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Hydrogenation and *N*-alkylation of anilines and imines *via* transfer hydrogenation with homogeneous nickel compounds†

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The nickel-catalyzed *N*-alkylation of a variety of arylamines *via* transfer hydrogenation in the absence of pressurized hydrogen and basic or acidic additives was achieved in a tandem reaction. This process was further extended to the C═N bond reduction and *N*-alkylation of a variety of imines with ethanol, the latter acting as a hydrogen and acetaldehyde source, which allowed for the reduction and subsequent condensation to yield the corresponding *N*-alkylated products.

Introduction

Metal-catalyzed C═N bond reduction and tandem alkylation (through a transfer hydrogenation (TH) process)[1,2] has been primarily studied with compounds containing precious metals such as Pd,[3] Ru,[4–7] Rh,[8] and Ir,[7,9,10] but is much less developed using cheap, first-row transition-metal compounds.[11–14] Preparation of secondary and tertiary amines[15,16] is of relevance because they are valuable building blocks in the fine chemical industry[15,16] and for fungicides,[17,18] additives,[19] pharmaceuticals,[20,21] and agrochemicals.[22] These secondary and tertiary amines are usually synthesized using conventional organic methodologies such as amine alkylation through nucleophilic substitution with toxic reagents that include aryl- or alkyl-halides. The use of precious metals, besides their high cost and limited availability, is associated with high toxicity,[1,2,23] for which it is necessary to replace them with less toxic or cheap reagents.[2] Thus, the exploration of alternatives like the first-row transition-metal catalysts for TH reactions is attractive due to their availability in the Earth's crust, and so far, however, few reports on the *N*-alkylation of primary amines with alcohols catalyzed by Fe, Co and Ni have been published.[11–14,24]

Regarding the relevant reports on the use of Earth-abundant metals, Gandon and Bour *et al.* have recently documented the synthesis of unsymmetrical tertiary amines using an iron-catalyzed system by a process of ethylation of imines with ethanol through a borrowing hydrogen process (which involves a TH process), with moderate to good yields.[25] Also, Kirchner and co-workers reported the alkylation of arylamines with primary alcohols in the presence of a base (*t*-BuOK) using Co(II)-catalysts that were stabilized by PCP pincer ligands.[13]

Our group has also been interested in the reduction of imines with the first-row transition-metal compounds in low oxidation states, particularly with the use of Ni(0), pressurized hydrogen and methanol as a solvent, where no evidence of the involvement of the solvent in the *N*-alkylation of fluoroimines has been found.[24] The amino reduction reactions of imines and anilines along with *N*-alkylation reactions have been reported with a few homogeneous and heterogeneous nickel catalysts.[26–31] Ni-RANEY® catalyzed reductive *N*-alkylation of amines and anilines was reported by Rice *et al.*[28] and Ainsworth[27] using alcohols as sources of hydrogen. Recently, Nandan and co-workers have re-visited the reaction with Ni-RANEY® in xylene under reflux conditions resulting in the hydrogen autotransfer of alcohols.[30] Regarding the homogeneous process with nickel, Banerjee *et al.* reported the *N*-alkylation of anilines with benzyl alcohol[29] using $NiBr_2$ as the catalyst precursor and *t*-BuOK as the additive. Barta and co-workers reported a similar reaction using $[Ni(COD)_2]$ and KOH,[26] and these studies highlight the need to use bases such as *t*-BuOK and KOH in the TH process to obtain good conversions and selectivities.

We disclose herein our results dealing with the *N*-alkylation of anilines and the C═N bond reduction and *N*-alkylation of imines, with nickel catalysts, without basic additives and H_2. These experiments used P-donor ancillary ligands and several alcohols, such as ethanol, methanol and 2-propanol, which acted as solvents and reagents in the reaction.

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Results and discussion

Optimization of reaction conditions

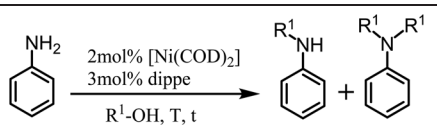
Initially, we assessed a variety of alcohols as solvents and reagents, with the $[Ni(COD)_2]$/dippe system, COD = 1,5-cyclooctadiene, and using aniline as the substrate. We considered the conditions used in previous work of our group;[32] the catalytic system was composed of 2 mol% $[Ni(COD)_2]$ and 3 mol% dippe.

