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# Reactions of diethylamine and ethylene catalyzed by Pt<sup>II</sup> or Pt<sup>0</sup>: transalkylation vs. hydroamination

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**Keywords:** Platinum / Ethylene hydroamination / Amine transalkylation / DFT calculations / Aqueous catalysis

PtBr<sub>2</sub>/*n*Bu<sub>4</sub>PBr (without solvent) or K<sub>2</sub>PtCl<sub>4</sub>/NaBr (in water), previously shown to efficiently catalyze the hydroamination of ethylene by aniline, are poor catalysts for the hydroamination of ethylene by diethylamine. A DFT study on the hydroamination mechanism indicates that the energetic span of the C<sub>2</sub>H<sub>4</sub>/Et<sub>2</sub>NH catalytic cycle is close to that of the C<sub>2</sub>H<sub>4</sub>/PhNH<sub>2</sub> cycle. The poor

performance is attributed to rapid catalyst degradation with reduction to metallic platinum. The produced Pt<sup>0</sup>, on the other hand, catalyzes a transalkylation process, partially transforming Et<sub>2</sub>NH into Et<sub>3</sub>N, EtNH<sub>2</sub>, and NH<sub>3</sub>. The latter process is inhibited by C<sub>2</sub>H<sub>4</sub>. Mechanistic considerations on the Pt<sup>0</sup>-catalyzed transalkylation process are presented.

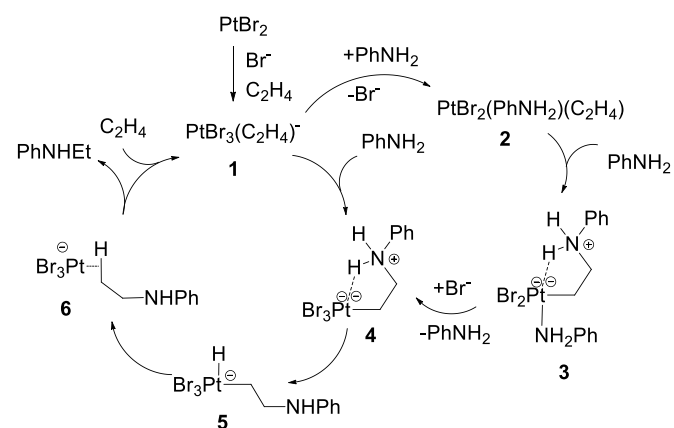
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## Introduction

Amines are important compounds for the bulk and fine chemical industries. There is great current interest in optimizing the hydroamination reaction, an atom economical process that results in the N-H addition of ammonia or an amine to an unsaturated substrate to produce a higher amine.<sup>[1]</sup> Amongst all the hydroamination reactions, the most difficult one is the intermolecular version with non-activated olefins and solutions based on transition metal catalysis are actively pursued.<sup>[1-3]</sup> With regard to industrial applications, short chain aliphatic olefins and especially ethylene constitute the most attractive starting materials. In the last 6 years a number of papers have appeared on the hydroamination of ethylene and other α-olefins catalysed in particular by Pt-based systems. These include the addition of substituted anilines to ethylene<sup>[4]</sup> and 1-hexene<sup>[5]</sup> catalyzed by PtBr<sub>2</sub>/*n*-Bu<sub>4</sub>PBr (**I**), including our recent extension to aqueous media (PtBr<sub>2</sub>/NaBr<sub>(aq)</sub>, **I'**),<sup>[6]</sup> the addition of carboxamides to RHC=CH<sub>2</sub> (R = H, Me) catalyzed by [PtCl<sub>2</sub>(H<sub>2</sub>C=CH<sub>2</sub>)<sub>2</sub>]/PPh<sub>3</sub> (**II**)<sup>[7]</sup> and that of sulfonamides or anilines to more strained olefins catalyzed by (COD)Pt(OTf)<sub>2</sub> (**III**).<sup>[8]</sup> For each type of catalyst the turnover number (TON) or product yield was shown to increase as the amine basicity decreases and no activity was found when the conjugate acid of the amine has a pK<sub>a</sub> value above a certain cut-off value. Although comparisons are complicated by the different conditions used for each of these three catalytic systems, **I** appears the most active one, allowing ethylene hydroamination with 4-MeOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> – the most basic amine for which an activity has been reported for a Pt-based catalyst.<sup>[4]</sup> Attempts to probe more basic amines for system **I** were not performed, probably because of expectations on the basis of the observed pK<sub>a</sub> trend. Attempts to use more basic secondary amines were described only for system **II**, with negative results

when using secondary amines.<sup>[7]</sup> The catalytic system **III** was shown to be inactive already when using aniline (pK<sub>a</sub> = 4.63).<sup>[8]</sup>

In recent work, we have explored the details of the PtBr<sub>2</sub>/Br<sup>-</sup> catalyzed addition of aniline to ethylene at the experimental and computational levels, by isolating a number of low-energy intermediates and off-loop species and studying their solution equilibria,<sup>[9]</sup> and by carrying out a computational investigation of the catalytic cycle,<sup>[10-11]</sup> the main features of which are summarized in Scheme 1. The nucleophilic addition to the coordinated and activated ethylene substrate is more facile for the neutral compound *trans*-[PtBr<sub>2</sub>(NHEt<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>)] (**2**), and also for the bis(ethylene) complex *trans*-[PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (not shown in Scheme 1), than for the anionic resting state [PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> (**1**), but the only zwitterionic intermediate capable to complete the catalytic cycle is [Br<sub>3</sub>Pt<sup>(-)</sup>(CH<sub>2</sub>CH<sub>2</sub>N<sup>(+)</sup>H<sub>2</sub>Ph)] (**4**), obtainable directly from **1**.



