DOI: 10.1002/ejic.201100624

Reactions of Diethylamine and Ethylene Catalyzed by Pt^{II} or Pt^0 – Transalkylation vs. Hydroamination

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Keywords: Homogeneous catalysis / Aqueous catalysis / Platinum / Hydroamination / Amines / Transalkylation / Density functional calculations

$PtBr_2$/$n$$Bu_4PBr$ (without solvent) or K_2PtCl_4/NaBr (in water) have been shown to efficiently catalyze the hydroamination of ethylene by aniline and 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_2H_4/Et_2NH catalytic cycle is close to that of the C_2H_4/$PhNH_2$ cycle. The poor performance is attributed to rapid catalyst degradation with reduction to metallic platinum. Pt^0, on the other hand, catalyzes a transalkylation process, partially transforming Et_2NH into Et_3N, $EtNH_2$ and NH_3. This process is inhibited by C_2H_4. Mechanistic considerations for the Pt^0-catalyzed transalkylation process are presented.

Introduction

Amines are important compounds for the bulk and fine chemical industries. There is great current interest in optimizing the hydroamination reaction, which is 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.[1] Amongst hydroamination reactions, the most difficult is the intermolecular process with nonactivated olefins, and solutions based on transition metal catalysis are actively pursued.[1–3] With regard to industrial applications, short-chain aliphatic olefins and ethylene constitute the most attractive starting materials. In the last six years, a number of papers have appeared on the hydroamination of ethylene and other α-olefins catalyzed by Pt-based systems. These include the addition of substituted anilines to ethylene[4] and 1-hexene[5] catalyzed by $PtBr_2$/$n$$Bu_4PBr$ (**I**) and our recent extension to aqueous media ($PtBr_2$/$NaBr_{(aq)}$, **I′**),[6] the addition of carboxamides to $RHC{=}CH_2$ (R = H, Me) catalyzed by $[PtCl_2(H_2C{=}CH_2)]_2/PPh_3$ (**II**)[7] and that of sulfonamides or anilines to more strained olefins catalyzed by $(COD)Pt(OTf)_2$ (**III**).[8] 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_a 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 to be the most active and allows ethylene hydroamination with $4\text{-}MeOC_6H_4NH_2$, which is the most basic amine for which an activity has been reported with a Pt-based catalyst.[4] Attempts to probe more basic amines with **I** were not performed, probably because of expectations based on the observed pK_a trend. Attempts to use more basic secondary amines have been described for **II** with negative results.[7] Catalytic system **III** has been shown to be inactive when using aniline (pK_a = 4.63).[8]

We have recently explored the details of the $PtBr_2/Br^-$ catalyzed addition of aniline to ethylene experimentally and computationally by isolating a number of low-energy intermediates and off-loop species and studying their solution equilibria[9] and by carrying out a computational investigation of the catalytic cycle,[10–11] the main features of which are summarized in Scheme 1. Nucleophilic addition to the coordinated and activated ethylene substrate is more facile for neutral *trans*-$[PtBr_2(Et_2NH)(C_2H_4)]$ (**2**) and *trans*-$[PtBr_2(C_2H_4)_2]$ (not shown in Scheme 1) than for the anionic resting state $[PtBr_3(C_2H_4)]^-$ (**1**). However, the only zwitterionic intermediate able to complete the catalytic cycle is $[Br_3Pt^{2-}(CH_2CH_2N^+H_2Ph)]$ (**4**), which can be obtained directly from **1**.

As 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_2NH and obtained direct evidence for the generation of the zwitterionic adduct $[(Et_2HN)Br_2Pt^-CH_2CH_2N^+HEt_2]$.[12] An excess amount of Et_2NH was shown to promote an equilibrium deprotonation of this species to yield the aminoalkyl derivative $[(Et_2N)Br_2PtCH_2CH_2NEt_2]^-$, which then decomposes to Pt^0 and other uncharacterized species. This behaviour is similar to that of other complexes obtained by the addition

