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Intermolecular Highly Regioselective Hydroamination of Alkenes with Ligandless Platinum(II) Catalysts in Ionic Solvents: Activation Role of *n*-Bu$_4$PBr[†]

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The reaction of aniline with 1-hexene catalyzed by PtBr$_2$ (0.3%) in the presence of *n*-Bu$_4$PBr (65 equiv/Pt) at 150 °C affords the expected hydroamination products with a 95% Markovnikov regioselectivity (*N*-(2-hexyl)aniline). An activating role of *n*-Bu$_4$PBr has been evidenced, which is due to the presence of the bromide ions. This accelerating effect is discussed in terms of increased basicity of the platinum center in a zwitterionic intermediate. The ligandless, inexpensive, and nontoxic PtBr$_2$−*n*-Bu$_4$PBr−H$^+$ catalytic system allows reaching a TON = 243 after 96 h at 150 °C (70% yield, 95% Markovnikov regioselectivity). The same results are obtained for reactions performed in the air.

Introduction

The catalytic hydroamination of alkenes is a subject of worldwide research, especially because such atom efficient addition reactions would be of great preparative value for the production of both basic and fine chemicals of industrial interest.[1] Intense efforts during the last thirty years have led to great improvements for the hydroamination of vinylarenes[2] and 1,3-dienes,[3] as well as for the *intramolecular* hydroamination of tethered aminoalkenes.[4] However, efforts directed toward the *intermolecular* hydroamination of nonactivated alkenes have met with less success and is still a challenge for chemists. Since the first report by Coulson in 1971 on the Rh- or Ir-catalyzed hydroamination of ethylene with highly basic secondary amines,[5] only a few catalytic systems, based on rhodium or iridium, and more recently on organolanthanides, have been shown to exhibit some activity for such reactions.[6]

A breakthrough seems to have been performed in our group by the discovery of a new catalytic system consisting of Pt(II) salts in ionic solvents.[7,8] A thorough study of the catalytic performances of such systems as a function of reaction parameters led us to show that PtBr$_2$ (0.3%) in *n*-Bu$_4$PBr (solvent) is particularly efficient for the hydroamination of ethylene with various anilines at 150 °C, leading to turnover numbers up to 250[8] (although solid at RT, *n*-Bu$_4$PBr melts near 100 °C, and is thus considered as an ionic solvent rather than a molten salt). At nearly the same time, Widenhoefer et al. reported the hydroamination of ethylene with the N−H bond of carboxamides using a catalytic system consisting of [PtCl$_2$(CH$_2$=CH$_2$)$_2$]$_2$ (2.5%) and PPh$_3$ (5%) in dioxane at 120 °C.[9]

Examination of literature data on the hydroamination of alkenes indicate that, in numerous cases, catalytic systems that exhibit activity for the hydroamination of ethylene failed when applied to higher olefins. Such is the case for the RhCl$_3$-catalyzed hydroamination with piperidine,[5] but also, for example, for the alkali metal

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Table 1. Reaction of Aniline with 1-Hexene Catalyzed by PtBr$_2$ in n-Bu$_4$PBr:[a] Influence of the 1-Hexene/Platinum Ratio

run	1-hexene (equiv/Pt)	**3** + **4** (TON)[b]	**3/4** ratio	**5** (TON)[b]	**6** (TON)[b]
1	100	10	nd	<1	~1
2	350	17	95/5	<1	4
3	500	25	95/5	<1	4
4	700	42	95/5	<1	5
5	800	37	95/5	<1	8
6	900	33	95/5	<1	9

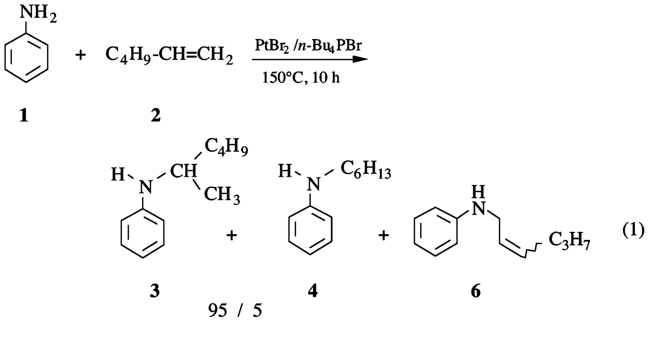
[a] PtBr$_2$, 0.13 mmol; n-Bu$_4$PBr/aniline/PtBr$_2$ = 150/350/1 (mmol). Reactions conducted at 150 °C for 10 h. [b] TON = turnover number.

catalyzed hydroaminations with diethylamine.[10] Thus, it was interesting to test the catalytic performances of the PtBr$_2$−n-Bu$_4$PBr system for the hydroamination of a higher olefin such as 1-hexene. Furthermore, it was important to determine the regioselectivity of this reaction, in view of possible enantioselective intermolecular hydroamination reactions of simple alkenes.