Scheme 1. Mechanism of the PtBr<sub>2</sub>/Br<sup>-</sup> catalyzed hydroamination of ethylene by aniline.

Since the zwitterionic intermediates invoked for this system, such as **3** and **4**, are too high in energy to be experimentally observed, we have carried out model investigations using the more basic and nucleophilic Et<sub>2</sub>NH, obtaining direct evidence for the generation of the zwitterionic adduct [(Et<sub>2</sub>HN)Br<sub>2</sub>Pt<sup>(-)</sup>(CH<sub>2</sub>CH<sub>2</sub>N<sup>(+)</sup>HEt<sub>2</sub>)].<sup>[12]</sup> An excess amount of NHEt<sub>2</sub> was shown to promote an equilibrium

deprotonation of this species, yielding the aminoalkyl derivative  $[(\text{Et}_2\text{N})\text{Br}_2\text{PtCH}_2\text{CH}_2\text{NEt}_2]^-$ , which then decomposes by giving rise to the deposition of  $\text{Pt}^0$  and to the generation of other uncharacterized species. This behaviour is similar to that of other complexes obtained by addition of basic amines to Pt-coordinated olefins.<sup>[13-15]</sup> This observation suggests that the catalyst deactivation process is triggered by the deprotonation of the intermediate zwitterionic species and this hypothesis has been confirmed by new catalytic tests: the addition of strong bases (KOH,  $\text{NHEt}_2$ ,  $\text{NEt}_3$ , or DBU) to the catalytic medium completely suppresses the production of the  $\text{PhNHEt}$  product, while the  $\text{Pt}^{\text{II}}$  catalyst is completely converted into metallic platinum.<sup>[16]</sup>

In this report, we present two new principles. The first one, derived from a computational investigation on the catalytic cycle with  $\text{NHEt}_2$ , is that more basic amines are indeed kinetically competent to complete the hydroamination catalytic cycle. Hence, the lack of catalysis is not due to an intrinsic lower catalytic efficiency but must be attributed to the above mentioned catalyst decomposition triggered by deprotonation, which is more favourable for stronger bases. The second one, derived from further catalytic experiments, deals with the discovery of a competitive amine transalkylation process, which is catalyzed by  $\text{Pt}^0$  under the hydroamination conditions.

## Results and Discussion

### (a) Initial catalytic tests.

We first attempted the ethylene hydroamination by  $\text{HNEt}_2$  under the same conditions previously used for the hydroamination of ethylene by aniline ( $\text{PtBr}_2/n\text{Bu}_4\text{PBr}$  catalyst, **I**)<sup>[4]</sup> and also under our recent extension of this system to aqueous media ( $\text{K}_2\text{PtCl}_4/\text{NaBr}(\text{H}_2\text{O})$  catalyst, **I'**)<sup>[6]</sup> These experiments yielded triethylamine in only close to stoichiometric amounts, see Table 1 (runs 1 and 2), while the starting compound conversion was negligible according to NMR. Extensive deposition of metallic Pt, as also reported for the aniline addition experiments,<sup>[4-6]</sup> was observed at the end of the reaction. Surprisingly, ethylamine, the formal product of dehydroamination, was also observed as a co-product in non negligible amounts.

Table 1. Pt-catalyzed hydroamination of  $\text{C}_2\text{H}_4$  by  $\text{Et}_2\text{NH}$ .<sup>[a]</sup>

run	cat.	Product (TON)	Other products (TON)
1	<b>I</b>	$\text{Et}_3\text{N}$ (~1)	$\text{EtNH}_2$ (3)
2	<b>I'</b>	$\text{Et}_3\text{N}$ (~2)	$\text{EtNH}_2$ (5)

[a] Conditions:  $[\text{Pt}] = 0.3\%$  relative to amine;  $[\text{Br}]/\text{Pt} = 150$ ; 15 ml of  $\text{H}_2\text{O}$  (only for system **I'**); 25 bar  $\text{C}_2\text{H}_4$  at 298 K, 10 h, 150°C.

We shall now first address the catalytic cycle of ethylene hydroamination by  $\text{NHEt}_2$  through a computational investigation, before analyzing the reason for the formation of the  $\text{EtNH}_2$  co-product.

### (b) Computational investigation of the hydroamination mechanism with $\text{Et}_2\text{NH}$ .

The energetics of the ethylene hydroamination by  $\text{Et}_2\text{NH}$  were analyzed by DFT, according to the established mechanism for the addition of aniline (Scheme 1).<sup>[11]</sup> In order to directly compare the results of the two system, the calculations were carried out at the same level of theory (see computational details). The addition of