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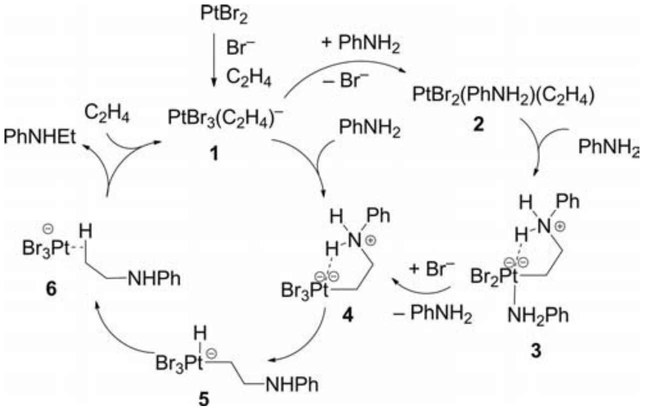
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100624.



Scheme 1. Mechanism of the $PtBr_2/Br^-$ catalyzed hydroamination of ethylene by aniline.

of basic amines to Pt-coordinated olefins.[13–15] This observation suggests that the catalyst deactivation process is triggered by deprotonation of the intermediate zwitterionic species, and this hypothesis has been confirmed by new catalytic tests: the addition of strong bases (KOH, Et_2NH, NEt_3 or 1,8-diazabicyclo[5.4.0]undec-7-ene) to the catalytic medium completely suppresses the production of PhNHEt, and the Pt^{II} catalyst is completely converted into metallic platinum.[16]

In this report, we present two new principles. The first, which is derived from a computational investigation on the catalytic cycle with Et_2NH, 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 intrinsically lower catalytic efficiency but must be attributed to catalyst decomposition triggered by deprotonation, which is more favourable for stronger bases. The second, which is derived from further catalytic experiments, deals with the discovery of a competitive amine transalkylation process, which is catalyzed by Pt^0 under hydroamination conditions.

Results and Discussion

(a) Initial Catalytic Tests

We first attempted ethylene hydroamination by Et_2NH under the same conditions previously used for the hydroamination of ethylene by aniline (**I**)[4] and under our recent extension of this system to aqueous media (**I′**).[6] These experiments yielded triethylamine in close to stoichiometric amounts (Table 1; Runs 1 and 2), whereas the starting compound conversion was negligible according to NMR spectroscopy. Extensive deposition of metallic Pt was observed at the end of the reaction, which has been reported for the aniline addition experiments.[4–6] Surprisingly, ethylamine, the formal product of dehydroamination, was also observed as a coproduct in nonnegligible amounts.

Table 1. Pt-catalyzed hydroamination of C_2H_4 by Et_2NH.[a]

Run	Catalyst	Product (TON)	Other products (TON)
1	**I**	Et_3N (≈ 1)	$EtNH_2$ (3)
2	**I′**	Et_3N (≈ 2)	$EtNH_2$ (5)

[a] Conditions: [Pt] = 0.3% relative to amine; [Br]/Pt = 150; H_2O (15 mL, only with **I′**); 25 bar C_2H_4 at 298 K, 10 h, 150 °C.

We shall address the catalytic cycle of ethylene hydroamination by Et_2NH through a computational investigation before analyzing the reason for the formation of the $EtNH_2$ coproduct.

(b) Computational Investigation of the Hydroamination Mechanism with Et_2NH

The energetics of ethylene hydroamination by Et_2NH were analyzed by DFT according to the established mechanism for the addition of aniline (Scheme 1).[11] In order to directly compare the results of the two systems, the calculations were carried out at the same level of theory (see computational details). The addition of Et_2NH to C_2H_4 is exoergic with $\Delta G°_{298} = -3.7$ kcal mol^{-1} (cf. –6.0 for $PhNH_2$) in the gas phase and $\Delta G°_{298}{}^{CPCM} = -6.1$ kcal mol^{-1} (cf. –8.0 for $PhNH_2$) with the inclusion of the solvent effect in aniline (CPCM = conductor-like polarizable continuum model). The energetic details of the catalytic cycle are summarized in Figure 1. Beyond the generation of zwitterion $[(Et_2HN)Br_2Pt^-CH_2CH_2N^+HEt_2]$ (**3′**), which was also observed experimentally,[12] ligand exchange occurs to yield the tribromido derivative $[Pt^{(2-)}Br_3(CH_2CH_2N^{(+)}HEt_2)]^-$ (**4′**). Contrary to the $PhNH_2/C_2H_4$ cycle, a local minimum could not be located for a five-coordinate Pt^{IV} hydride complex $[PtHBr_3(CH_2CH_2NEt_2)]^-$ (**5′**) derived from **4′** by intramolecular proton transfer. Every attempt to optimize such a complex led back to **4′**, which is consistent with the greater basicity of the N atom relative to the aniline system. However, a transition state was located for the transfer of the ammonium proton to the carbon atom, which directly transformed **4′** into the σ complex $[PtBr_3(\eta^2\text{-H-}CH_2CH_2NEt_2)]^-$ (**6′**) from which the Et_3N product may be released by exchange with C_2H_4 to start a new cycle. This proton transfer is assisted by the Pt centre, as shown by the relatively short Pt···H contact in the transition state (Figure 1).

