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Platinum-Catalyzed Intermolecular Hydroamination of Alkenes: Halide-Anion-Promoted Catalysis

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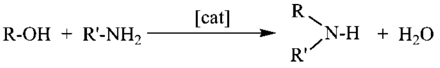
Tetraalkylphosphonium halides play the role of "promoters" for the previously unknown Pt^{II}-catalyzed hydroamination of alkenes. The promoting effect of these "cocatalysts" depends only upon their anionic moiety. The Pt^{II}/nBu_4PBr system exhibits an unprecedented catalytic activity (aerobic conditions) for the hydroamination of ethylene and 1-hexene (regioselectivity $> 95\,\%$, Markovnikov).

1. Introduction

Amines are important chemicals for both industry and everyday life.[1–4] Since the discovery of ammonia,[5] chemists have developed synthetic methods for the production of amines, and many methods are available.[6] However, most of them are unsuitable for industrial purposes, mainly because they involve very expensive starting materials, reagents, or purification steps. The condensation of ammonia [Equation (1)] or amines [Equation (2)] with alcohols in the presence of various catalysts, first pointed out by Sabatier et al. in 1909,[7,8] is nowadays the main method for the industrial production of light amines. This reaction is also used in some cases for the production of fatty amines or diamines.[2]

$$\text{R-OH} + \text{NH}_3 \xrightarrow{[\text{cat}]} \text{RNH}_2 + \text{H}_2\text{O} \tag{1}$$



$$\text{R-OH} + \text{R'-NH}_2 \xrightarrow{[\text{cat}]} \begin{matrix} \text{R} \\ \text{R'} \end{matrix}\!\!>\!\text{N-H} + \text{H}_2\text{O} \tag{2}$$

With the exception of methanol and ethanol, most primary alcohols are industrially produced from alkenes (hydroformylation–hydrogenation sequence).[9,10] It is thus obvious that the direct transformation alkene → amine would be a more economic process since it would suppress at least one step (Scheme 1) and would avoid the coproduction of water [Equations (1) and (2)].

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Jean-Jacques Brunet was born in Clermont-Ferrand, France, in 1945. He attended the Faculté des Sciences and the Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, where he received his Chemical Engineering degree in 1968. He obtained his PhD (Thèse d'Etat) in 1972 at the University of Nancy under the supervision of Pr P. Caubère. In 1985, he joined the Laboratoire de Chimie de Coordination of the CNRS (Toulouse), where he is one of the group leaders. Starting from organic synthesis and the study of reaction mechanisms, his current research interest lies now in organometallic chemistry and homogeneous catalysis directed towards organic synthesis, with some emphasis on carbonylation reactions and on the functionalization of alkenes by hydroamination.

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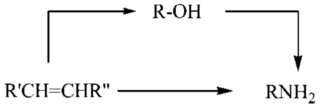
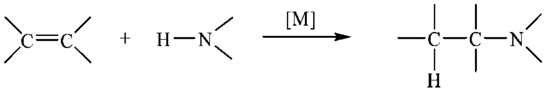


Scheme 1. From alkenes to amines.

The necessity to develop atom-economic reactions is often highlighted. The direct addition of the N–H bond of ammonia or amines on carbon–carbon multiple bonds (hydroamination) belongs to this desired class of reactions,[11] especially in the case of alkenes [Equation (3)], the subject of this review.



(3)

