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## Nickel-Catalysed Reductive Amination with Hydrosilanes

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Dedicated to Professor Irina Petrovna Beletskaya

Amines are central building blocks in organic synthesis for the preparation of natural products, pharmaceutical and agronomical compounds.<sup>[1]</sup> Among the various synthetic methods to prepare amines, the catalytic reduction of imines is one of the most efficient methods developed.<sup>[2]</sup> The stability of some imines is, however, rather limited, and their synthesis and purification can be tedious. On the other hand, direct reductive amination is an elegant and straightforward alternative to the synthesis of substituted amines, as the imine is generated in situ and reduced directly to the corresponding amines. The reducing agent is usually a borohydride derivative,<sup>[3]</sup> although several methods based on transition metal-catalysed hydrogenation, hydrogen transfer<sup>[4]</sup> and hydrosilylation<sup>[5]</sup> have been also developed. Hydrosilanes are versatile reducing agents that allow the use of mild conditions and good chemoselectivities.<sup>[6]</sup> In addition, the use of inexpensive silanes such as polymethylhydrosiloxane (PMHS), an abundant and non-toxic by-product of the silicone industry, or tetramethyldisiloxane (TMDS) offer useful alternatives for large-scale hydrogenations.<sup>[7]</sup>

The use of earth abundant transition metals has become an important goal in catalysis.<sup>[8]</sup> In the field of reduction, particularly in hydrosilylation, many efforts have been devoted to using inexpensive earth abundant metals such as iron,<sup>[9,10]</sup> zinc,<sup>[11]</sup> titanium<sup>[12]</sup> or copper.<sup>[13]</sup> Compared to the former metals of the first row of the periodic table, nickel has been employed much less.<sup>[14–16]</sup> Notably, only two examples of imine reduction have been reported, one by hydrogen transfer reaction<sup>[17]</sup> and the other by hydrosilylation.<sup>[18]</sup> In the field of reductive amination, catalytic reactions involving nickel are extremely scarce and mainly nickel nanoparticles have been involved in the hydrogen transfer reductive amination of aldehydes.<sup>[19]</sup> In 2012 and 2013, we have focused our attention on developing an efficient catalytic system for the reduction of carbonyl derivatives with nickel.<sup>[15–16]</sup> We have found that the simple salt

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Ni(OAc)<sub>2</sub> in the presence of tricyclohexylphosphine could be an efficient catalytic system for the reduction of aldehydes and ketones with PMHS as the silane.<sup>16]</sup> Here, we report the reductive amination of aldehydes by hydrosilylation by using an in situ-generated catalytic system from inexpensive nickel acetate and tricyclohexylphosphine.

To start our investigation, we selected benzaldehyde (1 equiv.) and *p*-methoxyaniline (1.5 equiv.) as the model substrates and the combination of Ni(OAc)<sub>2</sub> (5 mol%) and PCy<sub>3</sub> (10 mol%) as the catalytic system in the presence of 4 Å molecular sieves (Scheme 1, Table 1).<sup>[20,21]</sup> At 100°C in toluene with 4 equiv. of PMHS, the reaction led to 80% conversion into the amine **3** and 20% of benzyl alcohol **1** resulting from the



**Scheme 1.** Nickel-catalysed reductive amination of benzaldehyde with *p*-anisidine by hydrosilylation.

Table 1. Optimisation of the conditions of the reductive amination           reaction. <sup>[a]</sup>							
Entry	Silane [equiv.]	Solvent [mL]	Temp. [°C]	Time [h]	Yield <b>1/2/3</b> [%]		
1	PMHS (4)	toluene (2.5)	100	24	20/0/80		
2	TMDS (2.5)	toluene (2.5)	100	24	4/0/96		
3	PMHS (4)	THF (1)	70	24	6/0/94		
4	TMDS (2.5)	THF (1)	70	24	3/0/97		
5	TMDS (2.5)	THF (1)	50	24	1/81/18		
6 <sup>[b]</sup>	TMDS (2.5)	THF (1)	70	24	23/0/77		
7	TMDS (1.5)	THF (1)	70	16	< 3/0/ > 97		
8	TMDS (1)	THF (1)	70	16	0/>97/<3		
9 <sup>[c]</sup>	TMDS (1)	THF (1)	70	16	< 3/46/51		
10 <sup>[d]</sup>	TMDS (1.5)	THF (1)	70	16	8/ < 3/89		
11 <sup>[e]</sup>	TMDS (1.5)	THF (1)	70	24	$<\!3/0/\!>\!97$		

[a] Typical conditions: to a solution of Ni(OAc)<sub>2</sub> (5 mol%) and 4 Å molecular sieves (200 mg), PCy<sub>3</sub> (10 mol%), the amine (0.75 mmol, 1.5 equiv.), the aldehyde (0.5 mmol), and the silane (1–4 equiv.) were added in this order. The reaction mixture was then heated in an oil bath. After hydrolysis and extraction, the yields were determined by <sup>1</sup>H NMR and GC. [b] Without 4 Å molecular sieves, [c] Ni(OAc)<sub>2</sub> (2.5 mol%), PCy<sub>3</sub> (5 mol%). [d] 1 equiv. of amine. [e] 1.1 equiv. of amine; the silane was added after 8 h and the reaction mixture then stirred for an additional 16 h.