In this paper, we report extension of our results to the catalytic hydroamination of 1-hexene by aniline catalyzed by PtBr$_2$ in n-Bu$_4$PBr. The latter reaction is highly regioselective (≥95% Markovnikov) and proceeds with a TON up to 243 in the presence of an acid cocatalyst at 150 °C. The activating role of n-Bu$_4$PBr is clearly demonstrated and discussed.

Results and Discussion

The first experiment was performed by reacting aniline, **1**, with 1-hexene, **2**, in the presence of PtBr$_2$ in n-Bu$_4$PBr for 10 h at 150 °C in a stainless steel autoclave (run 1, Table 1). The very major product formed was the Markovnikov type addition product, *N*-(2-hexyl)aniline, **3**, first identified by comparison (GC retention time, GC/MS spectrum) with an authentic sample,[11a] and finally by ^{1}H NMR after isolation by GLC chromatography. GC analysis of run 1 also detected traces of side-products reported in Table 1, which could be identified through further experiments. The other regioisomer (anti-Markovnikov type), *N*-(n-hexyl)aniline, **4**, was formed in much lower amount (**4/3** ~5/95) (GC/MS comparison with an authentic sample).[11b] Other side-products were identified (GC/MS spectra) as 2-propylquinoline, **5** (m/z = 171, comparison of all fragmentations and relative intensities with literature data),[12] and *N*-(2-hexenyl)aniline, **6** (m/z = 175). Despite many efforts, the latter could not be isolated in a pure form. However, careful ^{1}H and ^{13}C NMR analysis with of a (**3** + **4** + **6**) mixture unequivocally indicated a $-CH_2-CH{=}CH-CH_2-$ moiety for **6**, which was definitely identified as the known (*E*)-*N*-(2-hexenyl)aniline.[13] Finally, another side-product, detected in trace amounts, could be identified as the branched imine ($C_6H_5-N{=}C(CH_3)-C_4H_9$, **7** ($m/z$ = 175, GC/MS comparison literature data).[14] In all further experiments reported in this work, **7** was always detected in only trace amounts and therfore has been omitted in equations and tables. The overall reaction can thus be summarized by eq 1.



As expected from previous results,[7,8] control experiments showed that the reaction conducted in n-Bu$_4$PBr was more efficient (10 cycles, run 1, Table 1) than that conducted in THF (<1 cycle).

For the hydroamination of ethylene under similar conditions, the amount of ethylene present in the autoclave under 25 bar pressure was ca. 100 mmol, i.e., 770 equiv/Pt.[8] Therefore, we examined the influence of the 1-hexene/Pt ratio on the course of the reaction.

As can be seen from Table 1, increasing the amount of 1-hexene increases the TON for (**3** + **4**) up to a maximum of 42 for a 1-hexene/platinum ratio near 700. Higher ratios slightly decrease the TON. The regioselectivity of **3/4** is 95/5 (±1%), whatever the amount of 1-hexene. In contrast, the formation of **6** continuously increases with increasing 1-hexene/Pt ratio. This observation raises questions about the fomation of **6**. Indeed, **6** may be considered as an oxidative amination product formed by β-elimination on the anti-Markovnikov zwitterionic addition complex (vide infra). It should thus be formed at the expense of **4**, a feature that is not observed since the **3/4** ratio is unchanged (within experimental error) whereas the yield of **6** increases.

The very high regioselectivity (Markovnikov/anti-Markovnikov) is rather unexpected. Indeed, although literature data are lacking about the stoichiometric addition of *aniline* on alkenes coordinated to platinum(II) complexes,[15−20] it has been reported that the Mark-

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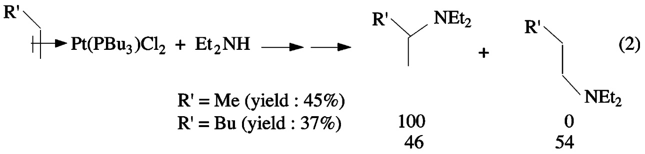
Table 2. Reaction of Aniline with 1-Hexene Catalyzed by $PtBr_2$ in n-Bu_4PBr:[a] Influence of the n-Bu_4PBr/Pt Ratio

run	n-Bu_4PBr equiv/Pt	(**3** + **4**) (TON)[b]	**3**/**4** ratio	**5** (TON)[b]	**6** (TON)[b]	(**3** + **4**)/**6** ratio
7	0	~1	nd	<1	<1	nd
8	10	21	95/5	~1	3	87/13
9	20	37	95/5	~1	4	90/10
10	30	41	95/5	~1	5	90/10
11	65	57	95/5	~1	5	92/8
12	90	46	95/5	~1	5	90/10
13	150	42	95/5	~1	5	90/10

[a] $PtBr_2$, 0.13 mmol; 1-hexene/aniline/$PtBr_2$ = 700/350/1 (mmol). Reactions conducted at 150 °C for 10 h. [b] TON = turnover number.

