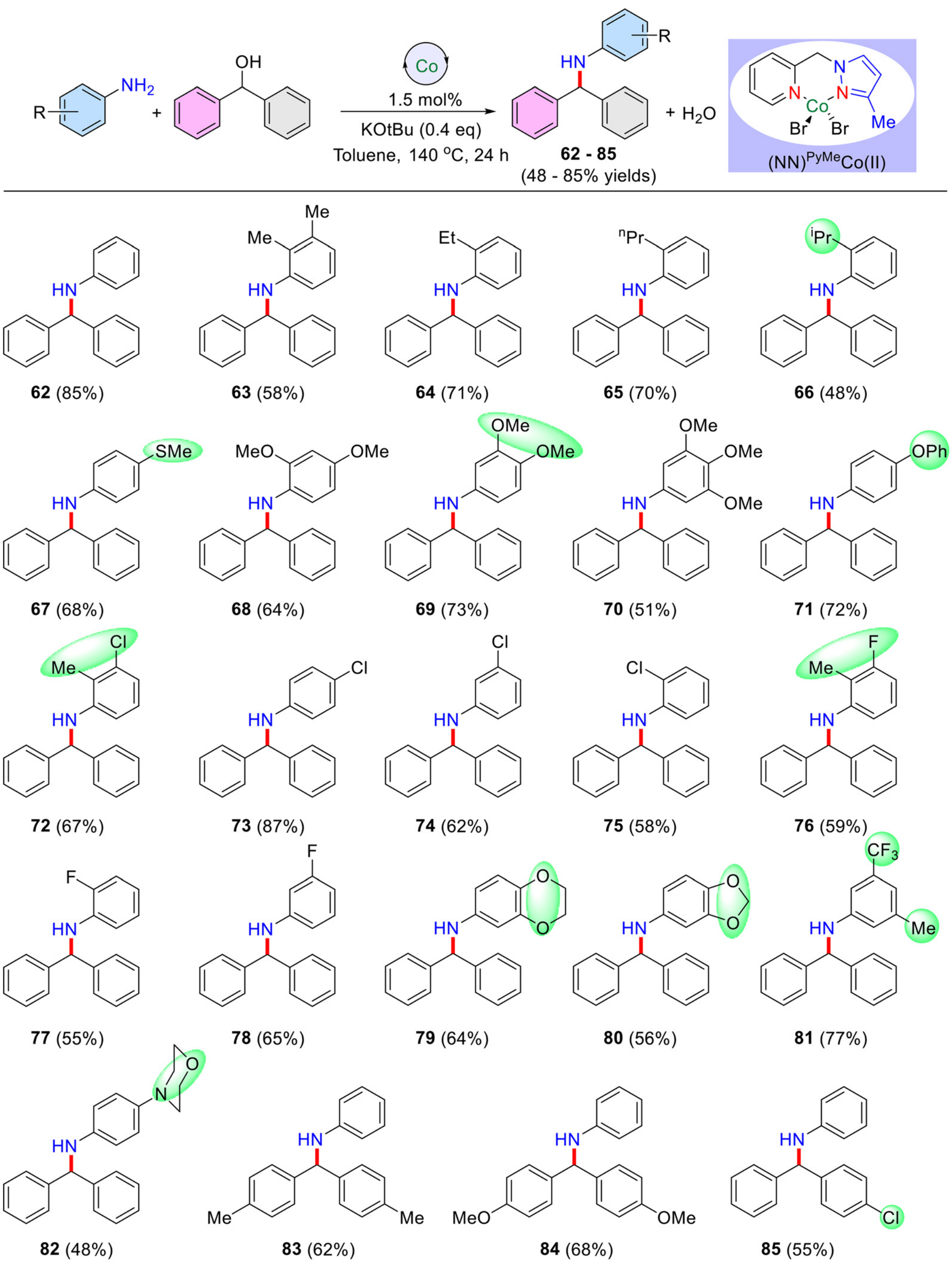
To expand the substrate scope, we examined a comprehensive list of activated primary alcohols (benzyl alcohol analogs) and some inactivated aliphatic alcohols for selective *N*-alkylation of aniline (Table 4). Initially, the homologous series of linear pentanol to heptanol were dehydrogenated for alkylation with aniline, resulting in low yields of 39–47% (Table 4, products **56–58**). With an increase in the $-CH_2-$ units in linear alcohols, there was a slight increase in the yield of *N*-alkylated products. 3-Phenylpropanol also yielded a moderate yield of 47% (Table 4, **59**). However, the dehydrogenative coupling of ethanol and methanol was not compatible with this method.