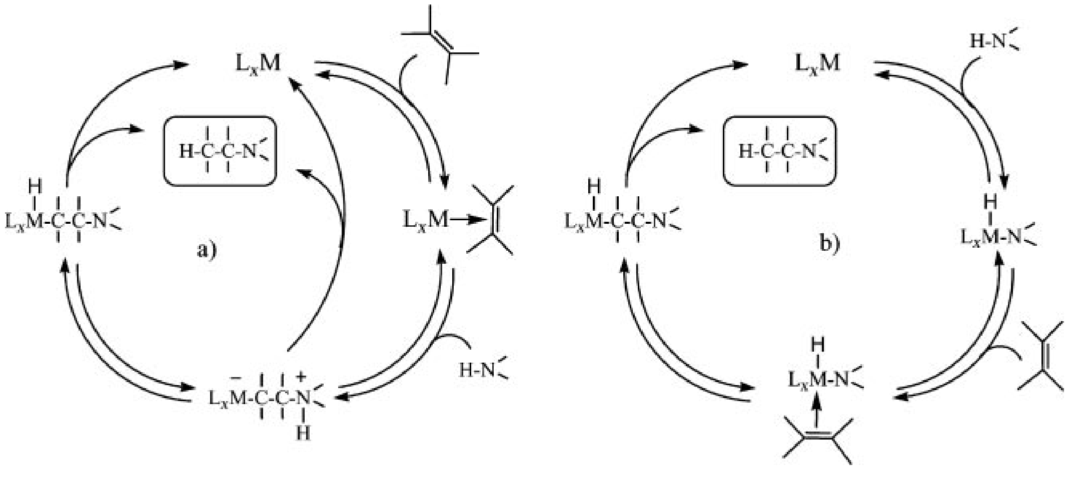
Consequently, intense efforts have long been devoted to the hydroamination of different kinds of multiple carbon–carbon bonds, alkenes, alkynes, vinylarenes, and dienes by intramolecular and intermolecular additions. Several reviews have been published since 1983.[12–23] The main conclusion that can be given (in 2006) is that significant progress has been made for the hydroamination of vinylarenes[24] and dienes,[25] which includes the inter- and intramolecular versions of this reaction. The hydroamination of vinylarenes must be highlighted since catalysts that allow fully regioselective additions (Markovnikov or anti-Markovnikov) and enantioselective Markovnikov additions have been designed.[26] In the case of nonactivated alkenes, several efficient catalytic systems have been reported for *intramolecular* hydroamination, which include highly enantioselective reactions.[22,23,27] In contrast, the *intermolecular* hydroamination of alkenes with *amines* is much less developed. Exceptions include the industrial production (BASF) of $t\mathrm{BuNH_2}$ by addition of ammonia to isobutene (zeolite catalyst),[21] the organolanthanide-catalyzed (neodymium, 20% catalyst) hydroamination of 1-pentene with $n\mathrm{PrNH_2}$ (fully regioselective Markovnikov addition),[27n] and the Li-catalyzed hydroamination of ethylene.[27p] This review is devoted to results developed in our group since 2002 for the platinum-catalyzed *intermolecular* hydroamination of nonactivated alkenes (some previous results with Rh catalysts are also included).

First, it is important to recall that the addition of ammonia or amines to ethylene is thermodynamically feasible (Table 1).[28] It is also noteworthy that the entropy term is highly negative, which means that very high temperatures would favor the reverse reaction and thus make the desired reaction impossible. However, this thermodynamic data gives no information on the activation barrier. It is conceivable that the approach of the nitrogen atom lone pair to the electron density of the carbon–carbon double bond of the alkene induces an electrostatic repulsion that corresponds to a high-energy barrier. The objective is thus to lower this energy barrier. Two possibilities can be considered:[14] (1) activation of the alkene (to make it more "electrophilic") and (2) activation of the amine (to make it more "nucleophilic"). The mechanisms corresponding to these two possibilities are represented in Scheme 2.[16]

Table 1. Thermodynamic data for the hydroamination of ethylene (T = 298 K, P = 101325 Pa).

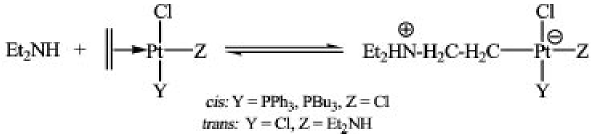
Reaction	$\Delta G°$ [kJ mol^{-1}]	$\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J mol^{-1} K^{-1}]
$C_2H_4 + NH_3 \rightarrow EtNH_2$	–14.4	–52.4	–127.4
$C_2H_4 + EtNH_2 \rightarrow Et_2NH$	–33.3	–78.6	–152.1
$C_2H_4 + Et_2NH \rightarrow Et_3N$	–29.9	–79.5	–166.2

The most significant results on the *homogeneously* catalyzed *intermolecular* hydroamination of nonactivated alkenes have already been reviewed.[21] However, in view of the subject of this article, it is interesting to note that intense efforts have been devoted to the addition of amines to alkenes coordinated to transition metals, especially $\mathrm{Pt^{II}}$ and $\mathrm{Pd^{II}}$. In the case of $\mathrm{Pt^{II}}$ alkene complexes,[29–34] attack by sufficiently basic amines (pK_a of conjugated acid > 5) has been shown to afford zwitterionic complexes [Equation (4)], one of which could be characterized by X-ray dif-