ovnikov addition of other amines was favored only when steric factors do not interfere. This conclusion was drawn from the study of *stoichiometric* reactions of dialkylamines such as Et_2NH with alkenes coordinated in *cis*-dichloro(olefin)(Bu_3P)Pt(II) complexes, *followed by reductive ($NaBH_4$) destruction* (eq 2).[17b]



These literature data reveal a great difference of regioselectivity between the (stoichiometric) hydroaminations of propene (100% Markovnikov) and 1-hexene (46% Markovnikov, 54% anti-Markovnikov) (both reactions were conducted under the same conditions: CH_2Cl_2, 0 °C).[17b] The catalytic hydroamination of 1-hexene with our Pt(II) system thus appears remarkable, from the point of view of both catalytic efficiency and regioselectivity.

Considering now the reagent ratio corresponding to the best results in terms of TON, we were interested in trying to understand the exact role of the phosphonium salt. The experimental conditions of run 4 (Table 1) involve 7 g of n-Bu_4PBr for 4.1 mL of aniline and 11.5 mL of 1-hexene. Under these conditions, the phosphonium salt cannot be truly considered as a solvent. However, as indicated before, the reaction using n-Bu_4PBr (7 g) (run 1, Table 1) gave a much higher TON than that conducted in THF (7.5 mL). We therefore studied the influence of the amount of n-Bu_4PBr for reactions conducted with a 1-hexene/aniline/$PtBr_2$ ratio of 700/350/1. As can be seen from Table 2, increasing the amount of n-Bu_4PBr from 0 to 65 equiv/$PtBr_2$ resulted in an increase of the hydroamination TON for (**3** + **4**) from ~1 to 57 (run 11, Table 2). Above this value, the hydroamination TON slowly decreased to 42 for higher n-Bu_4PBr/$PtBr_2$ ratios. Note that the formation of **6** also seems to be promoted by the presence of n-Bu_4PBr, but does not increase significantly with increasing amounts of n-Bu_4PBr (runs 8−13).

These experiments clearly show that the phosphonium bromide plays an activating role in the catalytic activity. Furthermore, these results suggest that the phosphonium bromide also has a limiting effect when used in larger amounts. This observation may suggest the intervention of the bromide ions of the phosphonium salt in an equilibrium toward active platinum species (vide infra).

Table 3. Reaction of Aniline with 1-Hexene Catalyzed by $PtBr_2$ in n-Bu_4PBr:[a] Influence of the Reaction Time

run	reaction time (h)	(**3** + **4**) (TON)[b]	**3**/**4** ratio	**5** (TON)[b]	**6** (TON)[b]	(**3** + **4**)/**6** ratio
14	10	57	95/5	1	5	92/8
15	24	91	95/5	3	6	94/6
16	48	120	95/5	5	7	95/5
17	72	135	95/5	6	7	95/5
18	96	152	95/5	6	7	96/4

[a] n-Bu_4PBr, 3 g; $PtBr_2$, 0.13 mmol; 1-hexene/aniline/$PtBr_2$ = 700/350/1 (mmol). Reactions conducted at 150 °C. [b] TON = turnover number.

On the basis of these results, we were led to examine the evolution of the reaction with time under the best conditions used so far (run 11, Table 2). These reactions were intended to detect possible catalyst poisoning, as previously observed for the hydroamination of ethylene with aniline.[8]

Results reported in Table 3 indicate some slowing of the formation of (**3** + **4**) with time, but this is much less pronounced than for the corresponding hydroamination of ethylene.[8] This observation may be due to the several facts. First, the main reaction product, *N*-(2-hexyl)aniline, is much more sterically demanding than *N*-ethylaniline, resulting in a slowed formation of inactive bis(*N*-alkylaniline)platinum(II) species. Second, this slowing could be due to the consumption of 1-hexene, thus lowering its concentration, which has been shown to be an important parameter (Table 1). Third, this observation could also be due to 1-hexene isomerization. Consequently, the composition of the alkene fraction was examined at the end of several runs (^{1}H NMR analysis). For run 14 (Table 3), the recovered alkene fraction was composed of 90% 1-hexene and ca. 10% of a 2- and/or 3-hexenes mixture. For run 18, the alkene fraction was composed of 75% 1-hexene and 25% 2- and /or 3-hexenes. These results indicate that the above catalytic system is a poor isomerization catalyst (whatever the reaction pathway) and suggest that the excess of 1-hexene necessary to obtain good turnover frequencies (see Table 1) should be recovered in large part.