$\text{Et}_2\text{NH}$  to  $\text{C}_2\text{H}_4$  is exoergic by  $\Delta G^\circ_{298} = -3.7$  kcal/mol (cf. -6.0 for  $\text{PhNH}_2$  in the gas phase and  $\Delta G^\circ_{298}^{\text{CPCM}} = -6.1$  kcal/mol (cf. -8.0 for  $\text{PhNH}_2$ ) with inclusion of the solvent effect in aniline. The energetic details of the catalytic cycle are summarized in Figure 1. Beyond the generation of the zwitterion  $[(\text{Et}_2\text{HN})\text{Br}_2\text{Pt}^{(-)}\text{CH}_2\text{CH}_2\text{N}^{(+)}\text{HEt}_2]$  (**3'**), which was also observed experimentally as already mentioned above,<sup>[12]</sup> ligand exchange occurs to yield the tribromido derivative  $[\text{Pt}^{(2-)}\text{Br}_3(\text{CH}_2\text{CH}_2\text{N}^{(+)}\text{HEt}_2)]^-$ , **4'**. Contrary to the  $\text{PhNH}_2/\text{C}_2\text{H}_4$  cycle, a local minimum could not be located for a 5-coordinate  $\text{Pt}^{\text{IV}}$  hydride complex  $[\text{PtHBr}_3(\text{CH}_2\text{CH}_2\text{NEt}_2)]^-$  (**5'**) derived from **4'** by intramolecular proton transfer. Every attempt to optimize such a complex led back to **4'**, consistent with the greater basicity of the N atom relative to the aniline system. However, a transition state was located for transfer of the ammonium proton to the carbon atom, directly transforming **4'** into the  $\sigma$ -complex  $[\text{PtBr}_3(\eta^2\text{-H-CH}_2\text{CH}_2\text{NEt}_2)]^-$ , **6'**, from which the  $\text{Et}_3\text{N}$  product may be released by exchange with  $\text{C}_2\text{H}_4$  to start a new cycle. This proton transfer is however assisted by the Pt atom, as shown by the relative short  $\text{Pt}\cdots\text{H}$  contact in the transition state (Figure 1).

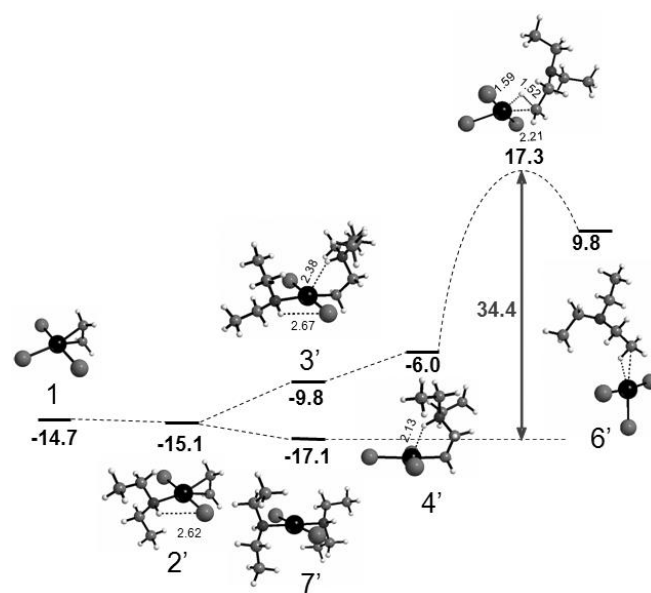


Figure 1.  $\Delta G^{\text{CPCM}}$  (aniline) profile in kcal mol<sup>-1</sup> for the  $\text{C}_2\text{H}_4$  hydroamination by  $\text{Et}_2\text{NH}$  on the  $\text{PtBr}_2/\text{Br}^-$  catalytic system at 298.15 K.

The overall barrier between the resting state and the rate-determining transition state<sup>[17]</sup> (34.4 kcal mol<sup>-1</sup>), is not significantly higher than that calculated for the corresponding  $\text{PhNH}_2/\text{C}_2\text{H}_4$  cycle (33.8 kcal mol<sup>-1</sup>).<sup>[11]</sup>  $\text{Et}_2\text{NH}$  coordination to  $\text{Pt}^{\text{II}}$  is more favorable than  $\text{PhNH}_2$  coordination, thus the resting state of the catalytic cycle in this case, according to the computational study, is the diamine complex *trans*- $\text{PtBr}_2(\text{NHEt}_2)_2$ , **7'**, rather than complex **1**. Complex *trans*- $\text{PtBr}_2(\text{PhNH}_2)_2$ , **7**, on the other hand, was calculated as 3.7 kcal mol<sup>-1</sup> less stable than **1**.<sup>[11]</sup> On the basis of this study, systems **I** and **I'** would be predicted as equally competent to catalyze the addition of  $\text{Et}_2\text{NH}$  and  $\text{PhNH}_2$  to  $\text{C}_2\text{H}_4$ . Hence, the reason for their poorer performance for  $\text{NHEt}_2$  must be attributed to the catalyst decomposition, which is related to the zwitterion deprotonation by the excess base, as confirmed by our recent study.<sup>[16]</sup> Note that the protonation transfer step is endoergic on the  $\Delta G^{\text{CPCM}}$  scale for both systems according to the previously published studies, but less so for the  $\text{NHEt}_2$  system (+15.3 kcal/mol for **3'**+ $\text{NHEt}_2$ )<sup>[12]</sup> than for the  $\text{PhNH}_2$  system (+19.8 kcal/mol for **3**+ $\text{PhNH}_2$ ).<sup>[11]</sup> The catalyst deactivation is then probably driven by the irreversibility of the subsequent steps leading to the metal reduction.