At 120 °C and with 2 mol% loading of $[Ni(COD)_2]$, the conversion was low (27%), but completely selective for *N*-ethylaniline **2a** (Table 1, entry 1). At 130 °C the conversion increased to 50%, with **2a** as the only product (Table 1, entry 2), and at the same temperature of reaction, but using 4 mol% $[Ni(COD)_2]$, changes in conversion and selectivity were not significant (Table 1, entry 3). A full conversion was obtained by maintaining the catalytic loading at 2 mol%, but increasing the reaction temperature to 150 °C (24 h) (Table 1, entry 4). Under these conditions, the selectivity of *N*-mono-ethylated aniline **2a** and *N*,*N*-di-ethylaniline **3a** was 73% and 27%, respectively.

A reduction in the reaction time from 24 h to 18 h resulted in 100% conversion and selectivity for the *N*-monoalkylated product **2a** (Table 1, entry 6) (under the same reaction conditions). Importantly, the conversion was lower when 2-propanol and methanol were used as solvents (Table 1, entries 7 and 8), and this may be due to the low stability of the corresponding intermediates (imines or enamines) involved when using these solvents.

In addition, a mercury drop test was performed (Table 1, entry 9), which resulted in 94% conversion, thus not causing a significant drop in conversion. Therefore, we conclude that this catalytic system is likely to be homogeneous and we consider the use of a catalytic loading of 2 mol% $[Ni(COD)_2]$, 3 mol% dippe, ethanol as the solvent (and the source of hydrogen and aldehyde), at 150 °C and 18 h of reaction time as the optimal conditions.

Table 1 Optimization of *N*-alkylation reaction[a]



1a 2a 3a

Entry	*T* (°C)	*t* (h)	R^1-OH	% Conversion	Selectivity **2a** : **3a**
1	120	24	EtOH	27	100 : 0
2	130	24	EtOH	50	100 : 0
3[b]	130	24	EtOH	40	100 : 0
4	150	24	EtOH	100	73 : 27
5	150	20	EtOH	100	92 : 8
6	150	18	EtOH	100	100 : 0
7	150	18	MeOH	13	100 : 0
8	150	18	2-Propanol	4	100 : 0
9[c]	150	18	EtOH	94	100 : 0

[a] General conditions: 1 mmol of aniline, $[Ni(COD)_2]$ (2 mol%), dippe (3 mol%) and dry ethanol (10 mL). [b] $[Ni(COD)_2]$ (4 mol%), dippe (6 mol%). [c] Mercury drop test.

Using the optimal reaction conditions, a variety of substituted anilines were assessed in the *N*-alkylation reaction. Toluidine substrates were employed (entries 2–4, Table 2) which resulted in 100% conversion and good selectivity towards the *N*-monoalkylated products (**2b**, **2c** and **2d**). Entry 3 was, however, the exception. In entry 3 the selectivity was found to be distributed between *N*-ethylaniline **2c** and *N*,*N*-diethylaniline **3c** (85% and 15% respectively). Using *m*-fluoroaniline, good conversion and selectivity were obtained and the presence of a minute amount of the corresponding enamine, which led to the formation of the *N*-dialkylated product **2ee**, was observed by GC-MS (Table 2, entry 5). The use of chlorinated anilines (Table 2, entries 6–8), *o*-chloroaniline and *p*-chloroaniline (Table 2, entries 6 and 8), resulted in low to fair conversions of these substrates (30% and 55%, respectively), likely due to the deactivating character of their substituents. This is in contrast to *m*-chloroaniline, which achieved 74% conversion (Table 2, entry 7). The electron withdrawing groups in the *ortho*-position of the phenyl ring were found to affect the reduction process; these electron withdrawing groups were less effective than those in the *meta*- and *para*- positions.[33] In addition, when using methoxyanilines, good conversions and selectivities were obtained and were comparable to the conversions obtained with *o*-, *m*-, and *p*-toluidine, due to their similar behavior to electron-donating substituents (Table 2, entries 9–11).

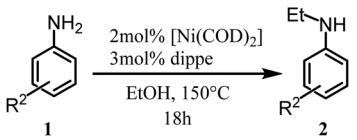
Considering the above results and the previous studies of our group and others,[24,32–36] we present a mechanistic proposal in Scheme 1 that is initiated by the oxidative addition of EtOH to [Ni(COD)(dippe)] (formed *in situ*) to produce "$[Ni(dippe)(H)_2]$" **A** and acetaldehyde, which then form the respective enamine **1-A** from aniline. This enamine is then coordinated to **A** to form the imine-complex **B**, and then the *N*-monoalkylated product **2** is obtained through the insertion of the enamine into the nickel hydride to yield **C**, followed by the reductive elimination of the product and the oxidative addition of EtOH to re-form complex **A**.

