# Base-catalyzed hydroamination of ethylene with diethylamine

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## Abstract

The catalytic hydroamination reaction of ethylene with diethylamine in the presence of lithium diethylamide has been reinvestigated to improve catalyst productivity. Various tertiary amines were synthesized and screened as ligands for the target reaction. Applying $N,N,N',N'$-tetramethylethylenediamine (TMEDA) or $N,N,N',N'',N''$-pentamethyldiethylentriamine (PMDTA) the rate of the reaction is increased, but also ligand degradation is observed. Using optimized parameters excellent yield (92%) and conversion (99%) were achieved under mild conditions. At higher temperature base-catalyzed hydroamination of higher olefins is also possible.
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## 1. Introduction

The addition of H–Nu (Nu = halogen, OR, NR$_2$, CN, CHO, etc.) across a carbon–carbon double bond is one of the most important and extensively used chemical transformations in organic synthesis. A prime example for this type of reaction is the hydroamination of ubiquitous available olefins (Scheme 1) [1]. Such addition reactions are perfectly suited for a sustainable production of aliphatic amines because of availability of substrates and 100% atom economy [2] or atom efficiency [3] of the process. Unfortunately, the direct nucleophilic addition of amines to non-activated olefins is hampered by several thermodynamic and kinetic barriers [4]. Thus, the development of a general hydroamination methodology is still an important challenge for catalysis. Nevertheless, in special cases, e.g. with aryl olefins or 1,3-dienes as substrates, catalysts such as Brønsted or Lewis acids, alkali [5] and transition metals [6], lanthanide or actinide complexes [7] permit successful hydroamination reactions. In the last decade we have been mainly involved in this area in the development of catalysts for carbonylative amination of olefins (so-called hydroaminomethylation) [8], transition metal- and base-catalyzed hydroamination of olefins [9] and alkynes [10].

With regard to industrial applications short chain aliphatic olefins constitute the most attractive starting materials for hydroamination reactions. For example, propene [11] and isobutene [12] have been reported to react with ammonia in the presence of zeolites forming isopropylamine (90–100% selectivity) and *tert*-butylamine (up to 99% selectivity), respectively. BASF has even commercialized a *tert*-butylamine process based on this reaction [13]. Due to the Brønsted or Lewis acid nature of the catalysts (zeolites) the Markovnikov product is formed because of the higher stability of the intermediate carbocation.

More recently, in a joint collaboration we became interested in the hydroamination of ethylene. Here, the use of acidic catalysts is less feasible because of the reduced stability of the intermediate carbocation. In addition, transition metal catalysts are not active or productive enough. Hence, we focused on the use of base catalysts for this reaction.

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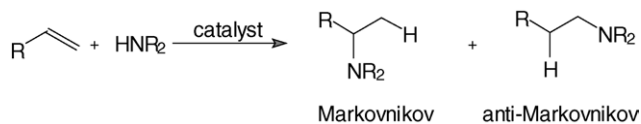
Scheme 1. Hydroamination of olefins.