### (c) Catalysis of transalkylation processes.

Based on these experimental and theoretical premises, we wondered whether catalytic hydroamination with Et<sub>2</sub>NH could be induced through protection of the zwitterionic complex by the addition of acid. Indeed, replacing H<sub>2</sub>O/NaBr by HBr<sub>aq</sub> gave marginally better results, with TON = 4 for Et<sub>3</sub>N, see run 3 (Table 2). However, the formation of EtNH<sub>2</sub> (ca. 18 cycles) was also observed. In addition to Et<sub>3</sub>N, EtNH<sub>2</sub>, and residual Et<sub>2</sub>NH, the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR monitoring also revealed the formation of a minor amount of EtOH (ca. 1 cycle).

Table 2. Additional reactions between C<sub>2</sub>H<sub>4</sub> and Et<sub>2</sub>NH.<sup>[a]</sup>

run	cat.	C <sub>2</sub> H <sub>4</sub> (bars)	Et <sub>2</sub> NH (% conv)	Et <sub>3</sub> N (TON)	EtNH <sub>2</sub> (TON)
3 <sup>[b]</sup>	K <sub>2</sub> PtCl <sub>4</sub>	25	7	~4	~18
4 <sup>[c]</sup>	-	25	0	0	0
5	K <sub>2</sub> PtCl <sub>4</sub>	25	~0	~1	0
6 <sup>[d]</sup>	K <sub>2</sub> PtCl <sub>4</sub>	-	52	92	23
7	Pt <sup>0</sup>	-	45	76	18
8	Pt <sup>0</sup>	25	~0	~1	0

[a] The experimental conditions are identical to those in Table 1, except for the nature and amount of catalyst, olefin and additive as indicated. [b] With 150 eq of HBr<sub>aq</sub> (48%) relative to Pt; a minor amounts of aromatic products (< 1%, resonances in the δ 110-150 range) and EtOH (ca. 1%, resonances at 17.7 and 57.2) were visible by <sup>13</sup>C{<sup>1</sup>H} NMR. [c] Same conditions as for run 3, without catalyst. [d] Minor amounts (< 2 %) of other products were also detected by <sup>13</sup>C{<sup>1</sup>H} NMR in the aliphatic region.

The next experiments were run with simplified catalytic systems. Run 4 was carried out in the presence of HBr (same conditions as run 3) without the Pt compound. The result demonstrates the absence of any acid-induced transformation. There are reports warning about the possible action of acids as hydroamination catalysts,<sup>[18-19]</sup> but they all concern less challenging processes such as intramolecular hydroaminations or the intermolecular addition across activated C=C bonds. Furthermore, the conditions employed here are not really acidic, since the amount of acid is a fraction of that of the amine (150 equiv. vs. 350 equiv), hence the reaction mixture contains a Et<sub>2</sub>NH<sub>2</sub><sup>+</sup>/Et<sub>2</sub>NH buffer. Run 5 was carried out in the absence of acid. These conditions are equivalent to those of run 2 (Table 1), except for the absence of NaBr. The results are also comparable to those of run 2. In fact, an even lower activity was recorded, in agreement with the known activating role of the bromide ions for this catalytic system.<sup>[4, 6]</sup> Further simplification of the system by running the reaction in the absence of ethylene (run 6), unexpectedly gave a large conversion into Et<sub>3</sub>N and EtNH<sub>2</sub>. Therefore, no external ethylene is necessary to generate the observed products, proving that these are not resulting from a hydroamination or dehydroamination process. The observed transformation can be rationalized as a simple transalkylation process. Furthermore, comparison of runs 5 and 6 demonstrates that the presence of ethylene inhibits this process.

On the basis of this new evidence, we wondered whether ammonia may also be formed by further transalkylation from the EtNH<sub>2</sub> primary product. The <sup>14</sup>N or <sup>15</sup>N analyses of the solution obtained from run 3 did not allow detection of any NH<sub>3</sub>. However, this result may be a consequence of the small conversion coupled with small sensitivity (for <sup>15</sup>N) or broad lines (for <sup>14</sup>N). An additional experiment was carried out starting from EtNH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> rather than from a Et<sub>2</sub>NH/HBr mixture. K<sub>2</sub>PtCl<sub>4</sub> was used as the catalyst, without the presence of ethylene, using the standard reaction time and temperature. The final mixture indeed revealed the formation of NH<sub>3</sub> (NH<sub>4</sub><sup>+</sup>) with a resonance at δ -357.6 in the <sup>14</sup>N

NMR spectrum, see Figure 2. The spectrum also exhibited a strong resonance at δ -344.4 for the residual EtNH<sub>2</sub>/EtNH<sub>3</sub><sup>+</sup>, and a weak one at δ -329.1 for Et<sub>2</sub>NH/Et<sub>2</sub>NH<sub>2</sub><sup>+</sup>. The identity of all these resonances was verified by comparison with genuine samples. A resonance for Et<sub>3</sub>N/Et<sub>3</sub>NH<sup>+</sup>, which should appear around δ -325, is not visible, once again because of the small conversion for this transalkylation process.

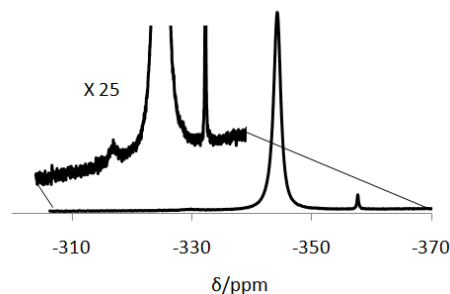


Figure 2. <sup>14</sup>N NMR spectrum of the solution obtained from EtNH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> in D<sub>2</sub>O, after 10 h at 150°C in the presence of K<sub>2</sub>PtCl<sub>4</sub> (0.3 %).