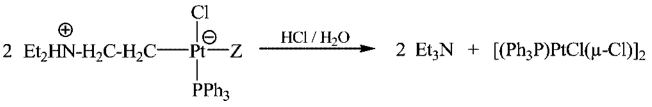
Scheme 2. a) Hydroamination by alkene activation; b) hydroamination by N–H activation.[16]

fraction study.[30d] However, liberation of the alkylated amine by cleavage of the carbon–platinum bond needs a further step (reaction with HCl or $NaBH_4$) [Equation (5)],[30–33] so that the hydroamination reaction is only *stoichiometric*.[34]



$$Et_2NH + \Vert\!\!\rightarrow \overset{Cl}{\underset{Y}{Pt}}\text{—}Z \rightleftharpoons \overset{\oplus}{Et_2HN}\text{-}H_2C\text{-}H_2C\text{—}\overset{Cl}{\underset{Y}{Pt^{\ominus}}}\text{—}Z \quad (4)$$

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



$$2\ \overset{\oplus}{Et_2HN}\text{-}H_2C\text{-}H_2C\text{—}\overset{Cl}{\underset{PPh_3}{Pt^{\ominus}}}\text{—}Z \xrightarrow{HCl/H_2O} 2\ Et_3N + [(Ph_3P)PtCl(\mu\text{-}Cl)]_2 \quad (5)$$

Soon after the publication of our paper on the Pt-catalyzed *hydroamination* of ethylene with aniline in ionic liquids (see below),[35] Widenhoefer et al. reported that the dinuclear Pt^{II} complex $[PtCl_2(C_2H_4)]_2$, associated with PPh_3, is an active catalyst for the intermolecular *hydroamidation* of ethylene with *carboxamides*.[36] Extension to the hydroamidation of alkenes with poorly basic *sulfonamides* catalyzed by $[PtCl_2(C_2H_4)]_2/[AgBF_4]$ has also been reported recently.[37]

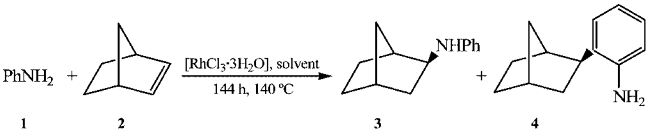
2. New Catalytic Systems for the Intermolecular Hydroamination of Alkenes

After our contribution on anionic Rh^I anilido species as possible hydroamination catalysts,[38–41] we were tempted to take advantage of our simultaneous involvement[42] in the use of molten salts or ionic liquids as possible candidates to replace classical organic solvents – an important aspect in the development of "greener" chemical processes.[43–46]

Examination of the patent by Coulson[47] on the Rh^{III}-catalyzed hydroamination of ethylene with secondary amines showed that highly polar solvents, such as hexamethylphosphoramide (HMPA), have a positive effect on the reaction. We showed that some ionic solvents apparently exhibit properties similar to those of the well-known but more hazardous (carcinogenic) dipolar aprotic solvents such as DMF or HMPA.[42]

2.1. Hydroamination of Norbornene by Aniline in Ionic Liquids

The above results led us to examine the Rh^{III}-catalyzed hydroamination of alkenes in ionic solvents. The hydroamination of norbornene with aniline was selected [Equation (6)], (see Table 2).



(6)

Table 2. $[RhCl_3{\cdot}3H_2O]$-catalyzed hydroamination of norbornene with aniline in ionic solvents.[a]

Run	Solvent	Reaction products: 3	4	TON Total (**3** + **4**)
1	thf (7.5 mL)	0	0	0
2	[EMIM][Cl] (3.0 g)	≈0	≈0	≈0
3	[BMIM][Cl] (3.6 g)	≈0	≈0	≈0
4	[BMIM][Cl] (7.2 g)	≈0	≈0	≈0
5	$[BMIM][PF_6]$ (6 g)	5.1	2.6	7.7
6	[BMIM][Br] (5.7 g)	8.3	1.5	9.8
7	[HMIM][Br] (7.1 g)	10.1	1.9	12
8	nBu$_4$PBr (7.1 g)	7.7	2.5	10.2

[a] 144 h at 140 °C, $[RhCl_3{\cdot}3H_2O]$: 0.13 mmol, norbornene: 13 mmol, aniline: 45 mmol.