The first well recognized hydroamination of ethylene was reported by Howk et al. already in 1954 [14]. In this process ammonia was added to ethylene in the presence of metallic sodium at 175–200 °C and 800–1000 bar pressure in an inert hydrocarbon medium forming almost equimolar amounts of ethyl-, diethyl- and triethylamine with a total yield of 70%. Sodium was found to be converted quantitatively to sodium amide after the reaction. Other alkali metal catalysts such as Li, K, NaH and LiH were equally active. The use of very high reaction pressures and temperatures are essential here; for instance only 0.7% conversion of ammonia is achieved at "lower" pressure (205 bar). Under similar conditions, other primary or secondary amines also react with ethylene. For example n-butylamine reacts with ethylene giving diethyl-n-butylamine (75% yield), in addition to some high boiling nitrogen containing materials. At temperatures below 200 °C, only the secondary product ethyl-n-butylamine is formed though in poor yields. Piperidine forms N-ethylpiperidine in good yield (~80%) [15] on reaction with ethylene (at 100 °C and 38 bar) using metallic sodium in the presence of traces of pyridine or by using $C_5H_{10}NLi$ as the pre-catalyst (90% yield). Similarly aniline is converted to N-ethylaniline using Na or NaNH$_2$ as pre-catalyst at 250–300 °C and 50–200 bar pressure [16]. The reaction temperature and pressure for the amination of ethylene can be considerably lowered by using alkali metal amides [17] and supported alkali metals as catalysts [18]. Since operating at lower temperatures these catalysts are particularly useful for the selective formation of monoalkylated amines. Thus, ethylene reacts with ammonia at 80–110 °C and 90–120 bar in the presence of catalytic amounts of cesium or rubidium amides forming moderate yields (28–34%) of ethylamine. Sodium and potassium amide catalysts give poorer yield for this reaction owing to their low solubility in liquid ammonia, but the eutectic mixture containing $KNH_2$–$2NaNH_2$ which melts at ~92 °C is more active (27% yield) [19]. Apart from inorganic alkali or alkaline earth metal amides derived from ammonia, organic amides derived from an amine, which are not considerably more acidic than the amine to be alkylated, can also be used as catalysts [20]. In general, the order of increasing basicity of amines is aromatic amines < ammonia < aliphatic amines. As a result in the ethylation of piperidine the more basic amide $Me_2NLi$ can be used as pre-catalyst, but the less basic $Ph_2NLi$ remains inactive [21]. Noteworthy, it has been shown that the addition of N,N,N′,N′-tetramethylethylenediamine (TMEDA) increases the rate of the reaction of primary and secondary amines with olefins using catalytic amounts of alkyl lithium [22]. Hence, these reactions run under much lower pressure and temperature than that needed for the metallic sodium catalysts. For

example, ethylene reacts with diethylamine in the presence of the LiNEt$_2$–TMEDA catalyst system at 70 bar and 140 °C forming triethylamine in 83% yield. However, the same reaction in the presence of Na or NaH as catalyst requires 1000 bar pressure and 225 °C to achieve 28% yield. Kinetic studies in the presence of TMEDA showed a first order dependence of the reaction rate with respect to ethylene and zero order dependence with respect to diethylamine.

Considering the LiNEt$_2$–TMEDA system for larger scale application the main problem is catalyst stability. Hence, we were interested in the mechanism of deactivation in base-catalyzed hydroaminations and in the development of more stable ligands. Here, we present a full account on our work.

## 2. Results and discussion

### 2.1. Hydroamination of ethylene

As a model system for the commercially interesting reaction of ammonia with ethylene, the hydroamination of ethylene with diethylamine in the presence of a lithium diethylamide–TMEDA catalyst system was studied (Scheme 2). As a starting point of our investigations we reproduced the result from Lehmkuhl and Reinehr [22] without any solvent (Table 1, entry 1). At 20 bar initial pressure of ethylene and 80 °C high conversion (96%) and a good yield (84%) of triethylamine are obtained. However, catalyst productivity (turnover number) is comparably low (TON = 10). Performing the reaction in non-polar solvents like toluene or cyclohexane gave excellent yield of triethylamine (Table 1, entries 3–4), while polar solvents THF and MTBE gave low yield (Table 1, entries 2 and 5). Due to the improved yield and the easy handling all further investigations were carried out in toluene as solvent.

Next, the reaction was carried out at different catalyst and TMEDA concentrations (Table 1, entries 6–12). The hydroamination of ethylene with diethylamine without ligand yielded only 22 and 15% of triethylamine at 9 or 3 mol% catalyst, respectively (Table 1, entries 6 and 8). However, addition of 5–10 mol% of TMEDA leads to good to excellent yield (up to 96%). In the presence of TMEDA also with 5 mol% of LiNEt$_2$ a nearly quantitative yield is observed (Table 1, entry 7). At lower catalyst concentration (2.5 mol%) it is necessary to increase the ethylene pressure to 40 bar or to increase the temperature to 110 °C in order to get good yield (93 and 69%, respectively) (Table 1, entries 11 and 14). The effect of temperature was examined by using 2.5 mol% LiNEt$_2$ catalyst and 5 mol% TMEDA (Table 1, entries 11–14). At room temperature the reaction proceeded extremely slowly with very
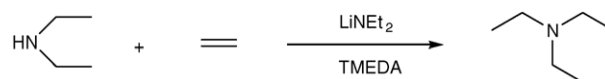


Scheme 2. Hydroamination of ethylene with diethylamine.