Motivated by the remarkable catalytic activity demonstrated in the *N*-alkylation of aniline with primary (aromatic and aliphatic) alcohols, we aimed to investigate the reactivity of the present phosphine-free $(NN)^{PyMe}COBr_2$ bidentate complex in the *N*-alkylation with sterically demanding secondary alcohols. Indeed, the *N*-alkylation of amines using secondary alcohols as alkylating agents is very challenging. This is due to the steric hindrance of secondary alcohols and the difficulty in dehydrogenating their corresponding ketones, followed by hydrogenation of the tetrasubstituted imine intermediate. Notably, the present bidentate pyridine–pyrazole (NN)–Co(II) complex has been proven to be an efficient and versatile precatalyst for the *N*-alkylation of amines with both primary alcohols and sterically hindered secondary alcohols. However, the present bidentate ligand has less steric crowding around the metal than the tridentate pincer ligand, which is often used for *N*-alkylation reactions. Our ligand has a pyrazole–pyridine unit with an angle of about 120 Å, which makes it easier for bulky secondary alcohols like biphenylmethanol to reach the metal. The metal can then catalyze the alcohol dehydrogenation and the imine hydrogenation. Also, the pyrazole ligand is a good π-acceptor, which stabilizes low-valent cobalt species and improves the kinetic stability of the Co(II)-complex. Thus, through a systematic exploration of various secondary alcohols, benzhydrol emerged as the optimal candidate, delivering 55% of the desired *N*-alkylated product under neat reaction conditions. However, due to its solid nature and the desire to maximize yield, modifications to the reaction conditions were implemented. Specifically, the addition of a suitable solvent, particularly toluene, was used to enhance the solubility of the reactants, leading to a substantial increase in yield, up to 78% yield. Additional optimization steps including increasing reaction temperature, reaction time, and base and catalyst loading ultimately afforded an outstanding 85% yield of the desired *N*-alkylated aniline. The optimized reaction conditions were found to be Cat. **I** (1.5 mol%), a reaction temperature of 140 °C, KO^tBu (50 mol%), and 1 mL of toluene as solvent, refluxed for 24 hours.

Having established the optimal reaction conditions, a broad range of anilines were selectively alkylated using benzhydrol (secondary alcohol) as the alkylating agent (Table 5). Notably, unsubstituted aniline reacted effectively, affording the desired *N*-alkylated product **62** in an excellent yield of 85%. Anilines bearing electron-donating groups such as –Me, –OMe, –iPr, –Pr, –Et, –OPh, and –SMe were well-tolerated, and the corresponding *N*-alkylated products **63–71** (Table 5) were obtained in yields ranging from 48% to 84%. The *ortho*-substituted aniline displayed lower yields due to its steric nature, however, long-chain ethyl and propyl groups at the *ortho* position yielded better results (up to 71% yield) than the simple methyl group (Table 5, product **63**).

Notably, aniline with halide functionalities such as –Cl and –F reacted favourably, yielding the products up to 69%. Difunctional anilines containing 2-Me,3-Cl (Table 5, **72**) and 2-Me,3-F (**76**) displayed respectable isolated yields of 67% and 59%, respectively. Moreover, 1,4-dioxanone, 1,3-dioxanone, trifluoro, and *para*-morpholine substituted anilines were effectively alkylated, affording the desired products (Table 5), **79** (64% yield), **80** (56% yield), **81** (77% yield), and **82** (48% yield), respectively. The other symmetrical diphenylmethanol bearing –Me, and –OMe groups gave the