Results reported in Table 3 also show that the formation of **6** does not increase significantly with time, and this raises again the question about the reaction pathway leading to **6**. In contrast, the formation of **5** slowly increases with time. The formation of **5** is believed to involve a platinum-catalyzed (aromatic C−H activation) generation of 2-propyl-1,2,3,4-tetrahydroquinoline, followed by dehydrogenation to give **5**. Such platinum- or rhodium-catalyzed transfer hydrogenations from 2-alkyltetrahydroquinolines have been previously observed during the hydroamination of ethylene with aniline.[6a,8]

Nevertheless, it is noteworthy that increasing the reaction time resulted in an increased overall selectivity: indeed, after 96 h (run 18, Table 3), the hydroamination products (**3** + **4**) are formed with a 43% yield (vs aniline), whereas **5** and **6** are each formed with a ≤2% yield.

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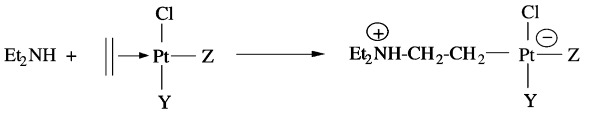
Considering now the activation effect evidenced above, how can we explain the role of *n*-Bu_4PBr in the hydroamination of alkenes with $PtBr_2$? Previous results on the hydroamination of norbornene with aniline have indicated that for a given cationic part all ionic solvents associated with a bromide ion gave higher catalytic efficiency than those associated with a chloride ion.[7,8] This observation was confirmed for the hydroamination of 1-hexene with aniline. Indeed under the conditions of run 11 (Table 2), replacing *n*-Bu_4PBr by *n*-Bu_4PCl resulted in the formation of (**3** + **4**) with TON = 5! It is thus clear that the anionic part of the phosphonium salt plays an important role: in contrast to chloride ions,[21] bromide ions strongly enhance the catalytic activity (see Table 2). Such halide ions effects have already been observed, e.g., for the palladium-catalyzed Heck reaction in ionic liquids, but are generally poorly understood.[22]

It has been known for a long time that alkenes coordinated to platinum(II) are susceptible to nucleophilic attack.[15] The case of amine nucleophiles has been particularly studied.[16−20] Stable zwitterionic complexes are formed by reaction of secondary amines, e.g., diethylamine, on coordinated ethylene in *cis*- or *trans*-[Pt(C_2H_4)Cl_2L] (eq 3). These have been isolated and characterized by NMR spectroscopy[17,18] and in one case by single-crystal X-ray diffraction.[17d]



(3)

cis : Y = PPh_3, PBu_3, Z = Cl
trans : Y = Cl, Z = Et_2NH

Although similar zwitterionic complexes have been observed with various amines, the reaction is limited to amines of sufficient basicity ($pK_a > 5$). For instance, *aniline* failed to give an addition compound when reacted with *trans*-[Pt(C_2H_4)(Et_2NH)Cl_2].[17b,d,18] Liberation of the alkylated amine by cleavage of the platinum−carbon bond of the zwitterionic complexes occurs *only* by treatment with HCl or $NaBH_4$.[17] The overall result is thus a *stoichiometric* hydroamination of ethylene.[23] These literature data make our results on the platinum(II)-catalyzed hydroamination of ethylene[8] or 1-hexene with aniline particularly remarkable.

A possible explanation of the activating role of *n*-Bu_4PBr is outlined below (eqs 4−9). For simplicity, the alkene considered is ethylene and the phosphonium cation has been omitted.

$$PtBr_2 + 2\,Br^- \rightleftharpoons [PtBr_4]^{2-} \xrightleftharpoons{CH_2=CH_2} [PtBr_3(C_2H_4)]^{\ominus} + Br^- \tag{4}$$

$$[PtBr_3(C_2H_4)]^{\ominus} + ArNH_2 \rightleftharpoons [PtBr_2(ArNH_2)(C_2H_4)] + Br^- \tag{5}$$

$$[PtBr_2(ArNH_2)(C_2H_4)] + ArNH_2 \rightleftharpoons [Ar\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\ominus}{Pt}Br_2(ArNH_2)] \tag{6}$$

$$[Ar\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\ominus}{Pt}Br_2(ArNH_2)] + Br^- \rightleftharpoons [Ar\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\ominus\,\ominus}{PtBr_3}] + ArNH_2 \tag{7}$$

$$[PtBr_3(C_2H_4)]^{\ominus} + ArNH_2 \rightleftharpoons [Ar\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\ominus}{Pt}Br_3]^{\ominus} \tag{8}$$

$$[Ar\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\ominus}{Pt}Br_3]^{\ominus} \xrightarrow{CH_2=CH_2} ArNH\text{-}CH_2\text{-}CH_3 + [PtBr_3(C_2H_4)]^{\ominus} \tag{9}$$

The equilibrium summarized by eq 4 represents both the solubilization of $PtBr_2$ in the phosphonium bromide and the coordination of ethylene. These steps are analogous to the formation of the Zeise's salt from K_2PtCl_4 and ethylene in water.[15] Note that it is known that in $[PtBr_3(C_2H_4)]^-$ the platinum−olefin bond is stronger than in the chloro equivalent.[24] It is also known that, in such complexes, the ethylene ligand is displaced by halides ions in high concentration,[15] a possible reason for the observation that too large amounts of phosphonium bromide have a slowing effect on the reaction rate (vide supra).