Table 1
Reaction of ethylene with diethylamine in the presence of LiNEt$_2$ and TMEDA

| Entry | Solvent (ml) | Cat. (mol%) | Ligand (mol%) | Cat.:L ratio | Pressure (bar) | Temperature (°C) | Time (h) | Conversion (%) | Yield (%) | TON |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | – | 8 | 28 | 1:3.5 | 20 | 80 | 18 | 96 | 84 | 10 |
| 2 | THF | 9 | 46 | 1:5 | 20 | 80 | 18 | 61 | 46 | 5 |
| 3 | Toluene | 9 | 46 | 1:5 | 20 | 80 | 18 | 100 | 97 | 11 |
| 4 | Cyclohexane | 9 | 46 | 1:5 | 20 | 80 | 18 | 98 | 95 | 11 |
| 5 | MTBE | 9 | 46 | 1:5 | 20 | 80 | 18 | 15 | 14 | 2 |
| 6 | Toluene | 9 | – | 1:0 | 20 | 80 | 18 | 23 | 22 | 3 |
| 7 | Toluene | 5 | 10 | 1:2 | 20 | 80 | 18 | 100 | 96 | 19 |
| 8 | Toluene | 3 | – | 1:0 | 20 | 80 | 18 | 15 | 15 | 5 |
| 9 | Toluene | 3 | 10 | 1:3.3 | 20 | 80 | 18 | 75 | 74 | 25 |
| 10 | Toluene | 2.5 | 10 | 1:4 | 20 | 80 | 18 | 39 | 38 | 15 |
| 11 | Toluene | 2.5 | 5 | 1:2 | 40 | 80 | 18 | 95 | 93 | 37 |
| 12 | Toluene | 2.5 | 5 | 1:2 | 40 | r.t. | 24 | 6 | 3 | 1 |
| 13 | Toluene | 2.5 | 5 | 1:2 | 40 | 40 | 12 | 10 | 8 | 3 |
| 14 | Toluene | 2.5 | 5 | 1:2 | 20 | 110 | 12 | 79 | 69 | 28 |
| 15 | Toluene | 2.5 | 10 | 1:4 | 11 | 80 | 18 | 33 | 33 | 13 |
| 16 | Toluene | 2.5 | 10 | 1:4 | 20 | 80 | 10 | 34 | 33 | 13 |
| 17 | Toluene | 2.5 | 10 | 1:4 | 20 | 80 | 18 | 39 | 38 | 15 |
| 18 | Toluene | 2.5 | 5 | 1:2 | 40 | 80 | 12 | 99 | 92 | 37 |
| 19 | Toluene | 2.5 | 5 | 1:2 | 60 | 80 | 12 | 100 | 99 | 40 |

Reaction conditions: 0.029 mol diethylamine, 15 ml solvent, 0.5 ml $n$-octane as an internal GC standard.
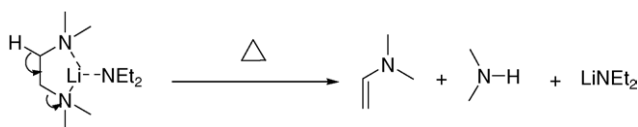


Scheme 3. Proposed degradation of TMEDA.

poor yield (3%). Increasing the temperature to 40 °C only 8% yield of triethylamine is obtained. At 80 °C the reaction proceeded smoothly with nearly quantitative conversion and good yield (93%). At >100 °C the chemoselectivity dropped significantly. Furthermore we investigated the influence of the ethylene pressure. The best yield (99%) is achieved with quantitative conversions at 60 bar pressure after 12 h (Table 1, entry 19).

After having obtained an excellent yield under ambient conditions we turned our interest to the problem of ligand degradation. Lehmkuhl and Reinehr [22] showed nicely that TMEDA forms under strong basic conditions $N,N$-dimethylaminoethene as a side-product (Scheme 3). We assumed that this base-induced fragmentation proceeds as a $syn$-elimination process, which should be easily influenced

by the structure of the ligand. Therefore, we tested different amine ligands, which resemble closely the TMEDA structure.