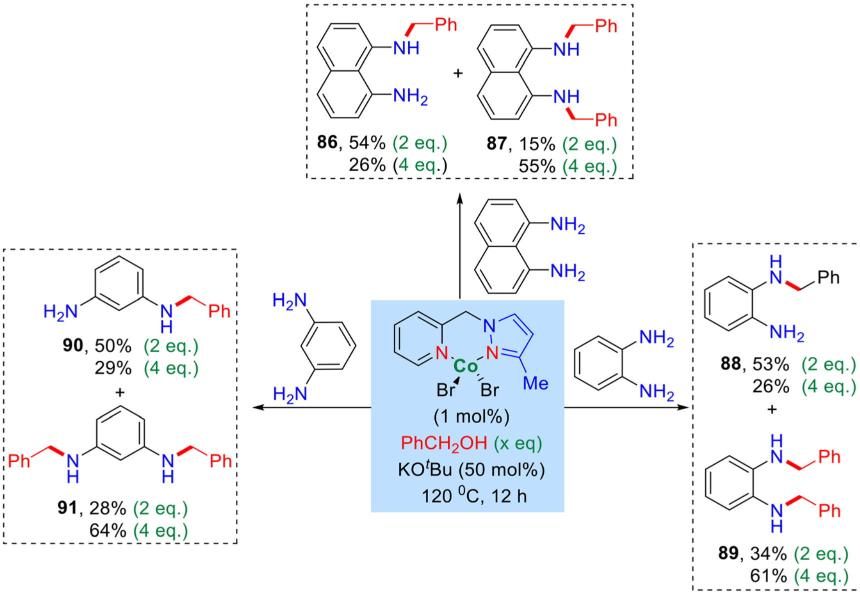
Table 5 $(NN)^{PyMe}Co(II)$-catalysed amination of alcohols: scope of secondary alcohols (diphenylmethanol derivatives)[a]



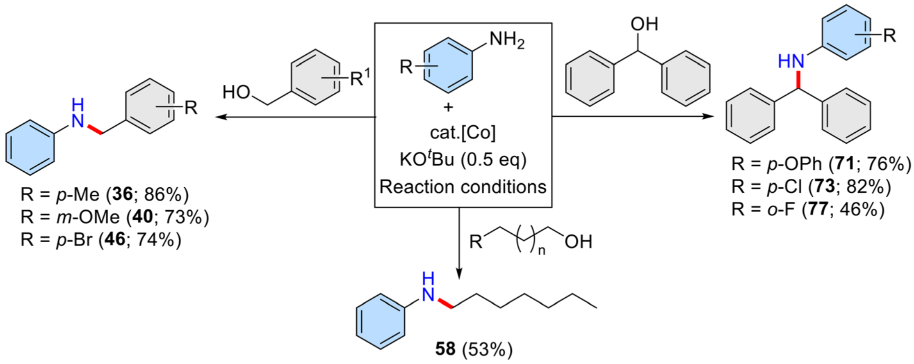
[a] Reaction conditions: aniline derivatives (0.5 mmol), diphenylmethanol (0.6 mmol), catalyst I (1.5 mol%), and KO^{t}Bu (0.25 mmol) heated at 140 °C (silicon oil-bath temperature) in 1 mL toluene for 24 h. Yield of isolated products are in parentheses.

N-alkylated products **83** in 62%, and **84** in 68% yields, respectively. In addition, unsymmetrical diphenylmethanol having a *p*-chloro substituent yielded 55% of the product **85** under optimized reaction conditions. Notably, other secondary alcohols such as cyclopentanol, cyclohexanol and 1-phenylethanol did not afford the desired secondary amine under present reaction conditions and their corresponding dehydrogenated carbonyl compounds were observed (~35%; GC and GCMS analyses).

In addition, we also investigated the alkylation of benzyl alcohol with diamine using diaminobenzene (1,2-, and 1,3-phenylenediamine) and 1,8-naphthylenediamine. The optimized reaction conditions led to the formation of both mono and bis-alkylated products (Scheme 3, products **86–91**).



Scheme 3 $(NN)^{PyMe}$Co(II)-catalysed *N*-akylation of diamines with benzyl alcohols.[a] [a]Reaction conditions: diamines (0.5 mmol), benzyl alcohol (*x* eq.), catalyst I (1 mol%), and KO^{t}Bu (0.25 mmol) heated at 120 °C (silicon oil-bath temperature) for 12 h. All are isolated yields of the products.