Equation 5 represents the displacement of a bromide ligand by aniline, a reaction similar to that involved in the synthesis of, for example, *trans*-[$PtCl_2$(C_2H_4)(amine)] from the Zeise's salt, K[$PtCl_3$(C_2H_4)], and an amine.[25] Note again that in the presence of a too large excess of bromide ions this equilibrium may be shifted to the left.

Equation 6 represents the *external*[17c] nucleophilic attack of aniline on the neutral [$PtBr_2$(C_2H_4)($C_6H_5NH_2$)] complex to generate a zwitterionic complex. However, as indicated before, zwitterionic complexes derived from the attack of aniline (reactions conducted at or below RT) have never been observed in NMR detectable quantities, a failure attributed to the too low basicity of aniline (equilibrium strongly shifted to the left?). However, in our hand, the hydroamination of 1-hexene by aniline conducted *at 150 °C* with $PtBr_2$ in the *absence* of *n*-Bu_4PBr (run 7, Table 2) afforded **3** in nearly stoichiometric amounts. This is evidence that attack by aniline on an alkene coordinated on $PtBr_2$ is possible provided that the reaction is conducted at high temperature. Note however that this result may be due to a temperature-promoted evolution of the zwitterionic complex by proton transfer (vide infra). DFT calculations by Togni et al. strongly suggest that, for the *catalytic* hydroamination of ethylene, the cleavage of the platinum−carbon bond by protonolysis should be the determining step.[26] In our opinion, this proton transfer should be facilitated by two parameters: the acidity of the N−H bond and the basicity of the platinum center. The acidity of the proton is directly related to the basicity of the aniline: the less basic the starting aniline, the easier the proton transfer to the negative center. This hypothesis seems confirmed by our observation that for the hydroamination of ethylene with anilines the less basic anilines gave the higher TONs.[8] For what concerns the basicity of the platinum center in the zwitterionic complex, eq 7 (ligand exchange of aniline for bromide) may represent a possibility to explain the activating role of the bromide ion by generating, at least transiently, a platinum center bearing *formally* two negative charges. Note that the direct addition of aniline on $[PtBr_3(C_2H_4)]^-$ (eq 8) should

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[21] The authors wish to thank Dr. I. Tkatchenko for helpful discussions about the coordinating ability of chloride ions.

[22] Handy, S. T.; Okello, M. *Tetrahedron Lett.* **2003**, *44,* 8395−8397, and references therein. Jeffery, T. *Tetrahedron* **1996**, *52*, 10113−10130. See also: Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254−278.

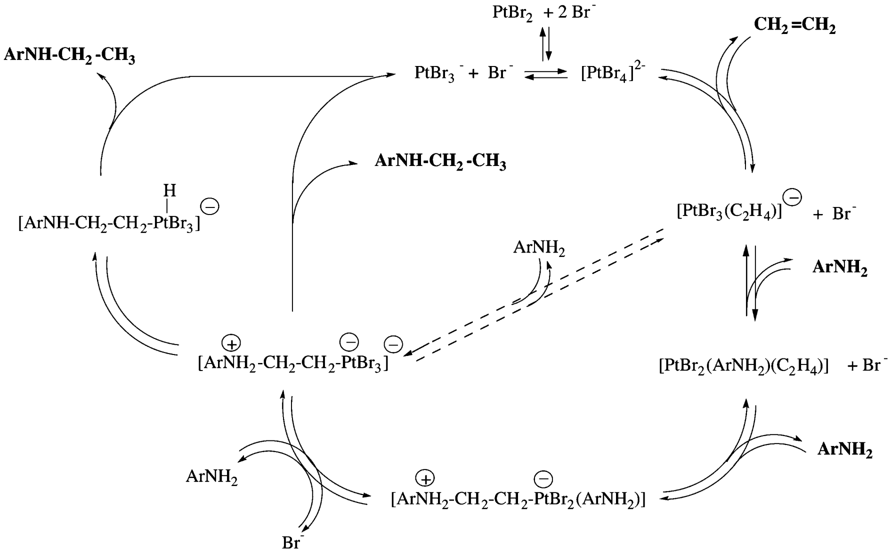
[23] Venanzi et al.[19] reported a platinum-promoted cyclization of aminoalkenes (e.g., 1-pentenylamine), which may appear catalytic in character. However, as noted by the authors, the reaction rates are so low that "its synthetic exploitation would not represent a significant improvement over existing stoichiometric processes".

[24] Denning, R. G.; Venanzi, L. M. *J. Chem. Soc. (A)* **1967**, 328−337.

[25] Cope, A. C.; Ganellin, C. R.; Johnson, H. W.; Van Auken, T. V.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1963**, *85*, 3276−3279. Hupp, S.; Dahlgreen, G. *Inorg. Chem.* **1976**, *15*, 2349−2353.