As expected,[47,48] no reaction was observed when thf was used as solvent (run 1, Table 2). The use of different imidazolium chlorides resulted in only traces of reaction products (runs 2 and 3). In contrast, the replacement of the chloride ion by $[PF_6^-]$ led to the formation higher-than-stoichiometric amounts of both **3** and **4** (run 5). A higher catalytic activity was obtained when imidazolium bromides were used (runs 6 and 7). Finally, the positive effect of the bromide ions was confirmed when nBu$_4$PBr (mp = 100–103 °C) was used as solvent (run 8).

Thus, the reaction of norbornene with aniline, catalyzed by $[RhCl_3{\cdot}3H_2O]$, does not occur in thf, but it can occur in the presence of imidazolium or phosphonium *bromides* as solvents. It is also worthy to note that the above ionic solvents allow the Rh^{III}-catalyzed hydroamination by a weakly basic amine ($pK_a = 4.63$).

In the early 2000s, Togni et al. published a very interesting theoretical study of the hydroamination through alkene activation and subsequent nucleophilic attack by the amine.[49] They considered d^8 transition-metal complexes of the type $[MCl(PH_3)_2]^{z+}$ {M = Co, Rh, Ir [$z = 0$] and M = Ni, Pd, Pt [$z = 1$]} for the hydroamination of ethylene with ammonia. For group 9 metals, nucleophilic attack was identified as the rate-determining step, while cleavage of the M–C bond was the rate-determining step for group 10 metals. Overall, metals from group 10 are more efficient than those from group 9 (lower activation barriers), and Ni^{II} precursors appeared to be the best candidates. These results led us to examine the catalytic activity of group 10 transition-metal precursors in combination with nBu$_4$PBr as solvent. For comparison, the reaction of aniline with norbornene under the same experimental conditions as those used for the Rh^{III} catalysts was considered.

The results reported in Table 3[50] show that group 10 transition-metal precursors exhibit some activity for the test reaction. However, contrary to that expected from the calculations by Togni and coworkers, the best results were clearly obtained with the Pt^{II} catalysts. The latter gave catalytic activities and chemoselectivities similar to those observed with [$RhCl_3 \cdot 3H_2O$] (Table 2).

Table 3. Hydroamination of norbornene with aniline in nBu$_4$PBr: catalysis by group 10 transition metals.[a]

Run	Catalytic precursor [mmol]	Reaction products: TON **3**	**4**	Total (**3** + **4**)
9	[$NiBr_2$] (0.40)	1.0	0	1.0
10	[$PdBr_2$] (0.17)	2.5	1.6	4.1
11	[$PtBr_2$] (0.13)	8.6	1.0	9.6
12	[$PtCl_2$] (0.13)	8.2	2.0	10.2
13	[PtI_2] (0.13)	9.8	1.2	11.0

[a] 144 h at 140 °C, norbornene: 13 mmol, aniline: 45 mmol, nBu$_4$PBr: 7 g.

The nature of the halide ion associated with the platinum precursor plays a minor role (runs 11–13, Table 3). This is not surprising since the [PtX_2]/nBu$_4$PBr ratio is 1:150, and this implies that the bromide ions are by far the main halogen ligands. Under these conditions, the platinum salts are soluble in the ionic solvent and can be considered as $[PtBr_4]^{2-}$ species [Equation (7)].[51]

$$[\mathrm{PtBr_2}] + 2\,n\mathrm{Bu_4PBr} \rightleftharpoons [\mathrm{PtBr_4}]^{2-} + 2\,[n\mathrm{Bu_4P}]^{+} \qquad (7)$$

The above results were particularly exciting because, as previously noted, no platinum-catalyzed alkene hydroamination had been reported until then. Since extensive information is available on the reactivity of Pt^{II}–ethylene complexes with amines,[29–34] we were prompted to examine the possible catalytic hydroamination of ethylene with aniline in the presence of the newly developed [$PtBr_2$]/nBu$_4$PBr system.

2.2. Hydroamination of Ethylene by Aniline in Ionic Liquids

Our first experiments were aimed at comparing the influence of the nature of the solvent on the reaction of aniline with ethylene (25 bar at room temperature) in the presence of catalytic amounts (0.3 %) of [$PtBr_2$]. In all cases, the reaction leads to the hydroamination product, N-ethylaniline (**6**) (with traces of N,N-diethylaniline, **7**), together with minor amounts of 2-methylquinoline (**8**) [Equation (8)].