A similar methodology was used for closely related imines that were synthesized *in situ* from *p*-tolualdehyde and *p*-toluidine. The best reaction conditions for this reaction were found to be 24 h and 150 °C (Table 3, entry 4), with a selectivity of 94% for product **5d**.

Considering the reaction conditions determined for entry 4, other alcohols were assessed (Table 3, entries 6 and 7). We determined that the reaction in methanol resulted in a conversion of 83% with a selectivity of 81% for amine **5d** and with 2-propanol the conversion was modest (78%), with good selectivity for **5d** (97%).

Because our interest was in obtaining the *N*-alkylated product (**7d**), we decided to use a higher catalytic loading of 5 mol% $[Ni(COD)_2]$ and 7 mol% dippe and a 48 h reaction time. Under these conditions, the conversion was 99% and there was low selectivity between amine **5d**, enamine **6d**, and *N*-ethylamine **7d** (64%, 1%, and 35% respectively) (Table 3, entry 8).

Table 2 Substrate scope for anilines[a]



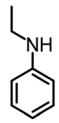
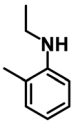
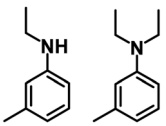
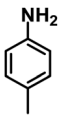
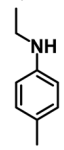
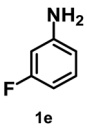
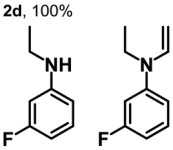
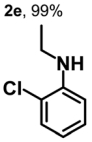
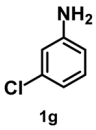
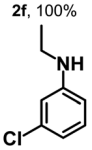
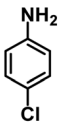
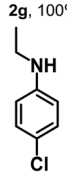
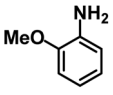
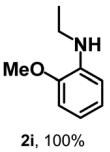
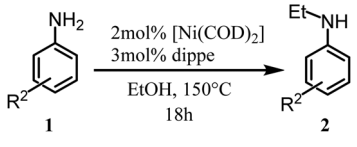
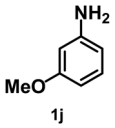
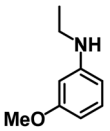
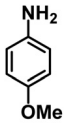
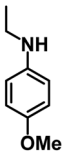
Entry	Substrate	% Conversion	% Selectivity
1	 1a	100	 2a,100%
2	 1b	100%	 2b, 100%
3	 1c	100	 2c, 85% 3c, 15%
4	 1d	100	 2d, 100%
5	 1e	100	 2e, 99% 2ee, 1%
6	 1f	30	 2f, 100%
7	 1g	74	 2g, 100%
8	 1h	55	 2h, 100%
9	 1i	100	 2i, 100%

Table 2 *(Contd.)*



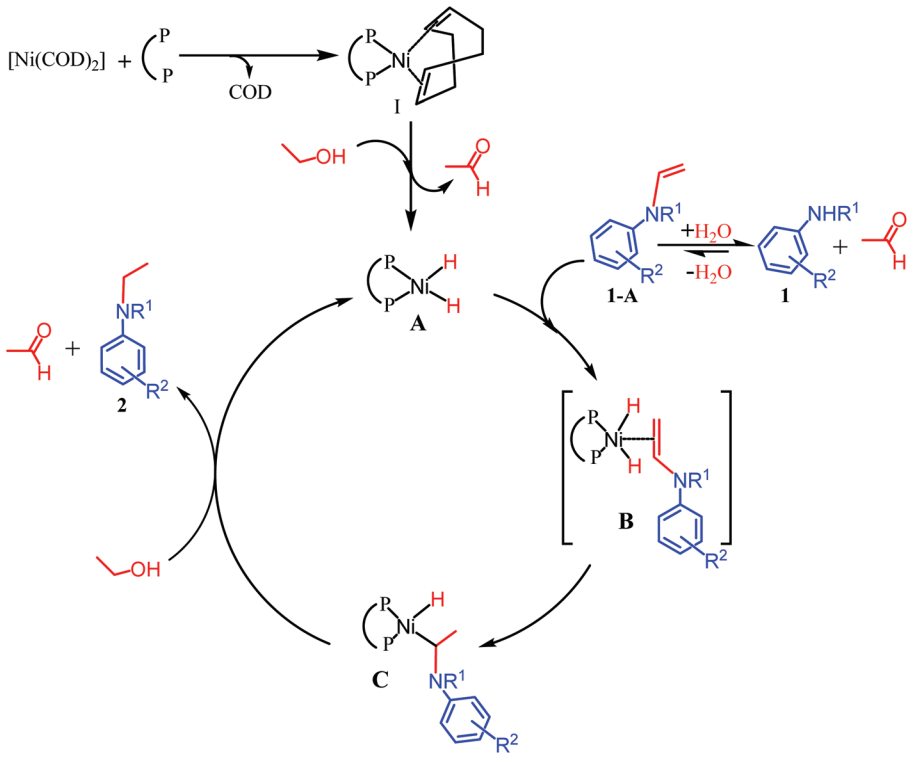
Entry	Substrate	% Conversion	% Selectivity
10	 1j	100	 2j, 100%
11	 1k	100	 2k, 100%