Transalkylation reactions for amine substrates have already been shown to occur under Pd<sup>0</sup> catalysis.<sup>[20-25]</sup> This intrigued us whether the same phenomenon may also occur in the presence of Pt<sup>0</sup>, because metallic platinum is generated in situ by decomposition of the Pt<sup>II</sup> system as shown above. Platinum-catalyzed amine transalkylation has previously been reported only by Brunet *et al.*, to the best of our knowledge, as a side process during the PtBr<sub>2</sub>-catalyzed heterocyclization of aniline to quinolines in the presence of Bu<sub>3</sub>N, but the authors could not establish whether the process is catalyzed by Pt<sup>II</sup> or by the Pt<sup>0</sup> formed during the reaction.<sup>[26]</sup> Indeed, using Pt<sup>0</sup> in place of K<sub>2</sub>PtCl<sub>4</sub> under otherwise identical conditions gave approximately the same conversion and product distribution of the transalkylation products (run 7, Table 2). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the final reaction mixture is shown in Figure 3. Once again, the process is inhibited by ethylene (run 8).

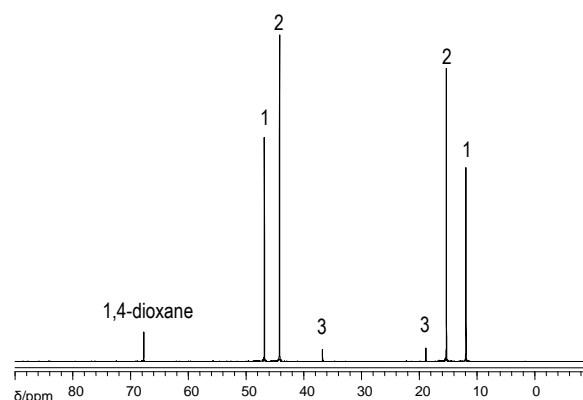


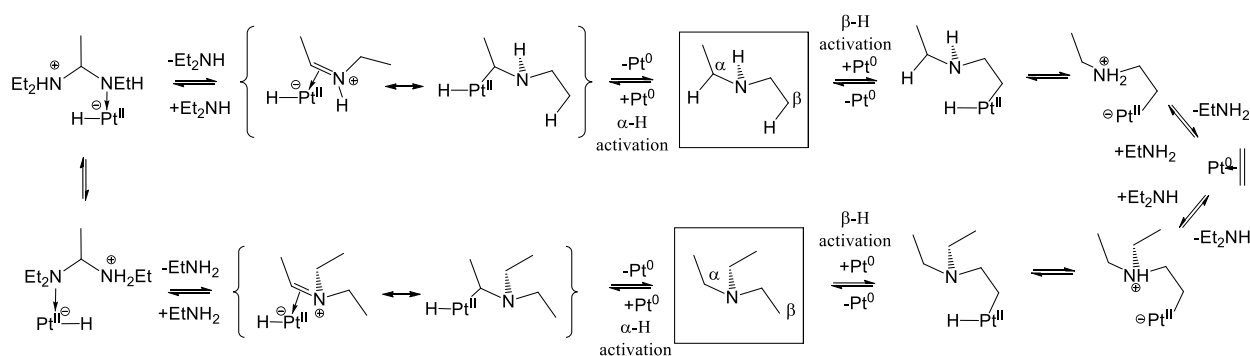
Figure 3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the final reaction mixture for run 7 (Table 2). 1: Et<sub>3</sub>N, 2: Et<sub>2</sub>NH, 3: EtNH<sub>2</sub> (internal standard: 1,4-dioxane, 1.3 mmol).

The mechanism proposed by Murahashi for the Pd<sup>0</sup>-catalysed transalkylation process involves metal insertion into the α-CH bond with formation of a hydrido iminium intermediate.<sup>[21]</sup> This pathway is illustrated on the left hand side of Scheme 2 for the related Pt<sup>0</sup> catalyst. The iminium ligand in this intermediate is then attacked by

a second amine molecule to generate a coordinated aminoallylammonium ligand, followed by exchange of the proton and the platinum centres and reversal of all steps. Following our recent computational investigation,<sup>[10-11, 16]</sup> however, we can also imagine an alternative pathway involving the reverse steps of the hydroamination reaction, starting with insertion of Pt<sup>0</sup> into a  $\beta$ -CH bond and leading to a Pt<sup>0</sup>-olefin intermediate, followed by hydroamination by a second amine molecule. This pathway is illustrated on the right hand side of Scheme 2. Note, however, that the hydroamination process was shown to occur via Pt<sup>II</sup>/Pt<sup>IV</sup> complexes, whereas in this case the Pt<sup>0</sup>/Pt<sup>II</sup> couple would operate.