Scheme 4 Large-scale synthesis & reusability of the homogeneous Co-catalytic system. Reaction conditions: aniline derivatives (5 mmol), alcohols (6 mmol), Cat. I (2 mol%), and KO^{t}Bu (2.5 mmol) heated for 36 h (120 °C and in the absence of solvent for compounds **36**, **40**, **46** and **58**; 140 °C in 6 mL toluene for compounds **71**, **73** and **77**) and the yield are isolated yields.

Notably, upon increasing the equivalent of benzyl alcohol, the yield of the bis-alkylated product increased while the yield of the mono-alkylated product decreased, as summarized in Scheme 3.

We have also shown the scalability of the molecularly defined Co(II)-complex catalysed *N*-alkylation reactions. In this regard, the present amination of alcohols catalysed by a (NN)Co(II)-bidentate complex under *solventless* conditions was examined for the large-scale (5.0 mmol scale) synthesis of diverse *N*-alkylated amines and it worked smoothly with excellent isolated yield of the expected products (Scheme 4).

Gratifyingly, the reusability of the present homogeneous Co-catalyzed *N*-alkylation of amines using alcohols was successfully demonstrated (Fig. 2). Thus, the reaction of *p*-toluidine with benzyl alcohol under standard reaction conditions was carried out by externally adding starting materials into the reaction mixture (without additional $(NN)^{PyMe}$cobalt complex **I**) after every 12 h and monitored the

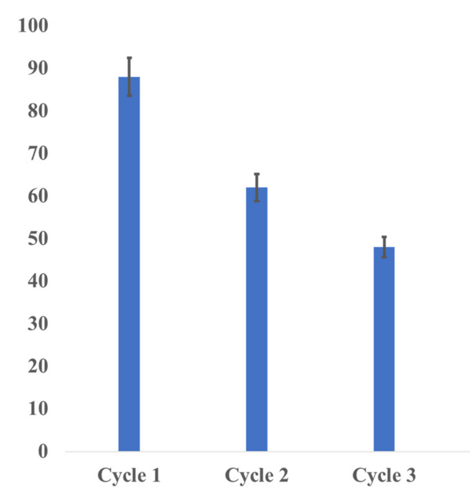
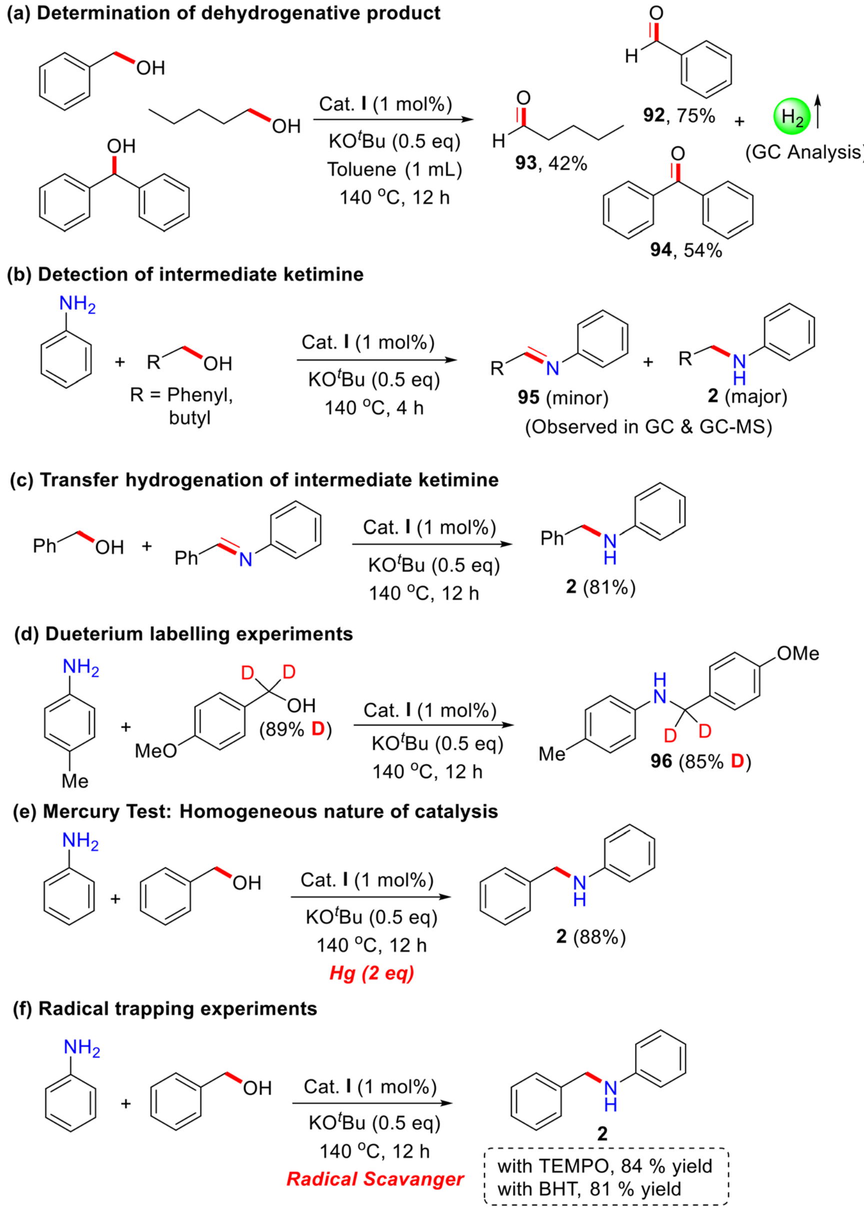