The results in Table 4 show that, contrary to literature data, the hydroamination reaction is catalyzed by [$PtBr_2$] in aniline or thf with significant TONs (runs 14 and15). It should be noted that no zwitterionic complex has ever been evidenced from the reaction of aniline with any Pt^{II}–ethylene complex.[29–33] This fact was explained by the insufficient basicity of aniline (pK_a = 4.63), relative to that of, for example, diethylamine (pK_a > 10) for which the zwitterionic addition complex had been fully characterized.[30d] We tentatively suggest that the addition of aniline to a Pt^{II}–ethylene complex occurs to a very small extent and that the equilibrium is displaced toward the right because the zwitterionic complex evolves at high temperatures (150 °C) to liberate N-ethylaniline.

Table 4. Hydroamination of ethylene with aniline: influence of the nature of the solvent.[a]

Run	Solvent	Reaction products: TON PhNHEt	PhNEt$_2$	"2-Me-quinoline"
14	aniline (10 mL)	23	1	3
15	thf (7.5 mL)	34	1	4
16	nBu$_4$PBr (7 g)	80	1	11

[a] [$PtBr_2$]: 0.13 mmol, ethylene: 25 bar at room temperature, aniline: 45 mmol, 10 h at 150 °C.

The beneficial effect of nBu$_4$PBr is again highlighted: under nonoptimized conditions, the highest catalytic activity ever reported for the hydroamination of ethylene (TON = 80) was obtained.

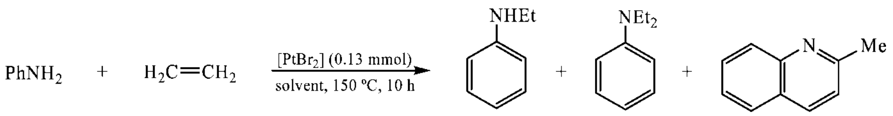
On the basis of the above observations, we briefly examined the influence of some classical reaction parameters.

The reaction temperature is an important parameter: at 150 °C, the TON was nearly twice that obtained at 120 °C (from 80 to 43 catalytic cycles after 10 h of reaction). Higher temperatures (180 °C) did not significantly improve the catalytic activity. Thus, further experiments were conducted at 150 °C.

The influence of the ethylene pressure was considered in the range 10–50 bar. By increasing the ethylene pressure from 10 to 50 bar, the formation of N-ethylaniline (TON from 73 to 90 after 10 h of reaction) was slightly increased. In contrast, the formation of the quinoline derivative was significantly favored by a high ethylene pressure (TON from 8 to 20).[52]

The next parameter that we examined was the amount of aniline used, whilst keeping all other parameters as stated in Table 4 (run 16An increase in the TON for the two main reaction products (TON for N-ethylaniline: from 30 to 99; TON for 2-methylquinoline: from 4 to 15) was observed by increasing the amount of aniline.

The evolution of the reaction with time was also considered. Runs were performed with different reaction times (1–10 h). The turnover frequency (TOF) for the formation of N-ethylaniline reached 37 h^{-1} for the first hour, which is apparently the highest TOF reported for ethylene hydroamination. The reaction rate then decreased, and the average



1 5 6 7 8 (8)

TOF for 10 h was 8 h^{-1}. In order to verify the possible poisoning by either of the two main reaction products, new runs were performed under the same conditions but in the presence of added 2-methylquinoline (1.5 mmol) or *N*-ethylaniline (15 mmol). After 10 h at 150 °C and in the presence of 2-methylquinoline, there was no significant difference in the reaction, whereas for the reaction conducted in the presence of added *N*-ethylaniline, a TON of less than 40 cycles was reached. Even more convincing is the following observation. A $[PtBr_2]$/aniline/*N*-ethylaniline (1:350:100 mmol) mixture was preheated (in the absence of ethylene) for 10 h at 150 °C. Ethylene was then added (25 bar at room temperature). This procedure resulted in a relatively inactive system for the production of **6**, but still active for the formation of **8** (9 cycles after 10 h). These results confirm that during the hydroamination reaction [Equation (8)], the increase in the concentration of *N*-ethylaniline induces a gradual poisoning of the catalyst.