direct reduction of the benzaldehyde (entry 1). By changing the silane from PMHS to TMDS (2.5 equiv.), the selectivity increased to 96% in favour of amine 3. At 70°C in THF, the selectivity towards the formation of the amine increased for both PMHS and TMDS (respectively 94 and 97%, entries 3 and 4). On decreasing the temperature to 50 °C, the imine intermediate 2 was obtained as the main product (81%, entry 5). We have also performed the reaction in the absence of 4 Å molecular sieves: the selectivity decreased and a 23:77 molar ratio mixture of benzyl alcohol 1 and amine 3 was obtained (entry 6). The quantity of TMDS could be decreased to 1.5 equiv. without any alteration of the selectivity (entry 7). In contrast, if the catalytic loading of nickel acetate was lowered to 2.5 mol%, a 1:1 mixture of the imine 2 and the amine 3 was obtained (entry 9). Finally, if the quantity of aniline was lowered from 1.5 to 1 equiv., 8% of benzyl alcohol 1 was detected, which showed that the formation of the imine was in competition with the reduction of the aldehyde (entry 10). To reduce the formation of the undesired alcohol but only use a stoichiometric amount of *p*-anisidine, a sequential procedure was used; the silane was added after 8 h of reaction and the desired amine then obtained quantitatively (entry 11).

With the optimised conditions in hand (1.1 equiv. amine, 1 equiv. aldehyde, 70°C, 8 h, then 1.5 equiv. TMDS, 70°C, 16 h), we focused on the scope of the reaction. At first, various amines were tested with aromatic aldehydes such as benzaldehyde and *p*-anisaldehyde (Table 2, entries 1–6): with the activated p-methoxyaniline, the corresponding amines were obtained with 97% isolated yields. In contrast, with non-activated aniline, the reduction of the imine required a longer reaction time of 40 h to reach completion and, with the electron-deficient 4-fluoroaniline, 4 equiv. of TMDS were needed to obtain the secondary amine in good yields (79-82%). The electronics of the amine partners seemed to have a strong influence on the reaction because, with an electron-rich amine, the reaction was performed in short time, whereas the presence of electron-withdrawing group induced longer reaction times (8 vs. 40 h). The group tolerance was also studied on the aldehyde partner by reaction with 1.1 equiv. of *p*-anisidine. Thus, the tolerance towards acidic phenol moieties was also demonstrated, as was the selectivity towards esters and amides functional groups; the resulting reactions led to high conversions of amines (87-97%) and isolated amines with non-altered functional groups isolated in moderate to good yields (46-80%; entries 7-9). In contrast, with p-cyano- and p-nitro-benzaldehyde derivatives, the conversions towards the desired amine were low or moderate (41 and 14%, respectively).

The reaction of aldehyde with benzylamine proceeded well and the products were isolated with 85–95% yields, irrespective of the nature of the substituent on the aromatic ring of the aldehyde (entries 12–14). If the reaction was performed with aliphatic aldehydes such as hydrocinnamaldehyde and octanal, the corresponding secondary amines were obtained in good to excellent conversions and yields (entries 17–20). Notably, aliphatic amines such as dodecylamine were also suitable for the reductive amination (97% yield, entries 15, 16, 18 and 20).



[a] Typical conditions: To a solution of Ni(OAc)<sub>2</sub> (5 mol%) and 4 Å molecular sieves (400 mg), PCy<sub>3</sub> (10 mol%), amine (1.1 mmol, 1.1 equiv.) and aldehyde (1 mmol) were added in that order and stirred at 70 °C for 8 h. Then TMDS (1.5 mmol, 1.5 equiv.) was added and the reaction stirred for 16 h, after which hydrolysis was performed by adding MeOH (2 mL) and NaOH (2 mL), followed by stirring overnight. [b] Yields were determined by using <sup>1</sup>H NMR spectroscopy. [c] Isolated yields after purification by column chromatography in parentheses. [d] t=40 h instead of 16 h, [e] 4 equiv. TMDS, [f] 1.5 equiv. amine. [g] *p*-Methoxybenzyl alcohol was observed. [h] t=48 h instead of 8 h.

If using secondary amine such as the dipropylamine, the reaction was more difficult to perform. If reacting with *p*-methoxybenzaldehyde, no resulting product of reductive amination was detected and the sole product obtained was the corresponding alcohol (entry 21). Notably, the dipropylamine could be condensed with the hydrocinnamaldehyde with moderate conversion (58%; entry 22). The transformation of ketones under similar reductive amination conditions was unsuccessful, with only low amounts of amine obtained. In comparison to other transition metal catalysts (iron<sup>[51]</sup> and zinc<sup>[5h]</sup>), the activity of this nickel catalytic system was competitive in the reductive amination of aldehydes with siloxanes as the reducing reagent.