In addition to commercially available amines also new (1–6) ligands were synthesized. As shown in Scheme 4 permethylation of the amino groups were achieved via the Eschweiler–Clarck reaction or methylation by using methyl iodide (Scheme 4).
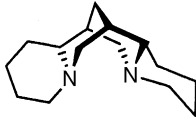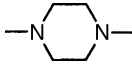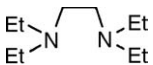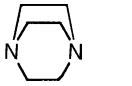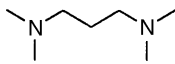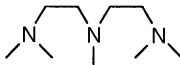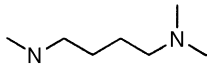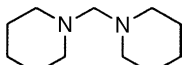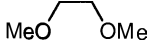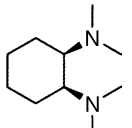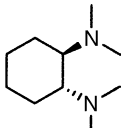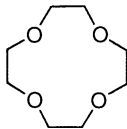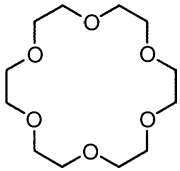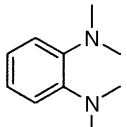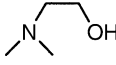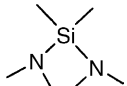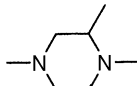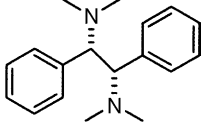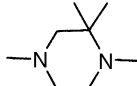
Selected results of the comparison of different cyclic, non-cyclic bidentate and tridentate amine ligands with TMEDA and also bidentate and polydentate ether are shown in Table 2.

As expected the reaction without any ligand present gave very poor yield, however in the presence of 5 mol% TMEDA 99% conversion and 92% yield are obtained (Table 2, entries 1–2). Significant yield of triethylamine is only observed using $N,N,N',N'',N''$-pentamethyldiethylentriamine (PMDTA) and sparteine as ligand (Table 2, entries 13 and 16). In the presence of most non-cyclic and cyclic bidentate amines only low conversion and yield are observed. Surprisingly, no conversion at all is seen in the presence of $cis$- and $trans$-1,2-bisdimethylaminocyclohexane, 1,2-bisdimethylaminostilbene and all ether ligands (Table 2,
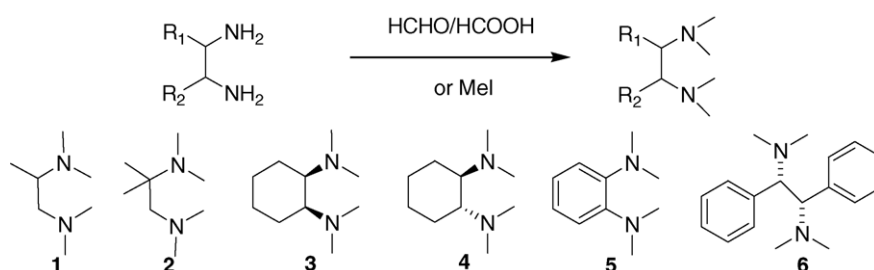


Scheme 4. Synthesis of ligands.

Table 2
Influence of different ligands on the hydroamination of ethylene

| Entry | Ligand | Conversion (%) | Yield (%) | Entry | Ligand | Conversion (%) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | – | 8 | 7 | 13 | | 38 | 36 |
| 2 | TMEDA | 99 | 92 | 14 | | 10 | 9 |
| 3 | | 20 | 19 | 15 | | 7 | 6 |
| 4 | | 10 | 9 | 16 | | 99 | 90 |
| 5 | | 8 | 7 | 17 | MeO...O...OMe | – | – |
| 6 | | 19 | 17 | 18 | MeO...OMe | – | – |
| 7 | | 1 | >1 | 19 | | – | – |
| 8 | | – | – | 20 | | – | – |
| 9 | | 10 | 9 | 21 | | – | – |
| 10 | | 14 | 13 | 22 | | 18 | 14 |
| 11 | | 13 | 11 | 23 | | – | – |
| 12 | | 14 | 14 | | | | |

Reaction conditions: 0.029 mol diethylamine, 2.5 mol% $LiNEt_2$, 5 mol% ligand, 40 bar initial pressure of ethylene, 80 °C, 12 h, 15 ml toluene, 0.5 ml *n*-octane as an internal GC standard.

entries 7, 8, 17–21, 23). Also 2-dimethylaminoethanol as ligand showed no activity.