[26] Senn, H. M.; Block, P. E.; Togni, A. *J. Am. Chem. Soc.* **2000**, *122*, 4098−4107.

Scheme 1

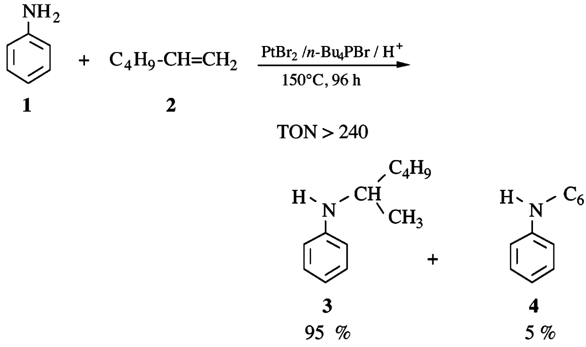


lead to the same highly reactive zwitterionic complex. Equation 9 finally represents the liberation of the alkylated aniline. This last step may proceed either by direct protonolysis of the platinum–carbon bond or via a platinum hydride, followed by reductive elimination. DFT calculations suggest that the protonolysis pathway is thermodynamically preferred.[26] Although it is difficult to address this question on the basis of our experimental data, the possible generation of a highly basic platinum center, as proposed above, may favor a platinum hydride pathway for reactions performed in the presence of n-Bu$_4$PBr. These overall mechanistic proposals are summarized by Scheme 1.

Another point has to be considered. Indeed, it is well known that the *stoichiometric* addition of amines on ethylene coordinated to palladium(II) complexes often gives low yields because of the simultaneous, irreversible formation of inactive Pd(II)(amine)$_2$ complexes.[27] Such may be the case also for Pt(II) complexes. During the *catalytic* hydroamination of ethylene with aniline, a gradual poisoning effect was observed, which could be attributed to the reaction product, *N*-ethylaniline, on the basis of experimental evidence.[8] Apparently, the possible poisoning by aniline itself is not significant, and the poisoning effect of *N*-ethylaniline does not prohibit catalysis, at least to some extent. It is tentatively proposed that, during the catalytic reaction in the presence of n-Bu$_4$PBr, the poisoning effect by the alkylated aniline is slowed by the presence of the excess of bromide ions. The latter may prevent the competitive formation of catalytically inactive species by keeping the platinum species in the forms involved in eqs 4 and 5.

To summarize the above considerations about the role of the anion associated with the phosphonium salt, we tentatively propose that the "inhibiting" effect of the chlorides ions mainly intervenes through eqs 4 and 5. The highly coordinating properties of chloride anions strongly shift both equilibriums to the left ($PtBr_2Cl_2^{2-}$, $PtBr_3Cl^{2-}$, or $PtCl_4^{2-}$). In contrast, the much less coordinating bromide ions do not inhibit eqs 4 and 5 and allow the catalytic cycle to proceed (eq 6). The activating effect of the bromide ions is believed to operate mainly by increasing the "basicity" of the platinum atom in the zwitterionic complexes (eq 7), thus promoting the proton transfer and liberation of the alkylated aniline, whatever the intimate reaction pathway.

Finally, the role of an added catalytic source of protons was examined. Indeed, for the hydroamination of ethylene, a catalytic source of protons (either an anilinium salt or simply CF_3SO_3H) has been shown to increase the catalytic activity of the $PtBr_2$–n-Bu$_4$PBr system. Reactions performed under the conditions of run 11 (Table 2) but in the presence of anilinium sulfate (3 equiv/Pt) formed (**3** + **4**) with 70 cycles for a 10 h reaction time, 180 cycles for a 48 h reaction time, and finally 243 cycles for 96 h (70% yield based on aniline, highly reproducible on several runs) without change in the **3**/**4** ratio (95/5). Interestingly, under the above conditions, the formation of both **5** and **6** is limited to only traces (TON < 1).



(10)

Analysis of the alkene fraction composition at the end of the reaction (eq 10) indicated 23% isomerization to the 2- and/or 3-hexenes mixture, suggesting again a possible recovery of a large part of the excess of 1-hexene.

Control experiments (96 h at 150 °C) showed that, in the absence of n-Bu$_4$PBr, the $PtBr_2$–H^+ system formed (**3** + **4**) with a TON of ca. 10, thus proving that the major activation is induced by the phosphonium bromide. Last, in the absence of $PtBr_2$, the n-Bu$_4$PBr–H^+ system

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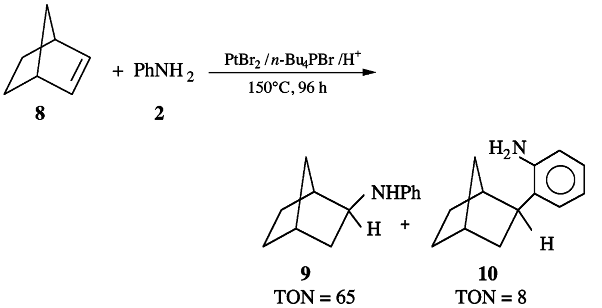
[27] Gasc, M. B.; Lattes, A.; Perié, J. J. *Tetrahedron* **1983**, *39*, 703–731.

formed (**3** + **4**) with a TON of 2 (vs H^+ catalyst), indicating that simple Brönsted catalysis is not significant.