The overall barrier between the resting state and the rate-determining transition state[17] (34.4 kcal mol^{-1}) is not significantly higher than that calculated for the corresponding $PhNH_2/C_2H_4$ cycle (33.8 kcal mol^{-1}).[11] Et_2NH coordination to Pt^{II} is more favorable than $PhNH_2$ coordination, thus the resting state of the catalytic cycle, according to the computational study, is *trans*-$PtBr_2(Et_2NH)_2$ (**7′**) rather than **1**. However, *trans*-$PtBr_2(PhNH_2)_2$ (**7**) was calculated to be 3.7 kcal mol^{-1} less stable than **1**.[11] On the basis of this study, systems **I** and **I′** are predicted to be equally competent to catalyze the addition of Et_2NH and $PhNH_2$ to C_2H_4. Hence, the reason for their poorer performance with Et_2NH must be attributed to catalyst decomposition, which is related to zwitterion deprotonation by excess base as confirmed by our recent study.[16] Note that the proton transfer

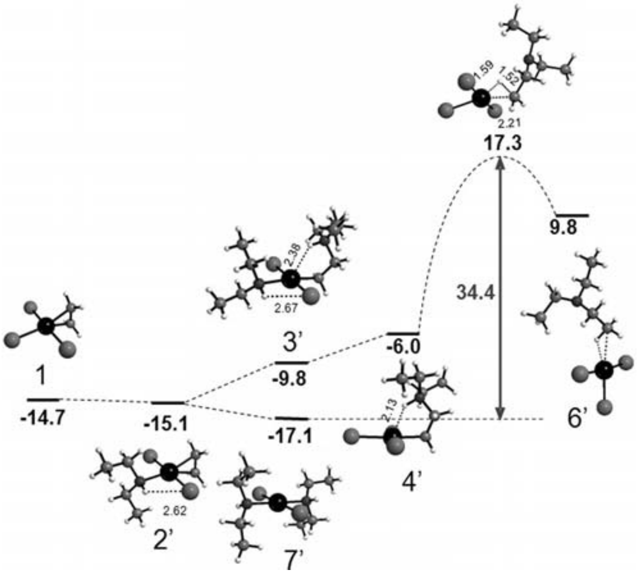


Figure 1. ΔG^{CPCM} (aniline) profile [kcal mol^{-1}] for C_2H_4 hydroamination by Et_2NH with the $PtBr_2/Br^-$ catalytic system at 298.15 K.

step is endoergic on the ΔG^{CPCM} scale for both systems according to previously published studies, but less so for the Et_2NH system (+15.3 kcal mol^{-1} for **3′** + Et_2NH)[12] than for the $PhNH_2$ system (+19.8 kcal mol^{-1} for **3** + $PhNH_2$).[11] The catalyst deactivation is probably driven by the irreversibility of the subsequent steps that lead to metal reduction.

(c) Catalysis of Transalkylation Processes

Based on these experimental and theoretical premises, we wondered whether catalytic hydroamination with Et_2NH could be induced through protection of the zwitterionic complex by the addition of acid. Indeed, replacing H_2O/NaBr by $HBr_{(aq)}$ gave marginally better results, with TON = 4 for Et_3N (Table 2; Run 3). However, the formation of $EtNH_2$ (ca. 18 cycles) was also observed. In addition to Et_3N, $EtNH_2$ and residual Et_2NH, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic monitoring also revealed the formation of a minor amount of EtOH (ca. one cycle).