[a] General conditions: 1 mmol of aniline, $[Ni(COD)_2]$ (2 mol%), dippe (3 mol%) and dry ethanol (10 mL).

An increase in temperature and reaction time improved the selectivity towards the production of **7d** (Table 3, entries 9 to 12). The addition of molecular sieves at 170 °C resulted in better selectivity of **7d** over **5d** (89% and 11%, respectively) (Table 3, entry 12). Finally, the use of dcype (1,2-bis(dicyclohexylphosphino)ethane) as the ancillary ligand (instead of dippe) resulted in 100% conversion and 97% selectivity towards **7d** (Table 3, entry 13).

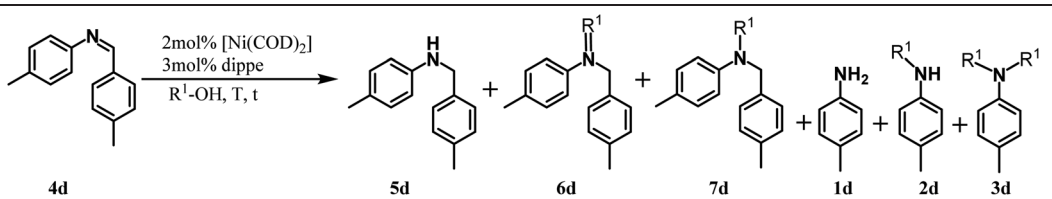
With these optimal reaction conditions in hand, we assessed the reactivity of closely related substrates that are depicted in Scheme 2. At 170 °C the reaction resulted in very good conversion and selectivity towards the *N*-alkylated product with ethanol (Scheme 2, b–d). It is noteworthy that the use of *o*-toluidine resulted in a very low yield, and this is probably due to steric effects.

The use of other alcohols was also assessed with 2-propanol and methanol. With these solvents the *N*-alkylated products were not observed, and only the production of the corresponding amine (**5d**) was observed (Scheme 3). For methanol, it is possible that the corresponding imine formed (**6**) may be unstable;[37] in addition, aliphatic alcohols are more difficult to activate than aromatic or unsaturated alcohols.[38] Also, among methanol and ethanol, methanol has a relatively high dehydrogenation energy (ΔH = +84 kJ mol^{-1}) with respect to ethanol (ΔH = +68 kJ mol^{-1}).[39] However, because the reduction of imine **4** was observed, the low selectivity towards the *N*-alkylated product would be related to the instability of the iminic intermediate **6**, rather than to the dehydrogenation of the alcohol. Regarding 2-propanol, the produced ketone after TH does not form the corresponding imine, and likely a Lewis acid is required to promote the condensation of the aniline and the ketone.[40]



Scheme 1 Mechanistic proposal for the *N*-alkylation TH-process.

Table 3 The reduction and *N*-alkylation of imines[a]