The hydroamination of other alkenes was also briefly examined. Under the conditions of eq 10 (aniline/olefin/n-$Bu_4PBr/PtBr_2/H^+$ = 350/700/65/1/3) the hydroamination of *trans*-2-hexene occurred with TON = 6 (85% *N*-(2-hexyl)aniline, 15% *N*-(3-hexyl)aniline). As expected, the hydroamination of cyclohexene proved to be even more difficult, yielding *N*-cyclohexylaniline (GC/MS comparison with a commercial sample) with TON = 3. Interestingly, the hydroamination of norbornene (eq 11) yielded the expected *N*-(2-norbornyl)aniline, **9** (TON = 65), together with the hydroarylation product **10** (TON = 8).[28]

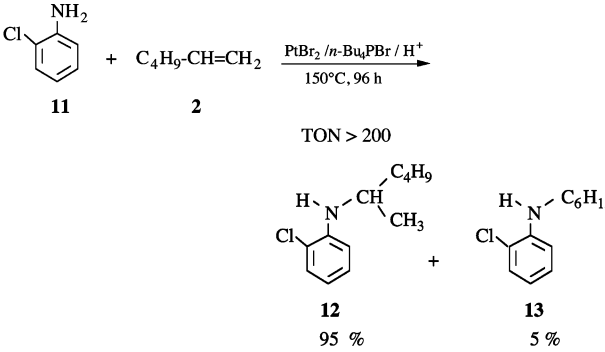


(11)

These results clearly show that the optimization of the hydroamination of 1-hexene is also beneficial in the case of norbornene, since it allowed great improvement (activity and selectivity for the hydroamination) of our previous results for this reaction (TON for **9** = 13, TON for **10** = 5, after 6 days at 140 °C).[7]

In contrast, under the same conditions (vide supra), the hydroamination of 1-dodecene occurred with only TON = 20, although with a very high regioselectivity (>95% Markovnikov). After 96 h at 150 °C, isomerization of 1-dodecene to internal dodecenes reached 35%. Thus, the best conditions established for the hydroamination of 1-hexene are not directly applicable to that of 1-dodecene. It must be noted that, at 150 °C in the autoclave, the amount of condensed olefin is different for 1-hexene (bp = 62 °C) and for 1-dodecene (bp = 213 °C). According to the influence of the olefin/$PtBr_2$ ratio (see Table 1), this may explain the lower TON obtained for the hydroamination of 1-dodecene under these conditions.

Last, extension to the hydroamination of 1-hexene with 2-chloroaniline, catalyzed by the $PtBr_2$−n-Bu_4PBr−CF_3SO_3H system, resulted in the selective formation of the expected alkylated chloroanilines (**12** + **13**) with TON = 200 and a 95% Markovnikov selectivity (eq 12).



(12)

From a practical point of view, it is important to note that the above *Pt(II)-catalyzed hydroamination reactions can be conducted in the air without loss in yield* (no use of inert atmosphere at any step of the procedure). To the best of our knowledge, the ligandless, inexpensive, and nontoxic platinum(II)−n-Bu_4PBr−H^+ system disclosed in this work is the most efficient ever reported for the catalytic hydroamination of an α-olefin such as 1-hexene. Furthermore, an activating effect of bromides ions associated with the phosphonium salt has been clearly evidenced, a feature that may suggest reconsidering some aspects of platinum organometallic chemistry.

Experimental Section

Methods and Materials. Tetra(n-butyl)phosphonium bromide (Janssen), tetra(n-butyl)phosphonium chloride (Aldrich), *N,N*-dibutylaniline (Acros), and platinum salts (Strem) were used as received. Arylamines (Fluka or Acros) and 1-hexene (Fluka) were distilled before use. Unles otherwise noted in the text, all sample manipulations of transition metal complexes were carried out under argon using standard Schlenk tube and vacuum line techniques.

Instrumentation. GC analyses were performed on a Hewlett-Packard HP 4890 (FID) chromatograph (HP 3395 integrator) equipped with a 30 m HP1 capillary column and GC/MS analyses on a Hewlett-Packard HP 6890 apparatus equipped with a HP 5973 M ion detector. NMR analyses were performed on a Bruker AM 250 or Avance 500 apparatus. Catalytic experiments were conducted in a 100 mL stainless steel autoclave with a glass liner and a magnetic stirring bar.