The next experiments were run with simplified catalytic systems. Run 4 was carried out in the presence of HBr under the same conditions as Run 3 without the Pt compound. The result demonstrates the absence of any acid-induced transformation. There are reports warning of the possible action of acids as hydroamination catalysts[18,19] 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, as the amount of acid is a fraction of that of the amine (150 vs. 350 equiv.), hence the reaction mixture contains a $Et_2NH_2^+/Et_2NH$ 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, even lower activity was recorded, in agreement with the known activating role of bromide ions for this catalytic system.[4,6] Further simplification of the system by running the reaction in the absence of ethylene (Run 6) unexpectedly gave a large conversion to Et_3N and $EtNH_2$. Therefore, external ethylene is not necessary to generate the observed products, which proves that these products do not result 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.

Table 2. Additional reactions between C_2H_4 and Et_2NH.[a]

Run	Catalyst	C_2H_4 [bar]	Et_2NH [% conv.]	Et_3N [TON]	$EtNH_2$ [TON]
3[b]	K_2PtCl_4	25	7	≈ 4	≈ 18
4[c]	–	25	0	0	0
5	K_2PtCl_4	25	≈ 0	≈ 1	0
6[d]	K_2PtCl_4	–	52	92	23
7	Pt^0	–	45	76	18
8	Pt^0	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 equiv. of $HBr_{(aq)}$ (48%) relative to Pt; minor amounts of aromatic products (< 1%, resonances in the 110–150 ppm range) and EtOH (ca. 1%, resonances at 17.7 and 57.2 ppm) were visible by $^{13}C\{^1H\}$ NMR spectroscopy. [c] The same conditions as for Run 3 but without catalyst. [d] Minor amounts (< 2%) of other products were also detected by $^{13}C\{^1H\}$ NMR in the aliphatic region.

On the basis of this new evidence, we wondered whether ammonia could also be formed by further transalkylation from the $EtNH_2$ primary product. ^{14}N and ^{15}N NMR spectroscopic analysis of the solution obtained from Run 3 did not show any NH_3. However, this result may be a consequence of the small conversion coupled with small sensitivity (for ^{15}N) or broad lines (for ^{14}N). An additional experiment was carried out starting from $EtNH_3^+Cl^-$ rather than a Et_2NH/HBr mixture. K_2PtCl_4 was used as the catalyst without the presence of ethylene and using the standard reaction time and temperature. The final mixture indeed revealed the formation of NH_3 (NH_4^+) with a resonance at –357.6 ppm in the ^{14}N NMR spectrum (Figure 2). The spectrum also exhibited a strong resonance at –344.4 ppm, which corresponds to residual $EtNH_2/EtNH_3^+$, and a weak one at –329.1 ppm, which corresponds to $Et_2NH/Et_2NH_2^+$. The identity of all these resonances was verified by comparison with genuine samples. A resonance for Et_3N/Et_3NH^+, which should appear at around –325 ppm, was not visible because of the small conversion for this transalkylation process.

Transalkylation reactions of amine substrates have already been shown to occur under Pd^0 catalysis.[20–25] We were intrigued as to whether the same phenomenon may also occur in the presence of Pt^0 because metallic platinum is generated in situ by the decomposition of the Pt^{II} system. To the best of our knowledge, Pt-catalyzed amine transalky-

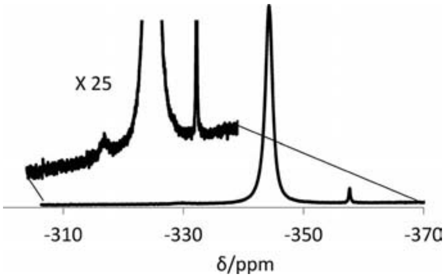


Figure 2. ^{14}N NMR spectrum of the solution obtained from $EtNH_3^+Cl^-$ in D_2O after 10 h at 150 °C in the presence of K_2PtCl_4 (0.3 %).

lation has only been reported by Brunet et al. as a side process during the $PtBr_2$-catalyzed heterocyclization of aniline to quinolines in the presence of Bu_3N but the authors could not establish whether the process was catalyzed by Pt^{II} or Pt^0 formed during the reaction.[26] Indeed, using Pt^0 in place of K_2PtCl_4 under otherwise identical conditions gave approximately the same conversion and product distribution of the transalkylation products (Table 2; Run 7). The $^{13}C\{^1H\}$ NMR spectrum of the final reaction mixture is shown in Figure 3. Again, the process is inhibited by ethylene (Run 8).