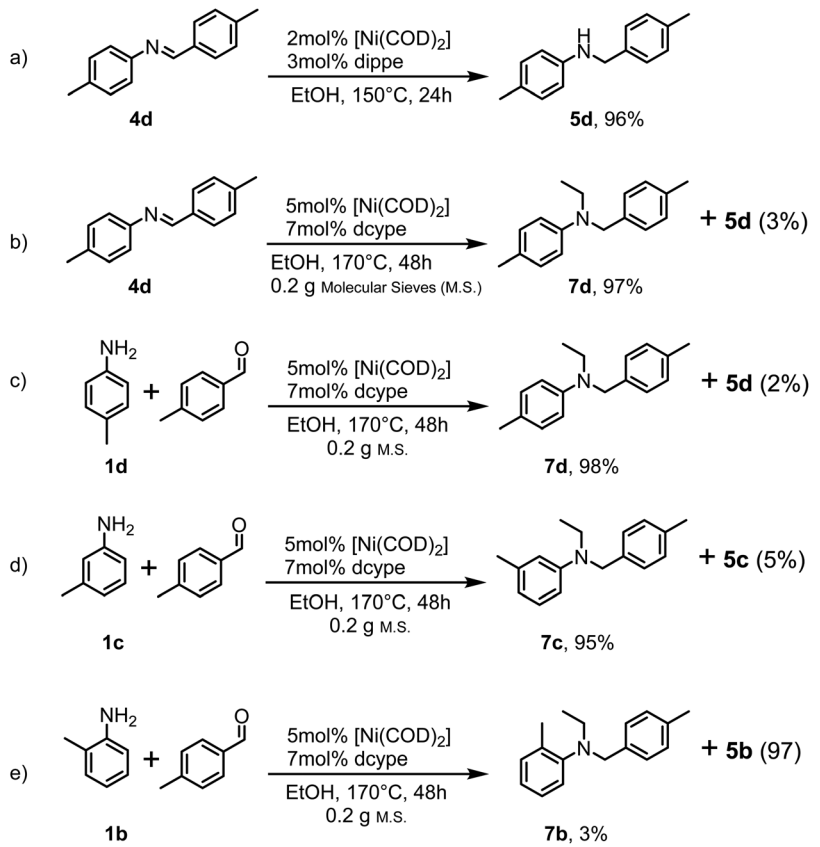


Entry	*T*/°C	*t* (h)	R^1-OH	% Conv.	**5d : 6d : 7d : 1d : 2d : 3d**
1	100	48	EtOH	0	—
2	130	48	EtOH	46	91 : 0 : 2 : 0 : 7 : 0
3	150	48	EtOH	93	94 : 1 : 0 : 0 : 5 : 0
4	150	24	EtOH	98	94 : 2 : 1 : 0 : 3 : 0
5	150	14	EtOH	7	97 : 0 : 3 : 0 : 0 : 0
6	150	24	MeOH	83	81 : 2 : 0 : 2 : 1 : 14
7	150	24	2-Propanol	78	97 : 0 : 0 : 3 : 0 : 0
8[b]	150	48	EtOH	99	64 : 1 : 35 : 0 : 0 : 0
9[b]	160	24	EtOH	100	56 : 0 : 42.8 : 0.2 : 1
10[b]	160	48	EtOH	100	60 : 6 : 34 : 0 : 0 : 0
11[b,c]	160	48	EtOH	100	12 : 0 : 87 : 0 : 0 : 1
12[b,c]	170	48	EtOH	100	11 : 0 : 89 : 0 : 0 : 0
13[c,d]	**170**	**48**	**EtOH**	**100**	3 : 0 : 97 : 0 : 0 : 0

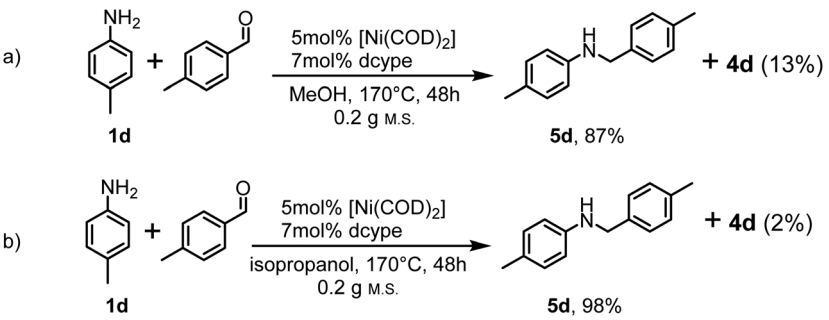
[a] General conditions: 1 mmol of imine, $[Ni(COD)_2]$ (2 mol%), dippe (3 mol%) and dry ethanol (10 mL). [b] 5 mol% $[Ni(COD)_2]$, 7 mol% dippe. [c] Molecular sieves (4 Å) were employed as the desiccant. [d] 5 mol% $[Ni(COD)_2]$, 7 mol% dcype.

Because the reduction of imines and further alkylation would involve the coordination of the –C═N– moiety to the nickel center, monitoring this reaction by NMR was used to identify some of the key intermediates. Thus, we used a similar methodology that has been previously used in our group and adapted it to the current case. This is presented in Scheme 4.[24,32,33]

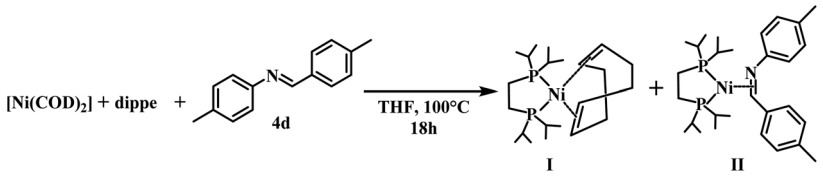
The corresponding $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture confirmed the presence of both compounds **I**



Scheme 2 Substrate scope for reduction and *N*-alkylation.