### 2.2. Mechanistic considerations

In order to understand the mechanism of catalyst deactivation we tried to identify potential degradation products of

the standard ligand. Hence, TMEDA was reacted with 0.5 and 1.0 equiv. of $LiNEt_2$ in the presence of diethylamine at room temperature, 40 and 80 °C for 4, 8, and 64 h (Fig. 1). To our surprise there is only little conversion of TMEDA seen. Even using 1.0 equiv. of $LiNEt_2$ at 80 °C for 8 h more than 90% of TMEDA remained unchanged! Interestingly, there is also no large difference in the degradation of TMEDA
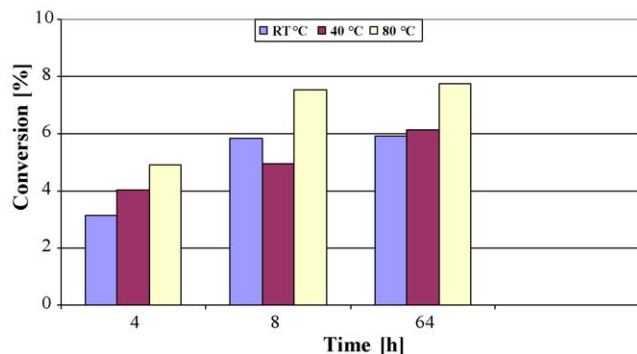
Fig. 1. Reaction of TMEDA with LiNEt$_2$ in the presence of diethylamine.



Fig. 2. Different lithium amide species.

between room temperature and 80 °C. Apparently the catalyst deactivation is not correlated to the amount of TMEDA degradation and deactivation of the active lithium amide species occurs already at room temperature. Due to low conversion of TMEDA (<10%) it was not possible to isolate any degradation products in pure form.

A potential catalyst deactivation pathway is the formation of lithium hydride by β-hydride elimination from lithium diethylamide species. Therefore LiH was used in the amination of ethylene under various conditions. Noteworthy, when we used 2.5 mol% LiH at 80 °C as catalyst in the reaction of ethylene with diethylamine no hydroamination product is observed. Even the use of 100 mol% of LiH (with respect to diethylamine) did not give any hydroaminated product in toluene or cyclohexane as solvents. This a hint that this compound is involved in the catalyst deactivation.

It is well-documented in the literature that the actual structure of lithium amides in solution is quite complex and that the concentration of different aggregates is influenced dramatically by minor modification of the conditions [23]. For example Collum and coworkers reported detail investigations of the coordination of polydentate amine- and ether ligands with lithium amide [24]. Depending on the ligand, lithium amide and solvents mainly monomers and dimers were observed in solution (Fig. 2).

Based on this we performed lithium NMR spectroscopy at room temperature with LiCl as an internal standard for the hydroamination reactions of ethylene in the presence of LiNEt$_2$ 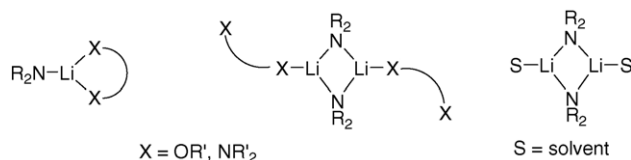and TMEDA. For the reaction mixture at room temperature a very broad signal between 0.1 and 3.5 ppm is observed, which shows that monomer, dimer and polymer species formed in the reaction mixture are in equilibrium. In addition, LiH might be present which forms at 0.44 ppm a broad peak. Despite variations of concentration and additives lithium NMR spectroscopy always only broad signal is observed.

In order to gain further insight into the mechanism, the addition of N-deuteriated diethylamine (CH$_3$-CH$_2$)$_2$ND to ethylene (40 bar) was performed at 80 °C for 12 h in the presence of LiNEt$_2$ and TMEDA (Scheme 5). As shown in Scheme 5 two deuteriated products 7 and 8 can be formed. These products are easily identified using $^{13}$C NMR spectroscopy.

The measured $^{13}$C NMR spectrum for the reaction mixture showed a triplet at $\delta = 11.18$, $^1J$ ($^{13}$C, $^2$D) = 19.3 Hz for the CH$_2$D group in the product 7. Furthermore 7 is confirmed by a DEPT spectrum. The formation of 8 is excluded because no signal for the CHD group is seen. Interestingly, we also observed ~5% deuterium exchange at the N-methyl group of TMEDA. As shown in Scheme 6 this deuterium exchange is explained by metallation of the N-methyl group and subsequent reaction with (CH$_3$-CH$_2$)$_2$ND. Similar results were observed when the reaction was carried out in toluene as solvent.