To test the possibility of the dehydroamination/hydroamination mechanism, we carried out two additional catalytic experiments, using only triethylamine as starting compound, under conditions identical to those of runs 7 and 8 of Table 2. Clearly, the  $\alpha$ -CH bond pathway cannot lead to any reaction, whereas the  $\beta$ -CH bond

pathway may result in the generation of Et<sub>2</sub>NH, with release of ethylene (dehydroamination). Under the conditions of run 8, namely in the presence of ethylene pressure, a minor but non negligible amount (ca. 1 cycle) of diethylamine was produced, whereas 5 cycles of the product were observed under the conditions of run 7 (no added ethylene). While these experiments do not exclude that the  $\alpha$ -CH bond activation mechanism is the main pathway when starting from diethylamine, they confirm that the  $\beta$ -CH bond activation mechanism is also taking place under these conditions. The inhibiting effect of the ethylene pressure may be rationalized by a saturation effect of the olefin coordination to the Pt<sup>0</sup> surface, blocking or retarding access of the platinum atoms by the C-H bonds. This rationalization is compatible, however, with both mechanisms. Additional investigations would be necessary to confirm the presence of an  $\alpha$ -CH bond pathway for this system, which are however outside of the scope of the present work.



Scheme 2. Two alternative pathways for the Pt<sup>0</sup>-catalyzed transalkylation reaction.

## Conclusions

The present study has revealed that the catalytic systems **I** and **I'**, are not efficiently adding the N-H bond of Et<sub>2</sub>NH across the C=C bond of ethylene, although a computational investigation suggests that they should be as competent to catalyze this transformation as the addition of the aniline N-H bond. The reason is attributed to rapid catalyst degradation with reduction to metallic platinum, favoured by the deprotonation of the key zwitterionic intermediate (**3'**), which was shown to form readily by an independent recent study.<sup>[12]</sup> This deprotonation is favoured by the high basicity of Et<sub>2</sub>NH.

Parallel studies have also shown that the produced metallic platinum is responsible for a transmetallation reaction, equilibrating Et<sub>2</sub>NH with Et<sub>3</sub>N, EtNH<sub>2</sub>, and even NH<sub>3</sub>. This appears to be the first report of Pt<sup>0</sup>-catalyzed amine transalkylation, a process that has previously been well established for Pd<sup>0</sup>. This process is inhibited by the olefin, presumably because of a surface saturation effect, blocking its access to the substrate C-H bonds. Among two different mechanistic pathways involving respectively the activation of the amine  $\alpha$ -CH and  $\beta$ -CH bonds, the latter was shown to be present by a control experiment, although the former could also play a role as previously suggested for the Pd<sup>0</sup>-catalyzed process.<sup>[21]</sup>

## Experimental Section

**General.** All solvents were of HPLC grade and were used as received. HNEt<sub>2</sub> (Fluka) was distilled and kept under argon in the dark. PtBr<sub>2</sub> (Alfa Aesar), K<sub>2</sub>PtCl<sub>4</sub> (Alfa Aesar) and nBu<sub>4</sub>PBr (Acros Organics) were used as received. Ethylene (purity  $\geq$  99.5%) was purchased from Air Liquide.

**Instrumentation.** NMR investigations were carried out on Bruker AV400 spectrometer at 298 K operating at 400.1 MHz (<sup>1</sup>H), 100.6 MHz (<sup>13</sup>C), 28.9 MHz (<sup>14</sup>N). The spectra were calibrated with the residual solvent resonance relative to TMS (<sup>1</sup>H, <sup>13</sup>C) and MeNO<sub>2</sub> (<sup>14</sup>N). D<sub>2</sub>O was used for lock.

**Typical procedures for the attempted hydroamination of ethylene by Et<sub>2</sub>NH.** (a) **With PtBr<sub>2</sub>/nBu<sub>4</sub>PBr.** The autoclave was charged with PtBr<sub>2</sub> (46 mg, 0.13 mmol) and nBu<sub>4</sub>PBr (440 mg, 1.3 mmol, 10 equiv), closed, and submitted to argon/vacuum cycles. Et<sub>2</sub>NH (4.7 mL, 45.5 mmol, 350 equiv) was syringed into the autoclave. Finally, the ethylene pressure was adjusted to 25 bar (ca. 100 mmol, 333 equiv) at RT. The temperature was then raised to 150°C. After 10 h, the autoclave was allowed to cool to room temperature and then slowly vented. An external standard (EtOH or 1,4-dioxane, 1.3 mmol) was added to the mixture. The solution was then analyzed by NMR spectroscopy using traces of CDCl<sub>3</sub> for instrument lock.

(b) **with K<sub>2</sub>PtCl<sub>4</sub>/HBr.** The autoclave was charged with K<sub>2</sub>PtCl<sub>4</sub> (54 mg, 0.13 mmol), closed, and submitted to argon/vacuum cycles. Water (or D<sub>2</sub>O), then Et<sub>2</sub>NH (4.7 mL, 45.5 mmol, 350 equiv), then aqueous HBr (gently) if necessary, were syringed into the autoclave and the ethylene pressure was adjusted to 25 bar (ca. 100 mmol, 333 equiv) at RT. The remainder of the experiment was carried out as above, except that D<sub>2</sub>O was used for the NMR lock. The amount of D<sub>2</sub>O was the minimum needed to homogenize the system.

**Typical procedures for the Et<sub>2</sub>NH transalkylation.** The autoclave was charged with K<sub>2</sub>PtCl<sub>4</sub> or Pt black (0.13 mmol), closed, and submitted to argon/vacuum cycles. Et<sub>2</sub>NH or Et<sub>3</sub>N (45.5 mmol, 350 equiv) was then added and the ethylene pressure (if needed) was adjusted to 25 bar (ca. 100

mmol, 333 equiv) at RT. The remainder of the experiment was carried out as above. A minor amount of D<sub>2</sub>O was added for the NMR lock.