Therefore, it was decided to perform the reaction in a biphasic medium consisting of nBu_4PBr and a high-boiling-point nonmiscible hydrocarbon. By performing the hydroamination of aniline with ethylene under the same conditions but in the presence of decane (4.5 mL for 7.2 g of nBu_4PBr), higher TONs (**6**: 115 cycles, **7**: 2 cycles and **8**: 17 cycles) were effectively reached.[53]

Finally, the possible influence of a proton source was examined. When the hydroamination of ethylene [Equation (8)] was performed in the presence of anilinium sulfate (3 equiv. per mol of $[PtBr_2]$), the TON increased from 80 to 130. Under biphasic conditions (nBu_4PBr/decane), the presence of anilinium sulfate led to an increase in the TON for *N*-ethylaniline from 115 to 145, the highest TON observed in the present work for the hydroamination of ethylene with aniline. Similar results were obtained when using CF_3SO_3H (3 equiv. per mol of $[PtBr_2]$) instead of anilinium sulfate.

As already mentioned, the reaction of amines with coordinated ethylene in $[Pt(C_2H_4)Cl_2L]$ complexes is only stoichiometric and, furthermore, is limited to amines of sufficient basicity ($pK_a > 5$). We have pointed out that aniline ($pK_a = 4.63$) reacts catalytically with ethylene in the presence of the $[PtBr_2]/nBu_4PBr$ system. Consequently, it seemed interesting to explore the scope of the reaction with regard to the basicity of the arylamine. Thus, anilines bearing different substituents were treated with ethylene under the conditions of [Equation (8)]. The results are reported in Table 5.

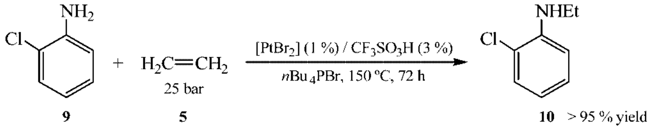
The results from Table 5 indicate that the lower the basicity of the arylamine, the higher the TON for the formation of the ArNHEt derivative. This observation is in contrast with that been reported for the stoichiometric reaction of amines with ethylene coordinated to Pt^{II} centers (see above). It must be noted, however, that the observed dependence of the TON on the basicity of the arylamine may be the result of several effects, such as an increase in reactivity of the expected zwitterionic intermediate (see below), and a reduction in the poisoning ability of the ArNHEt derivative (the lower the basicity of $ArNH_2$, the lower the poisoning effect of ArNHEt). Interestingly, hydroamination of ethylene with 2-chloroaniline was fully chemoselective (run 22).

Table 5. Hydroamination of ethylene:[a,b] influence of the basicity of arylamines.[c]

Run	Ar ($ArNH_2$)	pK_a	Reaction products: TON		
			PhNHEt	$PhNEt_2$	"2-Me-quinoline"
17	$4\text{-}MeOC_6H_4$	5.34	22	≈1	11
18	$4\text{-}MeC_6H_4$	5.08	55	≈1	17
19	C_6H_5	4.63	80	≈1	11
20	$2\text{-}MeC_6H_4$	4.44	85	≈1	11
21	$4\text{-}ClC_6H_4$	4.15	93	≈1	11
22	$2\text{-}ClC_6H_4$	2.65	110	–	–

[a] $[PtBr_2]$: 0.13 mmol, nBu_4PBr: 7.2 g. [b] 25 bar at room temperature, 10 h at 150 °C. [c] 45 mmol.

Finally, hydroamination of ethylene with 2-chloroaniline was performed by using the $[PtBr_2]/nBu_4PBr$ system in the presence of CF_3SO_3H (3 equiv. per mol of the Pt species). The reaction selectively afforded *N*-ethyl-2-chloroaniline with a TON of 250 after 10 h, corresponding to a 70% yield based on 2-chloroaniline. A nearly quantitative conversion of 2-chloroaniline was observed when using 1% of the catalyst system ($[PtBr_2]/3H^+$) in nBu_4PBr for 72 h at 150 °C [Equation (9)].



(9)

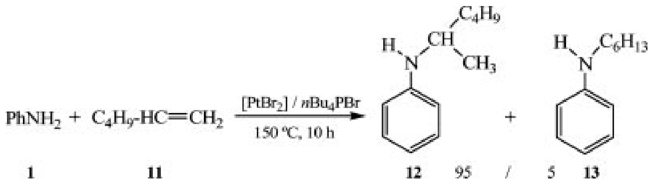
These results show, for the first time, that the platinum-catalyzed hydroamination of ethylene with arylamines is possible. The best results have been obtained for the hydroamination of ethylene with 2-chloroaniline by using a $[PtBr_2]/nBu_4PBr/3\ CF_3SO_3H$ system as catalyst. Such unprecedented catalytic performances for the hydroamination of ethylene led us to examine the catalytic activity of $[PtBr_2]/nBu_4PBr$ systems for the hydroamination of higher alkenes.