Fig. 2 Recyclability test of the cobalt-catalysed *N*-alkylation reaction (of *p*-toluidine with benzyl alcohol).

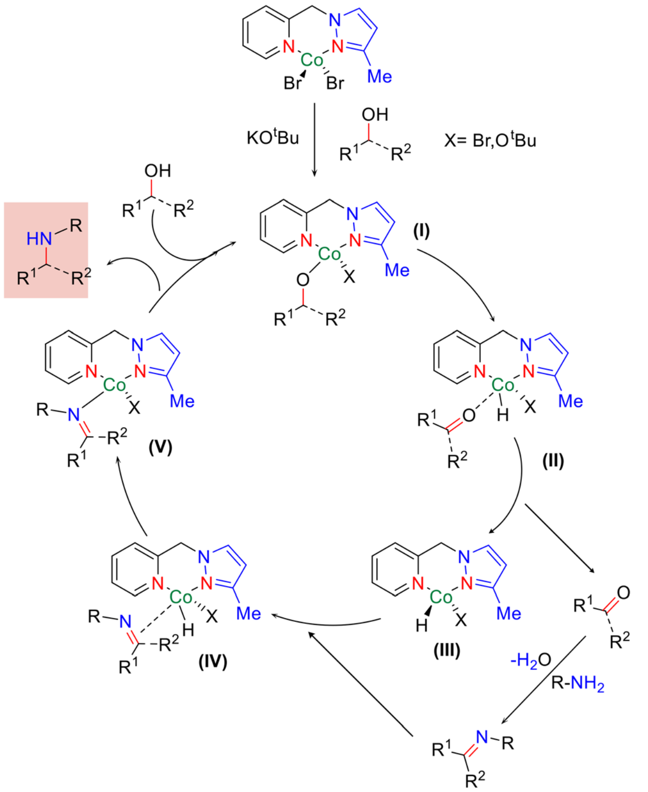


Scheme 5 Control experiments (a–f).

catalytic efficiency of the cobalt catalyst. Interestingly, the desired *N*-alkylated product (*N*-benzyl-4-methylaniline, **3**) was obtained in moderate yield after the 3rd cycle. The decrease in the catalytic activity after the 3rd cycle can be attributed to the gradual decomposition of the metal complex. Indeed, the reusability of soluble homogeneous catalytic systems for dehydrogenation and related reactions is rarely reported in the literature.[60–63]

For a detailed understanding of the bidentate Co-catalyzed *N*-alkylation reaction of aniline with primary and secondary alcohols, several control experiments were carried out under standard reaction conditions (Scheme 5). To investigate the dehydrogenation step, different alcohols (benzyl alcohol, 1-pentanol, and benzhydrol) were reacted in the absence of aniline, leading to the isolation of the corresponding aldehyde and ketone as products (**92–94**). The formation of hydrogen gas was detected using gas chromatography (Scheme 5a). Performing the reaction for 4 hours, both the *N*-alkylated product (major) and the corresponding imine intermediate (minor) (**95**) were observed in GC and GC–MS analyses (Scheme 5b). Furthermore, treatment of the imine intermediate with the corresponding alcohol under the optimized reaction conditions resulted in the desired *N*-alkylated product in excellent yield (Scheme 5c).