Scheme 3 Scope of alcohols in the reduction of **4**.



Scheme 4 Formation of [(dippe)Ni(η^2-C,N)-PhHC = NPh] (**II**).

and **II** (Fig. 1), with doublets at 65.15 ppm and 71.55 ppm, with a J_{P-P} of 61 Hz, assigned to complex **II**, in which the imine is coordinated side-on.[24,33] In addition, two singlets were observed at 51.59 ppm and 70.14 ppm and were assigned to free dippe and [Ni(dippe)(COD)], respectively.

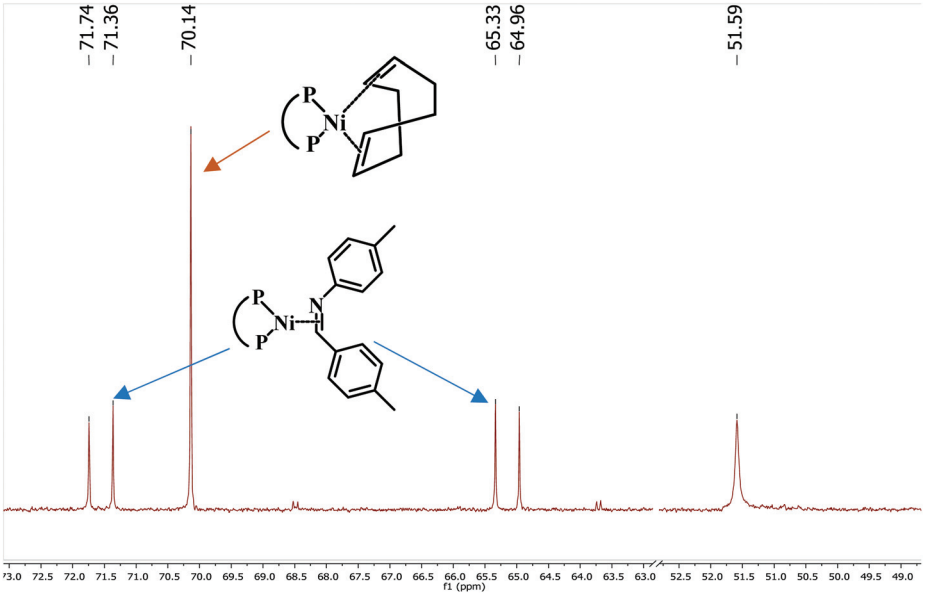


Fig. 1 The $^{31}P\{^{1}H\}$-NMR spectrum of a mixture of **I** and **II** in THF-d^8.

The ^{1}H-NMR spectrum (Fig. 2) shows a signature signal at 4.97 ppm (dd, J_{P-H} = 7.4 Hz and 2.9 Hz) assigned to the imine moiety coordinated to the metal which is characteristic of the coupling with non-equivalent phosphorus[33] and an up-field shift of the signal.[41,42] Considering the results outlined herein and in previous closely related reports,[24,32–36] a mechanism for the tandem hydrogenation and subsequent *N*-alkylation of imines is presented in Scheme 5, which is similar to the aniline alkylation mechanism presented in Scheme 1 (*vide supra*).

Here, imine **4** is coordinated to an active species **A** to yield amine **5** (the right side of the cycle), followed by the formation of enamine **6** by the condensation reaction with acetaldehyde formed *in situ* to produce intermediate **D**, followed by hydrogenation and reductive elimination to afford product **7**.