To try to develop better insights into the reaction conditions, several stoichiometric experiments were conducted in order to identify which type of active catalysts could be generated under our catalytic conditions. Recently Ananikov and Beleskaya have shown that Ni(acac)<sub>2</sub> and PMe<sub>2</sub>Ph were leading to Ni<sup>0</sup>-phosphines complexes, with the concomitant oxidation of one phosphine in the presence of traces of water.<sup>[22]</sup> As we have shown that Ni(acac)<sub>2</sub> could also be used as nickel precursor instead of Ni(OAc)<sub>2</sub> and that the basic dimethylphenylphosphine could be used instead of tricyclohexylphosphine for the reduction of carbonyl derivatives,<sup>[16a]</sup> we have investigated the reaction Ni(acac)<sub>2</sub> with Ph<sub>3</sub>SiH in the presence of PMe<sub>2</sub>Ph in a molar ratio of 1:1:3 in toluene to try to identify any product resulting from an oxidative addition of the silane onto the nickel. The mixture was stirred for a five minutes at room temperature until all solid dissolved, then layered with pentane and stored at -18 °C, which allowed the isolation of large blue-purple crystals. (Scheme 2) The molecular structure of **4**,



Scheme 2. Stoichiometric reactions of  $\mathsf{Ni}(\mathsf{acac})_2$  with phosphines. Cy = cyclohexyl.

which was identified by X-ray diffraction, revealed that only the complex *trans*-[Ni(acac)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] already described by Ananikov could be isolated. Notably, if the same reaction was performed at 70 °C for 8 h, despite a colour change from yellow to orange-red, no identifiable species could be detected.<sup>[23]</sup> Surprisingly, performing the same reaction with PCy<sub>3</sub>, large green crystals of **5** were formed, the molecular structure of which, as determined by X-ray diffraction analysis, was [Ni-



Figure 1. ORTEP view of the complex 5 drawn at 50% probability. Hydrogen atoms were omitted for clarity. The ligands acac are disordered over two positions, only one of which is depicted.

 $(acac)_2(PCy_3)],$  with only one phosphine coordinated, evidencing an 18-electron, five-coordinated square-pyramidal structure (see Figure 1).  $^{\rm [24]}$ 

Finally, by mixing Ni(OAc)<sub>2</sub>, PCy<sub>3</sub> and Ph<sub>2</sub>SiH<sub>2</sub>, the mixture turned orange-red after 3.5 h at 100 °C. The reaction solution was then transferred into an NMR tube for analysis. The main compound revealed a signal at -2.04 ppm in the <sup>1</sup>H NMR spectrum for Ni(H–Si) and a signal at +45.9 ppm in the <sup>31</sup>P NMR spectrum, which was in accordance with the complex [{Ni(PCy<sub>3</sub>)}<sub>2</sub>(µ-SiHPh<sub>2</sub>)<sub>2</sub>], as described by Osakada but synthesised from Ni(cod)<sub>2</sub>, PCy<sub>3</sub> and Ph<sub>2</sub>SiH<sub>2</sub>.<sup>[25]</sup> These spectrometric data could confirm that the first step of the catalytic cycle was the reduction of Ni<sup>II</sup> to Ni<sup>0</sup> species.<sup>[22,25]</sup>

In conclusion, we have developed an efficient nickel-catalysed reductive amination of aldehydes by using an in situ-generated catalyst from Ni(OAc)<sub>2</sub> and tricyclohexylphosphine. At 70 °C, with tetramethyldisiloxane as the hydrosilane, the corresponding secondary amines were obtained in moderate to good isolated yields. This in situ-generated nickel system from Ni(OAc)<sub>2</sub> and phosphine provides a good alternative to Ni(cod)<sub>2</sub> in catalysis.

## **Experimental Section**

A 10 mL oven dried Schlenk tube containing a stirrer bar was charged with 4 Å molecular sieves (200 mg) and Ni(OAc)<sub>2</sub> (10 mg, 0.05 mmol). After purging with argon (3 cycles), THF (2 mL) was added, followed by PCy<sub>3</sub> (168  $\mu$ L, 0.1 mmol), amine (1.1 mmol) and aldehyde (1.0 mmol). The reaction mixture was stirred in a preheated oil bath at 70 °C for 8 h. TMDS (264  $\mu$ L, 1.5 mmol) was then added and the reaction mixture stirred at 70 °C for an additional 16 h. After cooling to RT, MeOH (2 mL) was added followed by 2 m NaOH (2 mL) under vigorous stirring. The reaction mixture was stirred further for 16 h at RT, then extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography by using an ethyl acetate/petroleum ether mixture (5:95 to 20:80) to achieve the desired product.

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