The independent deuterium labeling experiments were carried out; almost 85% deuterium incorporated was observed at the α-methylene carbon of *N*-alkylation products (**96**) under the present catalytic condition These results demonstrated that the reaction proceeds *via* the BH/HT pathway. Additionally, the presence of mercury under



Scheme 6 A plausible mechanism.

standard reaction conditions led to an excellent yield of 88% of the *N*-alkylated product, indicating that the present Co-catalyst is homogeneous in nature (Scheme 5e). Indeed, we didn't observe any nanoparticle formation after the catalytic reaction (SEM analysis). Moreover, in the presence of radical quenchers, the reaction proceeded smoothly and didn't affect the product yields (Scheme 5f). These results suggest that this Co-catalysis does not follow the single electron transfer (SET) or free radical pathway. Various reports describe that the Co–hydride complex is an important intermediate in dehydrogenation and related reactions (for example, C–C and C–N bond formation) using amine and alcohol as alkylating agents *via* the borrowing hydrogenation strategy.[55,64,65] Recently, our research group also contributed to cobalt catalysis.[51,53,66,67] Plausibly, we predict the *in situ* formation of a Co–H intermediate from alcohol; however, it is very challenging to isolate due to its highly unstable nature. The Chirik group reported similar cobalt–hydride species using bis(silylene)pyridine cobalt(III) precatalyst using strong reducing agents like $NaHBEt_3$ and $LiHBEt_3$.[68] Using the same reaction procedure, several reactions were performed for the isolation and characterization of Co–H species with our catalytic system, using the $NNPy^{Me}$–Co(II) bi-dentate complex and $LiHBEt_3$ as a hydride donor. However, our attempts were unsuccessful. We propose two possible reasons for this outcome: (i) the research group of Chirik used a pincer complex, which is much more stable than the bidentate system we employed. The use of $LiHBEt_3$ as a hydride donor might have decomposed our catalyst system. (ii) The Co(II) species is paramagnetic, which makes the NMR characterization of the cobalt complex challenging.

Based on control experiments and literature precedents,[51,55,69] we have proposed a plausible catalytic cycle for the *N*,*N*-bidentate Co-catalysed amination of primary and secondary alcohols to aniline, as shown in Scheme 6. Initially, the alkoxide complex (**I**) was observed to form under the applied catalytic conditions. Subsequently, β-hydride elimination yielded the Co–hydride complex (**II**) with the generation of the corresponding carbonyl compound (**III**). The condensation of aniline with a carbonyl compound (**III**) resulted in imine formation, which further coordinated to give complex (**IV**). Reduction of the imine bond led to the amino–cobalt complex (**V**). Furthermore, abstraction of the proton of the alcohol resulted in the desired *N*-alkylated product, regenerating complex (**I**) and completing the catalytic cycle. Indeed, the isolation of the proposed intermediates and detailed mechanistic investigation are in progress in our laboratory.

In summary, we present an environmentally benign and highly selective direct synthesis of *N*-alkylation of anilines using primary (including unactivated aliphatic) and sterically demanding secondary alcohols (benzhydrol) *via* the borrowing hydrogen strategy using an air-stable, phosphine-free, non-precious cobalt(II)–NN–bidentate complex. The *N*-alkylation reaction demonstrated significant efficiency, as evidenced by the high degree of substrate and functional group tolerance observed. The reaction operates under *solventless* conditions with a low catalyst loading. Large-scale synthesis of *N*-alkylated amines and reusability of the present homogeneous Co-catalysis are additional advantages of the present strategy. Furthermore, the replacement of tridentate pincer ligands with bidentate ligands in the metal complex system represents a promising avenue for future research.

Conflicts of interest

The authors declare no competing financial interest.

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