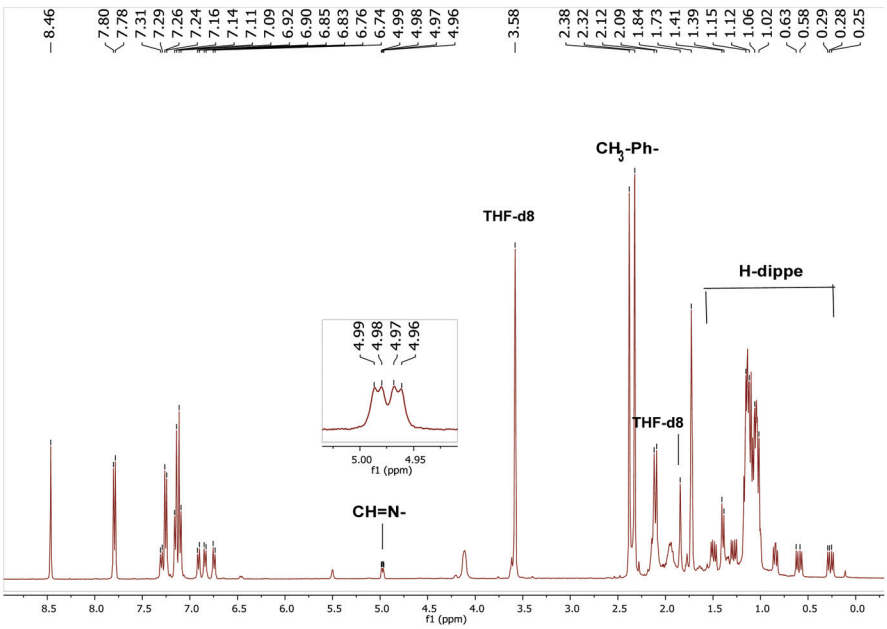
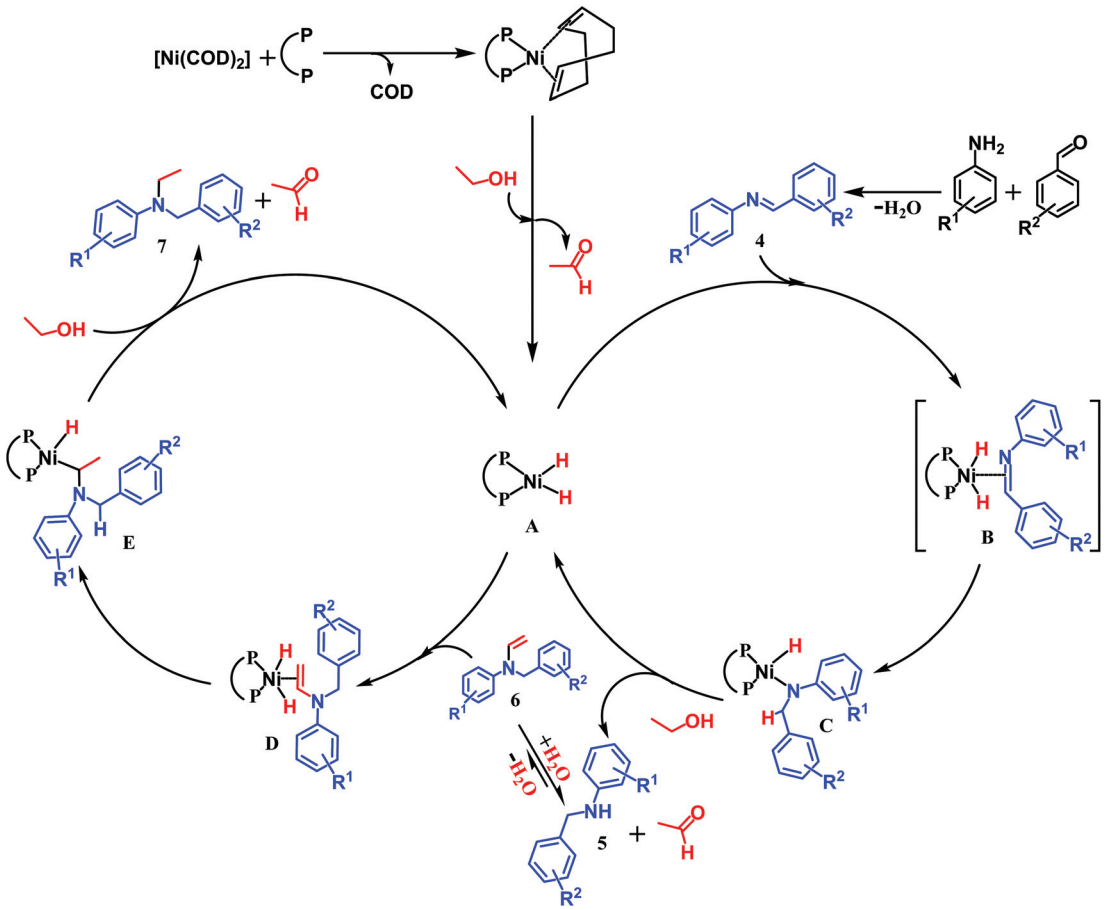


Fig. 2 The ^{1}H-NMR spectrum of a mixture of **I** and **II** in THF-d^8.



Scheme 5 Mechanistic proposal for the amino-reductive and *N*-alkylation TH process of imines.