### 2.3. Hydroamination of higher olefins

Hydroamination of larger aliphatic olefins to anti-Markovnikov amines is basically not known and rather tricky compared to activated olefins such as aryl olefins or 1,3-dienes. Hence, functionalization of such olefins with anti-Markovnikov regioselectivity is viewed for decades as one of the major challenges of catalysis [25]. Until to date only a few examples are known where non-activated higher alkenes have
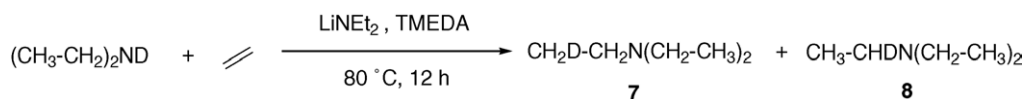


Scheme 5. Hydroamination of ethylene with deuteriated diethylamine.
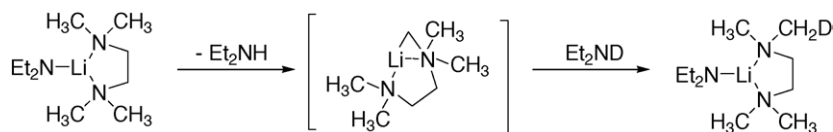


Scheme 6. Proposed mechanism for the formation of partially deuteriated TMEDA.
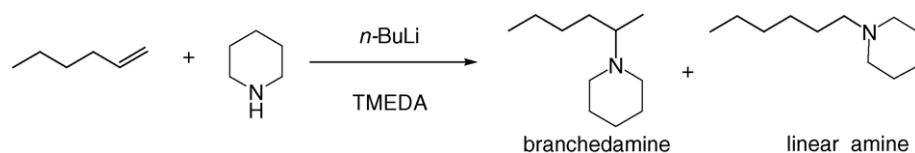
Scheme 7. Hydroamination of 1-hexene with piperidine.

been hydroaminated at all [14,19,26]. Olefins like propylene, isobutylene, 1-butene, 1-hexene and cyclohexene are found to form the corresponding Markovnikov amination products in very low yield. When higher olefins were reacted with amines, disproportionation of the amine is observed. However, in a recent study by us [27], a catalyst system consisting of n-BuLi and TMEDA was found to be active for the hydroamination of norbornene with piperidine forming N-norbornylpiperidine (75% yield at 150 °C) [28]. Similarly, the hydroamination of norbornadiene with morpholine in the presence of the catalyst system n-BuLi–KO-t-Bu yields 45% of the monohydroamination product [29].

As a model for the hydroamination of higher aliphatic olefins the reaction of 1-hexene with piperidine in the presence of n-BuLi and TMEDA was studied (Scheme 7). Selected results are summarized in Table 3. All reactions were carried out in ACE pressure tubes. The reaction without any solvent at 120 °C gave 5% conversion and 4% total amine yield with a linear to branched-ratio of 1:3. In the presence of toluene as solvent a similar yield is obtained (Table 3, entry 2). Other tested polar and non-polar ether solvents did not work at all.

Further optimization of this reaction applying different temperatures was carried out in toluene as solvent (Table 3, entries 6–9). All reactions were performed in the presence of 20 mol% n-BuLi and 20 mol% TMEDA for 20 h with a 1:2 piperidine to 1-hexene ratio. In general the branched amine is obtained as major product (linear/branched = ~1:4). The best result of the corresponding amines is obtained at 130 °C (10% yield). Although this yield is not useful for preparative applications to the best of our knowledge we do not know any higher amination yield for this reaction. At higher temperatures catalyst deactivation and isomerization of 1-hexene are

problematic. It is worth mentioning that further variation of reaction conditions as well as additions of ligands and additional transition metal catalysts did not lead to better results.