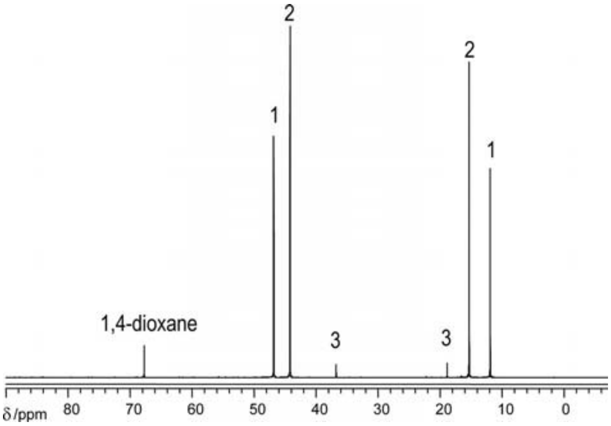
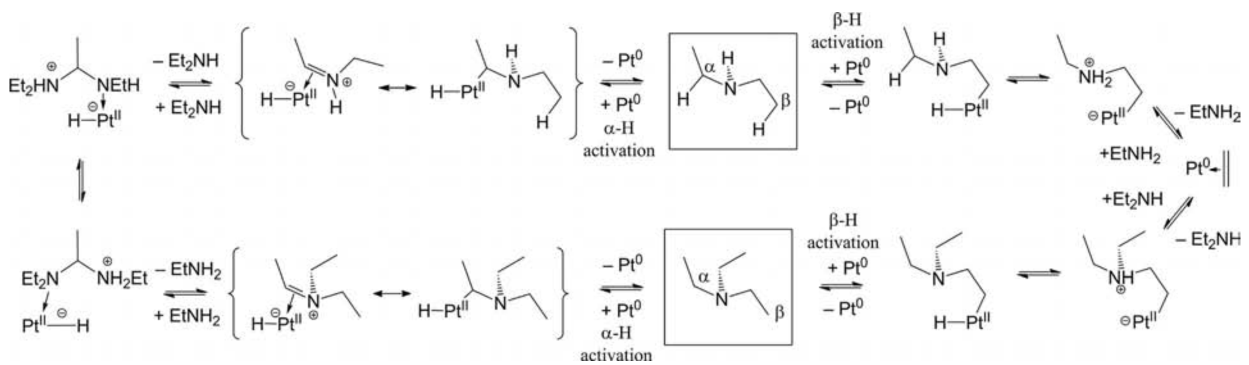


Figure 3. $^{13}C\{^1H\}$ NMR spectrum of the final reaction mixture from Run 7 (Table 2). Peak assignment, 1: Et_3N, 2: Et_2NH, 3: $EtNH_2$ (internal standard: 1,4-dioxane, 1.3 mmol).

The mechanism proposed by Murahashi for the Pd^0-catalyzed transalkylation process involves metal insertion into the α-CH bond with formation of a hydridoiminium intermediate.[21] This pathway is illustrated in Scheme 2 (left) for the related Pt^0 catalyst. The iminium ligand in this intermediate is then attacked by a second amine molecule to generate a coordinated aminoalkylammonium ligand, followed by exchange of the proton and the platinum centres and reversal of all steps. However, following our recent computational investigation,[10–11,16] we can imagine an alternative pathway that involves the reverse steps of the hydroamination reaction, which starts with insertion of Pt^0 into a β-CH bond and leads to a Pt^0–olefin intermediate, followed by hydroamination by a second amine molecule. This pathway is illustrated in Scheme 2 (right). Note, however, that the hydroamination process was shown to occur with Pt^{II}/Pt^{IV} complexes, whereas in this case the Pt^0/Pt^{II} couple would operate.