2.3. Hydroamination of Higher Alkenes

The literature indicates that, in most cases, systems that exhibit activity for the hydroamination of ethylene fail when applied to higher olefins.[48,54,55] Thus, it was interesting to consider the $[PtBr_2]/nBu_4PBr$ system for the hydroamination of a higher alkene 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.[22,23]

The first experiment was performed by reacting aniline with 1-hexene in the presence of $[PtBr_2]$ in nBu_4PBr (150 equiv. per mol of the Pt species) for 10 h at 150 °C [Equation (10)]. The major product formed was the Markovnikov-type addition product *N*-(2-hexyl)aniline (**12**). The other regioisomer (anti-Markovnikov-type), *N*-(*n*-

hexyl)aniline (**13**), formed in much lower amounts (**12**/**13** ≈ 95:5).[56] Other side-products were identified as 2-propylquinoline (**14**, trace amounts)[57] and *N*-(2-hexenyl)aniline (**15**).

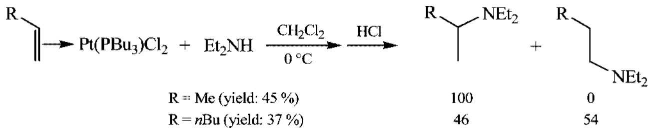


(10)

As expected, the reaction conducted in $n\text{Bu}_4\text{PBr}$ was more efficient (10 cycles) than that conducted in thf (<1 cycle, control experiments). As for the hydroamination of ethylene (see above), the influence of the 1-hexene/Pt ratio was considered.

When the amount of 1-hexene was increased, the TON for (**12** + **13**) increased up to a maximum of 42 for a 1-hexene/Pt ratio of about 700. Higher ratios tended to decrease the TON. The regioselectivity of **12**/**13** is 95:5 (±1%), irrespective of the amount of 1-hexene used.

The very high regioselectivity (Markovnikov/anti-Markovnikov) was rather unexpected. Indeed, although no literature data is available on the stoichiometric addition of *aniline* to alkenes coordinated to Pt^{II} complexes, it has been reported that the *Markovnikov* addition of other amines is favored only when steric factors do not interfere. This conclusion was drawn from the study of *stoichiometric* reactions of Et_2NH with *cis*-$[\text{Pt(olefin)(PBu}_3)\text{Cl}_2]$ complexes [Equation (11)].[30b]



(11)

These literature data reveal a great difference in regioselectivity between the (stoichiometric) hydroaminations of propene (100% Markovnikov) and 1-hexene (46% Markovnikov, 54% anti-Markovnikov).[30b] The catalytic hydroamination of 1-hexene with our Pt^{II} system thus appears remarkable, both from the point of view of catalytic efficiency and regioselectivity.

Considering now the ratio of the reagents for the best results in terms of TON, we were interested in better understanding the role of $n\text{Bu}_4\text{PBr}$. For the experiment, 7 g of $n\text{Bu}_4\text{PBr}$ for 4.1 mL of aniline and 11.5 mL of 1-hexene was used. Under these conditions, $n\text{Bu}_4\text{PBr}$ cannot truly be considered as a solvent. We therefore studied the influence of the amount of $n\text{Bu}_4\text{PBr}$ for reactions conducted with a 1-hexene/aniline/$[\text{PtBr}_2]$ ratio of 700:350:1. When the amount of $n\text{Bu}_4\text{PBr}$ was increased from 0 to 65 equiv. per mol of $[\text{PtBr}_2]$, an increase in the hydroamination TON for (**12** + **13**) from ca. 1 to 57 was observed. The TON slightly decreased to 42 when using higher $n\text{Bu}_4\text{PBr}/[\text{PtBr}_2]$ ratios. The regioselectivity **12**:**13** is unchanged, irrespective of the $n\text{Bu}_4\text{PBr}/[\text{PtBr}_2]$ ratio used.