## 3. Experimental

### 3.1. General information

Solvents were dried according to literature [30]. All reactions were carried out under an argon atmosphere. Starting materials were used as received from Aldrich, Fluka, Acros and Strem and unless otherwise noted were used without further purification. Amines were distilled from $CaH_2$. Alkenes were degassed, flushed with argon and stored over molecular sieves (4 Å). Absolute solvents were purchased from Fluka®. GC analyses were performed on a HP® 6890 equipped with a HP-5 capillary column (5% phenylmethylsiloxane, $l = 30$ m, $d = 250$ μm, $d_{film} = 0.25$ μm) and an FID detector. Quantitative GC analyses are referenced to internal standard n-octane or hexadecane. MS data were obtained on AMD 402/3 of AMD Intectra®. Electron impact spectra (EI) were recorded at 70 eV, chemical ionization (CI) was with iso-butane. GC–MS spectra were recorded on an HP 5890 with mass-selective HP 5989A detector (double focusing sector field mass spectrometer). $^1H$ and $^{13}C$ NMR data were recorded on a Bruker® ARX 400 with QNP probe head ($^1H$, 400.13 MHz; $^{13}C$, 100.61 MHz) at 25 °C. Resonances are reported in δ (ppm) relative to $CDCl_3$. Deuteriated $^{13}C$ NMR data were recorded on a Bruker® ARX 500 with QNP probe head ($^{13}C$, 125.77 MHz) at 25 °C. $^7Li$ NMR data were recorded on a Bruker® ARX 500 with QNP probe head ($^7Li$, 194.36 MHz) at 25 °C. Coupling constants $J$ are reported in

Table 3
Effect of solvent

| Entry | Solvent (ml) | n-BuLi (mol%) | TMEDA (mol%) | Temperature (°C) | Conversion (%) | Yield (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Branched amine | Linear amine |
| 1 | – | 20 | – | 120 | 5 | 3 | 1 |
| 2 | Toluene | 20 | 20 | 120 | 8 | 4 | 1 |
| 3 | THF | 20 | – | 80 | 1 | – | – |
| 4 | Diethyl ether | 20 | – | 80 | – | – | – |
| 5 | MTBE | 20 | – | 80 | – | – | – |
| 6 | Toluene | 20 | 20 | 80 | 3 | 2 | 1 |
| 7 | Toluene | 20 | 20 | 120 | 8 | 4 | 1 |
| 8 | Toluene | 20 | 20 | 130 | 15 | 8 | 2 |
| 9 | Toluene | 20 | 20 | 160 | 5 | 4 | 1 |

Reaction condition: 5 mmol 1-hexene, 2.5 mmol piperidine, 20 h, 100 μl n-octane GC standard.

Hz. The following abbreviations were used to specify multiplicity, shape, and other properties: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet; br, broad. Melting points (mp) of the solid compounds were recorded on a Leica Galen III on the glass slide and are uncorrected.

### 3.2. Reaction equipment

For standard pressurized reaction (ethylene), 25 and 100 ml mini bench top reactor of the 4560 series from Parr Instrument® were used [31]. The removable head is fitted with a PTFE gasket that is sealed with six cap screws in a split-ring cover clamp. The reactor is equipped with a magnetically driven stirrer with a variable speed motor, an external electric header, three safety check valves, 3000 psi gauge and safety rupture disk, a temperature sensor, and a PID controller with pressure and temperature display module. Reactions with air-sensitive compounds were performed using standard Schlenk techniques. For hydroamination of higher olefins described below, threaded ACE® pressure tubes (Aldrich) were used unless otherwise noted.

### 3.3. General procedure for base-catalyzed hydroamination of ethylene (GP I)

Hydroamination experiments were carried out in a Parr stainless steal reactor (100 or 25 ml). All above described reactions involved the use of very reactive and pyrophoric alkali metals and alkylamides, and were thus conducted in the strict absences of air and moisture. In a typical experiment, the reactor was charged with LiNEt$_2$ (2.5 mol%), diethylamine (0.029 mol), TMEDA (5 mol%), $n$-octane GC standard (0.5 ml), toluene (15 ml) under argon atmosphere. The reactor was pressurized with ethylene (40 bar) and the reaction was carried out at 80 °C for 12 h. After reaction, the reactor is cooled to room temperature and depressurized. The reaction mixture was transferred to a Schlenk flask under argon atmosphere, and then quenched by dry methanol (2 ml). Aliquots were taken from the reaction mixture and subjected to GC analysis for determination of conversions and yield. The products were identified by comparison with authentic samples by GC, furthermore products were confirmed by GC–MS.