Reactions. Hydroamination of 1-Hexene: Typical Procedure. The autoclave was charged with $PtBr_2$ (46.2 mg, 0.13 mmol) and n-Bu_4PBr (see Tables), closed, and submitted to argon-vacuum cycles. Degassed aniline (4.1 mL, 45 mmol) and 1-hexene (see Tables) were then syringed into the autoclave. The temperature was then raised to 150 °C. After the reaction times indicated in the tables, the autoclave was allowed to cool to room temperature. The reaction mixture was dropped into 50 mL of diethyl ether, stirred, and then filtered. The solid phase was extracted again with diethyl ether (3 × 50 mL). The external standard (*N,N*-dibutylaniline) was added to the collected ethereal phases and the solution analyzed by GC and GC/MS.

Isolation of *N*-(2-hexyl)aniline, 3. After extraction of the reaction products as described above (no added internal standard), the hydroamination product, *N*-(2-hexyl)aniline, was isolated by column chromatography over silica (hexane/ether: 100/10). ^1H NMR ($CDCl_3$, 250 MHz): δ(ppm) 7.15−7.21 (m, 2H), 6.58−6.71 (m, 3H), 3.45 (m, 1H), 1.33−1.56 (m, 7H), 1.32 (d, J = 6.3 Hz, 3H), 0.90−0.95 (m, 3H). GC/MS (EI, 70 eV) *m/z*: 177 (M^+), 120 ($M - C_4H_9$, base pic).

Identification of (*E*)-*N*-(2-Hexenyl)aniline, 6. After extraction of the reaction products as above and evaporation of the solvent, column chromatography isolated a (**3** + **4** + **6**) mixture free of any other reaction product (GC/MS analysis). Careful ^1H NMR analysis ($CDCl_3$, 500 MHz) of the 2−6 ppm region showed (besides the known signals of **3** and **4**) signals at δ (ppm) = 2.07 (m), 3.78 (d), 5.63 (m), and 5.74 (m), in relative integrated area 2/2/1/1. COSY experiments clearly indicated a [$-CH_2-CH{=}CH-CH_2-$] backbone corresponding (δ, J) to *N*-(2-hexenyl)aniline, **6**.[13] Integration of the ^1H NMR signals between 2 and 6 ppm indicated the same **4**/**6** ratio as

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[28] Compounds **9** and **10** were identified by comparison with authentic samples. Brunet, J. J.; Neibecker, D.; Philippot, K. *J. Chem. Soc., Chem. Commun.* **1992**, 1215−1216. Brunet, J. J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221−228.

that determined by GC analysis. Furthermore, the $^{13}C\{^{1}H\}$ NMR spectrum of the (**3** + **4** + **6**) mixture indicated all the signals reported for the [NH−CH$_2$−CH═CH−CH$_2$−] chain of (*E*)-*N*-(2-hexenyl)aniline.[13]

Analysis of the Hexenes Fraction. At the end of the reaction, the autoclave was maintained at 150 °C and the gases were quenched by slowly bubbling into ice-cooled $CDCl_3$. The solution was then transferred in a NMR tube and analyzed by ^{1}H NMR (250 MHz) at 293 K, indicating the presence of 1-hexene (vinylic protons: m (1H) at 5.7−5.9 ppm and m (2H) at 4.9−5.1 ppm) and 2- and/or 3-hexenes (*cis* + *trans*) (vinylic protons: m at 5.43 ppm).

Identification of *N*-(3-Hexyl)aniline. GC/MS (EI, 70 eV) *m*/*z*: 177 (M^+), 148 ($M - C_2H_5$), 134 ($M - C_3H_7$, base pic).

Identification of *N*-(2-Dodecyl)aniline. GC/MS (EI, 70 eV) *m*/*z*: 261 (M^+), 246 ($M - CH_3$), 120 ($M - C_{10}H_{21}$, base pic).

Identification of *N*-(*n*-Dodecyl)aniline. GC/MS (EI, 70 eV) *m*/*z*: 261 (M^+), 106 ($M - C_{11}H_{23}$, base pic).

Identification of 2-Chloro-*N*-(2-hexyl)aniline, **12.** Isolation as described above. ^{1}H NMR ($CDCl_3$, 250 MHz): δ(ppm) 7.34−7.38 (m, 1H), 7.19−7.25 (m, 1H), 6.65−6.77 (m, 2H), 4.25 (m, 1H, NH), 3.60 (m, 1H),1.46−1.70 (m, 6H); 1.32 (d, $J = 6.3$ Hz, 3H), 1.01−1.08 (m, 3H). GC/MS (EI, 70 eV) *m*/*z*: 213 ($M^+ + 2$), 211 (M^+), 198, 196, 156, 154 (base pic).

Identification of 2-Chloro-*N*-(hexyl)aniline, **13.** GC/MS (EI, 70 eV) *m*/*z*: 213 ($M^+ + 2$), 211 (M^+), 142, 140 (base pic).

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