**Computational Details.** The DFT calculations were carried out using the same methodology described in detail in our recent studies of the C<sub>2</sub>H<sub>4</sub>/PhNH<sub>2</sub> reaction,<sup>[10-11]</sup> namely using the B3LYP functional and the standard 6-31+G\* basis set for all atoms except Pt, for which the LANL2TZ(f) basis was used.<sup>[27]</sup> The calculations included a frequency analysis for all minima and transition states and solvation effects by single-point C-PCM<sup>[28-29]</sup> corrections on the gas-phase optimized geometries, from which the thermodynamic  $\Delta G^{\text{CPCM}}$  values were derived. All new optimized geometries are available in the SI.

**Supporting Information** (see footnote on the first page of this article): List of optimized Cartesian coordinates for all new geometries (2 pages).

## Acknowledgments

We are grateful to the CNRS (Centre National de la Recherche Scientifique), the ANR (Agence Nationale de la Recherche, Grant No. NT09\_442499), the IUF (Institut Universitaire de France) for financial support, as well as the CINES (Centre Informatique National de l'Enseignement Supérieur) and the CICT (Centre Interuniversitaire de Calcul de Toulouse, project CALMIP) for granting free computational time. PD thanks the MENESR (Ministère de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche, France) for a Ph.D. fellowship.

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## Entry for the Table of Contents

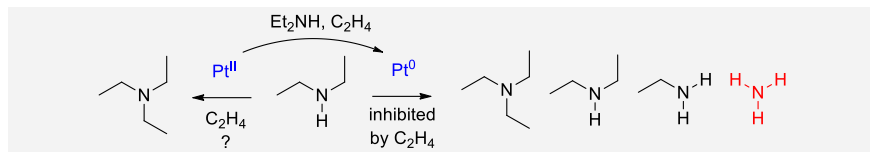
### Hydroamination vs. transalkylation

**Pavel A. Dub and Rinaldo Poli\***

..... Page No. – Page No.

Reactions of diethylamine and ethylene catalyzed by Pt<sup>II</sup> or Pt<sup>0</sup>: transalkylation vs. hydroamination

**Keywords:** Platinum / ethylene hydroamination / amine transalkylation / DFT calculations / aqueous catalysis



Pt<sup>II</sup> salts and Pt<sup>0</sup> promote different reactions for the amine/ethylene combination. Pt<sup>II</sup> is a catalyst for the

hydroamination process, whereas Pt<sup>0</sup> promotes transalkylation, a reaction which is inhibited by the olefin.

## Supporting Information

# Reactions of diethylamine and ethylene catalyzed by Pt<sup>II</sup> or Pt<sup>0</sup>: transalkylation vs. hydroamination.

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## SUPPORTING INFORMATION

Table S1. Cartesian coordinates for all new optimized structures.

<b>[trans-PtF<sub>2</sub>(HNEt<sub>2</sub>)] 6</b>				H	-3.841836000	0.600657000	1.369572000
SCF DONE: -5689.757768				H	-3.365738000	-0.110802000	2.915873000
				C	-3.002209000	0.159243000	1.917418000
				C	-2.464044000	-1.094874000	1.239493000
				H	-1.682458000	-1.557138000	1.847515000
				H	-3.265116000	-1.835589000	1.119337000
				Pt	0.066123000	0.027448000	-0.029007000
				Br	-0.761224000	2.381085000	-0.102415000
				Br	0.892481000	-2.328617000	0.037704000
				N	1.975072000	0.915211000	0.024775000
				H	1.729554000	1.845155000	0.380508000
				C	2.554710000	1.175992000	-1.338821000
				H	3.918729000	0.895746000	0.837516000
				C	2.977765000	0.344084000	0.977302000
H	-4.542268000	-0.729073000	-2.269058000				
H	-3.716283000	-2.181533000	-1.687123000				
H	-4.684750000	-1.193886000	-0.571183000				
C	-3.994261000	-1.153677000	-1.420202000				
H	-3.039300000	0.714621000	-0.818520000				
C	-2.762673000	-0.290150000	-1.139577000				
H	-2.163997000	-0.176913000	-2.047276000				
N	-1.838172000	-0.862951000	-0.109228000				
H	-1.576739000	-1.798488000	-0.437661000				
H	-2.227166000	0.922679000	2.021065000				



C	2.513747000	0.449389000	2.426003000
H	3.294263000	0.058542000	3.088709000
H	3.146009000	-0.697867000	0.702766000
H	2.318076000	1.490354000	2.713172000
H	1.601550000	-0.131995000	2.588342000
C	2.990007000	-0.071219000	-2.098985000
H	3.355632000	0.230925000	-3.087541000
H	3.802312000	-0.604244000	-1.593790000
H	2.158509000	-0.767937000	-2.231290000
H	1.783057000	1.716163000	-1.893261000
H	3.409850000	1.854795000	-1.204839000