### 3.4. Synthesis of diamine ligands: general procedure for the permethylation of amino groups by the Eschweiler–Clarck reaction (GP II) [32]

A solution of the diamine (1 mmol), formaldehyde (37% aqueous solution, 2.5-fold excess based on the number of methyl group produced), and formic acid (10 mmol) was heated overnight at 100 °C. The reaction mixture is cooled, concentrated by rotary evaporation, made basic with NaOH (2 N solution), and extracted with CHCl$_3$ (3× 20 ml). The combined organic layer were washed with brine and dried

over Na$_2$SO$_4$. Evaporation and distillation from sodium yielded the *N,N,N′,N′*-tetramethyldiamines.

#### 3.4.1. N,N,N′,N′-tetramethyl-1,2-propanediamine (1)

From propane-1,2-diamine, formaldehyde and formic acid according to Ref. [32].

#### 3.4.2. N,N,N′,N′-tetramethyl-1,2-diamino-2-methylpropane (2)

From 2-methylpropane-1,2-diamine, formaldehyde and formic acid according to Ref. [32].

#### 3.4.3. Cis-N,N,N′,N′-tetramethyl-cyclohexane-1,2-diamine (3)

From *cis*-cyclohexane-1,2-diamine, formaldehyde and formic acid according to Ref. [32].

#### 3.4.4. Trans-N,N,N′,N′-tetramethyl-cyclohexane-1,2-diamine (4)

From *trans*-cyclohexane-1,2 diamine, formaldehyde and formic acid according to Ref. [32].

#### 3.4.5. N,N,N′,N′-tetramethyl-benzene-1,2-diamine [33] (5)

From benzene-1,2-diamine, MeI and Na$_2$CO$_3$ according to Ref. [33].

#### 3.4.6. (1S,2S)-(+)-N,N,N′,N′-tetramethyl-diphenylethane-1,2-diamine [34] (6)

According to GP II (1*S*,2*S*)-(−)-diphenylethylendiamine (30 mmol), formaldehyde (300 mmol), formic acid (300 mol) were employed.

Molecular formula: C$_8$H$_{20}$N$_2$, MW: 268.40 g/mol, mp: 81 °C, isolated yield: 80%, off white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.12–7.07 (m, 4H, 5-H); 7.04–6.99 (m, 2H, 6-H), 6.99–6.95 (m, 4H, 4-H), 4.22 (s, 2H, 1-H); 2.23 (s, 12H, 2-H). $^{13}$C NMR (100.61 MHz, CDCl$_3$): $\delta$ = 138.2 (C-3), 127.8, 127.8 (C-4, C-5), 127.6 (C-6), 87.7 (C-1), 57.2 (C-2).

### 3.5. General procedure for base-catalyzed hydroamination of higher olefins (GP III)

Hydroamination experiments for higher olefins were carried out in threaded ACE® pressure tubes (Aldrich). All described reactions involved the use of very reactive and pyrophoric alkali metals and alkylamides, and were thus conducted in the strict absence of air and moisture. In a typical experiment, a pressure tube was charged with *n*-BuLi (20 mol%), piperidine (2.5 mmol), 1-hexene (5.0 mmol), TMEDA (40 mol%), *n*-octane GC standard (100 µl), toluene (5 ml) under argon atmosphere. The pressure tube is closed with Teflon cap and heated it in an oil bath at 130 °C for 20 h. After reaction the pressure tube is cooled to room temperature and the reaction mixture is quenched by dry methanol (1 ml) and analyzed by gas chromatography. The products

were identified by comparison with authentic samples by GC, furthermore products were confirmed by GC–MS.

## 4. Conclusion

In summary, the base-catalyzed hydroamination reaction of ethylene with diethylamine to give triethylamine was investigated. In agreement with previous data it has been shown that TMEDA as additive increases the rate of reaction and lead to excellent product yield (up to 99%) under ambient conditions. For the first time a similar effect was observed with a tridentate ligand (PMDTA). Model studies suggest that catalyst deactivation is not a result from TMEDA degradation. Potentially formed LiH is not a catalyst or mediator for the hydroamination reaction under ambient conditions. The catalytic hydroamination of *non*-activated 1-hexene is in principle possible, but yield of amines (up to 10%) and selectivity are unsatisfactory for further applications.

## Acknowledgements

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