Conclusions

In summary, a Ni-catalyzed tandem process achieved the *N*-alkylation of anilines with electron withdrawing and donating groups that were found to show excellent conversion toward *N*-ethylaniline. Similarly, the reduction of *N*-di-*p*-tolymethanimine **4** in the absence of pressurized hydrogen was achieved in the presence of ethanol, methanol and 2-propanol; however, the imine *N*-alkylation reaction was carried out through an extra tandem step (only for ethanol), which allowed the formation of the enaminic intermediate that is reduced to form the *N*-ethyl product **7**.

Experimental

The catalytic experiments were carried out using standard Schlenk techniques in an inert-gas/vacuum double manifold or under argon (Praxair, 99.998) in an MBraun UniLab glove box (<1 ppm H_2O and O_2). The alcohols were dried using standard methods, refluxed under an inert atmosphere with magnesium/iodine, and subsequently distilled and stored over molecular sieves under an argon atmosphere. All liquid reagents were purchased as reagent grade and were degassed before use. All anilines, aldehydes, molecular sieves and $[Ni(COD)_2]$ were purchased from Aldrich and stored in the glove box. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves in a glove box. [(dippe)Ni(η^2-C, N)-PhHC = NPh] was prepared according to methods described in previous reports,[33] and *N*-di-*p*-tolymethanimine **3** was prepared using the general procedure described elsewhere.[12,24,33] NMR spectra were recorded at room temperature on a 300 MHz Bruker AVANCE III spectrometer. ^{1}H NMR spectra (δ parts per million) were reported relative to the residual protio-solvent. $^{13}C\{^1H\}$ spectra showed the characteristic carbon signal of each solvent. $^{31}P\{^1H\}$ NMR chemical shifts (δ parts per million) were reported relative to external 85% H_3PO_4. Coupling constants (J values) are given in Hz. The following abbreviations are used for the NMR data: s = singlet, d = doublet, t = triplet, m = multiplet and br = broad. GC-MS determination was performed using an Agilent Technologies G3171A equipped with a column comprised of 5% phenylmethyl silicone, 30 m × 0.25 mm × 0.25 μm; internal standards were used for every sample recovered from the isolated product, done in triplicate. ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the reduction products were obtained in $CDCl_3$. The catalytic experiments were carried out in 4750-125 and 4700-25 mL stainless-steel Parr reactors.

General procedure for *N*-alkylation of anilines

A solution of [Ni(COD)$_2$] (2 mol%) and dippe (3 mol%) in 1 mL of ethanol was added to an aryl-substituted aniline (1.0 mmol) dissolved in 4 mL of ethanol and transferred to a stainless-steel Parr reactor (4750, 125 mL). The reaction mixture was stirred for 18 h at 150 °C and the reaction crude was filtered using Celite and analyzed using GC-MS and multinuclear NMR spectroscopy.

Mercury drop test

A similar procedure was followed, however, a mercury drop was added after the reagents and the reaction mixture were transferred into a stainless-steel Parr reactor (4750, 125 mL). The reaction mixture was stirred for 18 h at 150 °C and the reaction crude was filtered using Celite and analyzed using GC-MS.

General procedure for reduction of *N*-di-*p*-tolymethanimine 3

A solution of [Ni(COD)$_2$] (2 mol%) and dippe (3 mol%) in 1 mL of ethanol was added to *N*-di-*p*-tolymethanimine **3** (1.0 mmol) in 4 mL of ethanol and then transferred into a stainless-steel Parr reactor (4750, 125 mL). The reaction mixture was stirred for 24 h at 150 °C. The reaction crude was filtered using Celite and analyzed using GC-MS.

General procedure for reduction and *N*-alkylation of imines

A solution of [Ni(COD)$_2$] (5 mol%) and dcype (7 mol%) in 1 mL of THF was added to the imine (1.0 mmol) in 5 mL of alcohol and transferred to a stainless-steel Parr reactor (4750, 125 mL). The reaction mixture was stirred for 48 h at 170 °C. The reaction crude was filtered using Celite and analyzed using GC-MS.

Synthesis of the complex [(dippe)Ni(η^2-C, N)-PhHC = NPh]

A solution of [Ni(COD)$_2$] (0.025 mmol) and dippe (0.025 mmol) in 1 mL of THF was stirred for 1 h. *N*-di-*p*-tolymethanimine **3** (0.025 mmol) in 3 mL of THF was added and stirred for 12 h. Subsequently, it was concentrated *in vacuo* and monitored by NMR under argon in THF-d$_8$.

Conflicts of interest

The authors have no conflicts to declare.

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