**[PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>NHEt<sub>2</sub>)]<sup>-</sup> 4**

SCF DONE: -8126.038077

H	-2.104365000	3.182480000	2.643258000
H	-0.985991000	1.798682000	2.580794000
C	-1.696418000	2.394545000	1.998264000
H	-3.329584000	1.008874000	2.319265000
C	-2.844775000	1.527831000	1.485591000
H	-3.608691000	2.126870000	0.977219000
N	-2.378493000	0.478445000	0.517194000
H	-3.256952000	0.941364000	-1.364721000
H	-1.926917000	2.010390000	-0.848656000
H	-1.337036000	0.244029000	0.690546000
C	-1.181638000	0.151700000	-1.649473000
H	-0.879370000	0.722426000	-2.537086000
H	-1.582681000	-0.812310000	-1.988609000
H	-2.578626000	-1.541854000	0.016566000
C	-3.109046000	-0.828566000	0.652034000
H	-2.949035000	-1.154960000	1.684873000
C	-4.598830000	-0.760950000	0.328873000
H	-5.136338000	-0.042029000	0.959191000
H	-5.036263000	-1.750058000	0.508132000
H	-4.784598000	-0.507012000	-0.719644000
Br	-0.083000000	-2.573941000	-0.273127000
Pt	0.458235000	-0.128152000	-0.397091000
Br	0.962242000	2.315335000	-0.719374000
H	-1.127794000	2.855983000	1.185313000
C	-2.252005000	0.970351000	-0.923565000
Br	2.424404000	-0.403268000	1.275244000

**[PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>NHEt<sub>2</sub>)]<sup>-</sup> TS**

SCF DONE: -8126.017479

H	4.431289000	-2.828971000	1.824518000
H	3.042498000	-1.847482000	2.365568000
C	3.632913000	-2.150041000	1.494035000
H	4.867582000	-0.387816000	1.532235000
C	4.236714000	-0.919237000	0.807997000
H	4.911166000	-1.242616000	-0.010943000
N	3.220563000	0.021285000	0.331336000
H	3.265835000	-0.234385000	-1.794269000
H	2.401956000	-1.468194000	-0.865599000
H	0.918916000	0.174516000	0.254494000
C	1.269178000	0.306892000	-1.223532000
H	0.849623000	-0.122226000	-2.137791000
H	1.374329000	1.385166000	-1.347657000
H	2.736519000	2.046939000	0.218158000
C	3.623238000	1.429400000	0.395370000
H	3.924821000	1.629959000	1.431878000
C	4.755759000	1.871992000	-0.553414000
H	5.679058000	1.305058000	-0.377355000
H	4.979443000	2.935297000	-0.395518000

H	4.479459000	1.746570000	-1.607079000
Br	-0.768344000	2.527908000	0.139985000
Pt	-0.620385000	0.041713000	-0.113132000
Br	-0.354392000	-2.440329000	-0.371164000
H	2.966313000	-2.707741000	0.828742000
C	2.594798000	-0.394482000	-0.924018000
Br	-3.038931000	-0.220545000	0.419948000

**trans-[PtF<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PhNH<sub>2</sub>)]<sup>-</sup> 5**

SCF DONE: -685.150356

78	-1.003000000	0.000556000	-0.094129000
9	-0.957709000	1.975517000	-0.142570000
7	0.722778000	0.013187000	-1.330241000
9	-0.944481000	-1.973790000	-0.152465000
6	-3.059819000	-0.007446000	0.474548000
6	-2.267246000	-0.011668000	1.628413000
1	-2.082288000	0.911774000	2.172500000
1	-2.076889000	-0.940319000	2.161645000
1	-3.494540000	-0.932360000	0.102205000
1	-3.498969000	0.919392000	0.112257000
6	1.981448000	0.006284000	-0.600006000
1	0.649515000	-0.810354000	-1.930303000
1	0.647749000	0.849823000	-1.911776000
6	2.564827000	-1.213044000	-0.248144000
6	3.766929000	-1.213218000	0.463163000
6	4.375866000	-0.007365000	0.824261000
6	3.772263000	1.205310000	0.477540000
6	2.570265000	1.218740000	-0.233928000
1	2.071748000	-2.146346000	-0.507333000
1	4.223840000	-2.159999000	0.737754000
1	5.311320000	-0.012698000	1.376722000
1	4.233327000	2.146788000	0.763201000
1	2.082241000	2.157507000	-0.482909000

**[PtBr<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>NEt<sub>2</sub>)]<sup>-</sup> 5**

SCF DONE: -8126.031875

H	4.284230000	-2.872651000	1.770679000
H	3.307991000	-1.545087000	2.452857000
C	3.683570000	-1.986447000	1.522272000
H	5.360966000	-0.641196000	1.407734000
C	4.536353000	-0.967271000	0.759497000
H	5.007241000	-1.457718000	-0.116705000
N	3.780004000	0.226367000	0.375375000
H	3.445995000	0.215841000	-1.737897000
H	2.596878000	-1.019592000	-0.813617000
H	1.062668000	0.578673000	0.166355000
C	1.644825000	0.884163000	-0.753612000
H	1.076810000	0.763014000	-1.680932000
H	1.813687000	1.955089000	-0.607798000
H	3.894989000	2.290237000	0.142706000
C	4.576059000	1.452814000	0.334936000
H	4.982267000	1.617399000	1.342829000
C	5.735800000	1.505185000	-0.682885000
H	6.478463000	0.720909000	-0.490298000
H	6.247944000	2.474498000	-0.616247000
H	5.383063000	1.387391000	-1.714151000
Br	-1.345096000	2.478063000	0.183747000
Pt	-0.827127000	0.065005000	-0.083691000
Br	-0.061464000	-2.278182000	-0.445760000
H	2.814669000	-2.316700000	0.943876000
C	2.909262000	0.027625000	-0.787382000
Br	-3.113933000	-0.608494000	0.293189000