To test the plausibility of the dehydroamination/hydroamination mechanism, we carried out two additional catalytic experiments that used only triethylamine as the starting compound under conditions identical to those of Runs 7 and 8 in Table 2. Clearly, the α-CH bond pathway cannot lead to a reaction, whereas the β-CH bond pathway may result in the generation of Et_2NH with release of ethylene (dehydroamination). Under the conditions of Run 8, i.e. in the presence of ethylene, a minor but nonnegligible amount (ca. one cycle) of diethylamine was produced, whereas five cycles of the product were observed under the conditions of Run 7 (no added ethylene). Although these experiments do not exclude that the α-CH bond activation mechanism is the main pathway when starting from diethylamine, they confirm that the β-CH bond activation mechanism also takes 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^0 surface, which blocks or retards access to the platinum atoms by the C–H bonds. However, this rationalization is compatible with both mechanisms. Additional investigations are necessary to confirm the presence of an α-CH bond pathway for this system, which is outside of the scope of this work.



Scheme 2. Two alternative pathways for the Pt^0-catalyzed transalkylation reaction.

Conclusions

This study has revealed that the catalytic systems **I** and **I′** do not efficiently add the N–H bond of Et_2NH 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, which is favoured by the deprotonation of the key zwitterionic intermediate (**3′**).[12] This deprotonation is also favoured by the high basicity of Et_2NH.

Parallel studies have also shown that the metallic platinum produced is responsible for a transmetallation reaction, which equilibrates Et_2NH with Et_3N, $EtNH_2$ and even NH_3. This appears to be the first report of Pt^0-catalyzed amine transalkylation, a process that has previously been well established for Pd^0. This process is inhibited by the olefin, presumably because of a surface saturation effect, which blocks its access to the substrate C–H bonds. Among two different mechanistic pathways involving the activation of the amine α-CH and β-CH bonds, respectively, 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^0-catalyzed process.[21]

Experimental Section

General: All solvents were of HPLC grade and were used as received. Et_2NH (Fluka) was distilled and kept under argon in the dark. $PtBr_2$ (Alfa Aesar), K_2PtCl_4 (Alfa Aesar) and nBu$_4$PBr (Acros Organics) were used as received. Ethylene (purity ≥ 99.5%) was purchased from Air Liquide.

Instrumentation: NMR investigations were carried out with a Bruker AV400 spectrometer at 298 K operating at 400.1 MHz (^{1}H), 100.6 MHz (^{13}C) and 28.9 MHz (^{14}N). The spectra were calibrated with the residual solvent resonance relative to tetramethylsilane (^{1}H, ^{13}C) and $MeNO_2$ (^{14}N).

Typical Procedures for the Attempted Hydroamination of Ethylene by Et_2NH: (a) with $PtBr_2$/nBu$_4$PBr: An autoclave was charged with $PtBr_2$ (46 mg, 0.13 mmol) and nBu$_4$PBr (440 mg, 1.3 mmol, 10 equiv.) and submitted to argon/vacuum cycles. Et_2NH (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 room temp. 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 with traces of $CDCl_3$ to obtain an instrument lock.

(b) with K_2PtCl_4/HBr: The autoclave was charged with K_2PtCl_4 (54 mg, 0.13 mmol) and submitted to argon/vacuum cycles. Water (or D_2O), Et_2NH (4.7 mL, 45.5 mmol, 350 equiv.) and 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 room temp. The remainder of the experiment was carried out as above, except that D_2O was used to obtain the NMR lock. The amount of D_2O was the minimum needed to homogenize the system.

Typical Procedures for Et_2NH Transalkylation: The autoclave was charged with K_2PtCl_4 or Pt black (0.13 mmol) and submitted to argon/vacuum cycles. Et_2NH or Et_3N (45.5 mmol, 350 equiv.) was added and the ethylene pressure (if needed) was adjusted to 25 bar (ca. 100 mmol, 333 equiv.) at room temp. The remainder of the experiment was carried out as above. A minor amount of D_2O was added to obtain the NMR lock.

Computational Details: The DFT calculations were carried out according to the methodology described in detail in our recent studies on the $C_2H_4/PhNH_2$ reaction,[10–11] 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.[27] The calculations included a frequency analysis for all minima and transition states and solvation effects by single-point CPCM[28–29] corrections on the gas-phase optimized geometries, from which the thermodynamic ΔG^{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.

Acknowledgments

We are grateful to the Centre National de la Recherche Scientifique (CNRS), the Agence Nationale de la Recherche (ANR), grant number NT09_442499, and the Institut Universitaire de France (IUF) for financial support as well as the Centre Informatique National de l'Enseignement Supérieur (CINES) and the Centre Interuniversitaire de Calcul de Toulouse (CICT), project CALMIP, for granting free computational time. P. A. D. thanks the Ministère de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche (MENESR) for a Ph.D. fellowship.

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[1] J.-J. Brunet, D. Neibecker, in: *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, Germany, **2001**, pp. 91–141.
[2] J.-J. Brunet, N.-C. Chu, M. Rodriguez-Zubiri, *Eur. J. Inorg. Chem.* **2007**, 4711–4722.
[3] T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892.
[4] J. J. Brunet, M. Cadena, N. C. Chu, O. Diallo, K. Jacob, E. Mothes, *Organometallics* **2004**, *23*, 1264–1268.
[5] J. J. Brunet, N. C. Chu, O. Diallo, *Organometallics* **2005**, *24*, 3104–3110.
[6] P. A. Dub, M. Rodriguez-Zubiri, C. Baudequin, R. Poli, *Green Chem.* **2010**, *12*, 1392–1396.
[7] X. Wang, R. A. Widenhoefer, *Organometallics* **2004**, *23*, 1649–1651.
[8] D. Karshtedt, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646.
[9] P. A. Dub, M. Rodriguez-Zubiri, J.-C. Daran, J.-J. Brunet, R. Poli, *Organometallics* **2009**, *28*, 4764–4777.
[10] P. A. Dub, R. Poli, *J. Mol. Catal. A* **2010**, *324*, 89–96.
[11] P. A. Dub, R. Poli, *J. Am. Chem. Soc.* **2010**, *132*, 13799–13812.
[12] P. A. Dub, J.-C. Daran, V. A. Levina, N. V. Belkova, E. S. Shubina, R. Poli, *J. Organomet. Chem.* **2011**, *696*, 1174–1183.
[13] J. K. K. Sarhan, M. Green, I. M. Al-Najjar, *J. Chem. Soc., Dalton Trans.* **1984**, 771–777.
[14] G. Lorusso, C. R. Barone, N. G. Di Masi, C. Pacifico, L. Maresca, G. Natile, *Eur. J. Inorg. Chem.* **2007**, 2144–2150.
[15] G. Balacco, G. Natile, *J. Chem. Soc., Dalton Trans.* **1990**, 3021–3024.
[16] P. A. Dub, A. Béthegnies, R. Poli, submitted.
[17] R. Poli, *Comments Inorg. Chem.* **2009**, *30*, 177–228.
[18] B. Schlummer, J. F. Hartwig, *Org. Lett.* **2002**, *4*, 1471–1474.

[19] J. G. Taylor, L. A. Adrio, K. K. Hii, *Dalton Trans.* **2010**, *39*, 1171–1175.
[20] N. Yoshimura, I. Moritani, T. Shimamura, S. I. Murahashi, *J. Am. Chem. Soc.* **1973**, *95*, 3038–3039.
[21] S. I. Murahashi, T. Hirano, T. Yano, *J. Am. Chem. Soc.* **1978**, *100*, 348–350.
[22] S. I. Murahashi, T. Yano, *J. Chem. Soc., Chem. Commun.* **1979**, 270–271.
[23] Y. Shvo, R. M. Laine, *J. Chem. Soc., Chem. Commun.* **1980**, 753–754.
[24] S. I. Murahashi, N. Yoshimura, T. Tsumiyama, T. Kojima, *J. Am. Chem. Soc.* **1983**, *105*, 5002–5011.
[25] S. I. Murahashi, *Angew. Chem.* **1995**, *107*, 2670; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2443–2465.
[26] S. Anguille, J.-J. Brunet, N. C. Chu, O. Diallo, C. Pages, S. Vincendeau, *Organometallics* **2006**, *25*, 2943–2948.
[27] L. E. Roy, P. J. Hay, R. L. Martin, *J. Chem. Theory Comput.* **2008**, *4*, 1029–1031.
[28] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
[29] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.

Received: June 21, 2011