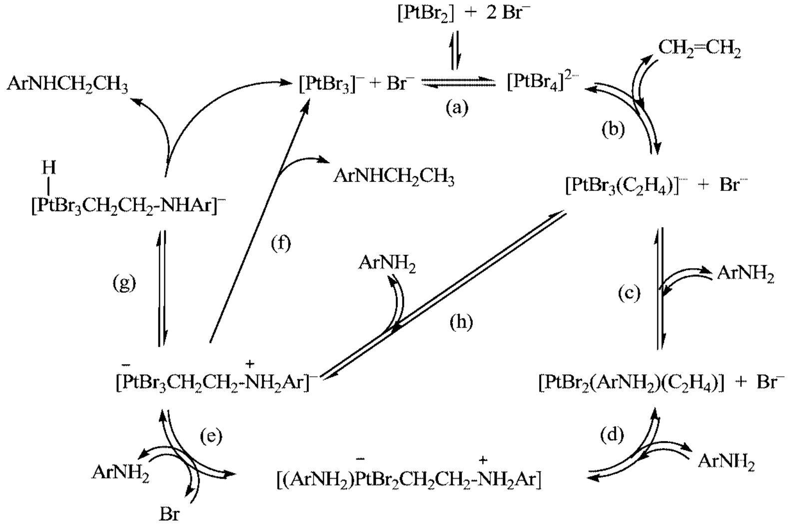
These experiments confirm that $n\text{Bu}_4\text{PBr}$ has a promoting role on the catalytic activity of the $[\text{PtBr}_2]$ precursor. Furthermore, they show that the phosphonium bromide has also a limiting effect when used in larger amounts. This observation may suggest the participation of the bromide ions of $n\text{Bu}_4\text{PBr}$ in an equilibrium implicating the active platinum species (vide infra).

On the basis of these promising results, we examined the evolution of the reaction with time under the best conditions determined so far. This study was intended to detect possible catalyst poisoning. The results indicate some activity decrease with time, but this is much less pronounced than that for the corresponding hydroamination of ethylene. This observation may be due to several facts. Firstly, the main reaction product, *N*-(2-hexyl)aniline is much more sterically demanding than *N*-ethylaniline, which results in the retarded formation of the inactive bis(*N*-alkylaniline)platinum(II) species. Secondly, this decrease in activity could simply be due to the decrease in the 1-hexene concentration, which was shown to be an important parameter (see above). Finally, this observation could also be due to the isomerization of 1-hexene. Hence, the composition of the alkene fraction was examined at the end of several runs (^{1}H NMR spectroscopic analysis). The results indicate that the $[\text{PtBr}_2]/n\text{Bu}_4\text{PBr}$ system is a poor isomerization catalyst (irrespective of the reaction pathway).[58]

The promoting effect of $n\text{Bu}_4\text{PBr}$ for the $[\text{PtBr}_2]$-catalyzed hydroamination of alkenes was thus confirmed, but remained to be explained. The study of the hydroamination of norbornene with aniline (vide supra) indicates that for a given cationic moiety, ionic solvents associated with a bromide ion give a higher catalytic efficiency than those associated with a chloride ion. This observation was confirmed for the hydroamination of 1-hexene with aniline. Indeed, replacement of $n\text{Bu}_4\text{PBr}$ by $n\text{Bu}_4\text{PCl}$ resulted in the formation of (**12** + **13**) with a TON of 5 (instead of 57). It is thus clear that the anionic part of the phosphonium salt plays an important role: in contrast to chloride ions, bromide ions strongly enhance the catalytic activity. Such halide ion effects have already been observed, but are generally poorly understood,[59–61] except in some cases.[62]

A possible explanation for the promoting role of $n\text{Bu}_4\text{PBr}$ is outlined below (Scheme 3). For simplicity, the alkene considered is ethylene and the $[n\text{Bu}_4\text{P}]^+$ cation has been omitted.

Equilibria (a) and (b) represent the solubilization of $[\text{PtBr}_2]$ in phosphonium bromide and the coordination of ethylene. These steps are analogous to the formation of the Zeise's salt from $\text{K}_2[\text{PtCl}_4]$ and ethylene in water.[29] Note that the platinum–olefin bond in $[\text{PtBr}_3(\text{C}_2\text{H}_4)]^-$ is known to be stronger than that in the chlorido equivalent.[63] In such complexes, the ethylene ligand is displaced by halide ions at high concentrations,[29] which could be the reason for the decrease in activity when very large amounts of $n\text{Bu}_4\text{PBr}$ are present (vide supra).



Scheme 3. Pt^{II}-catalyzed hydroamination of ethylene promoted by bromide ions.

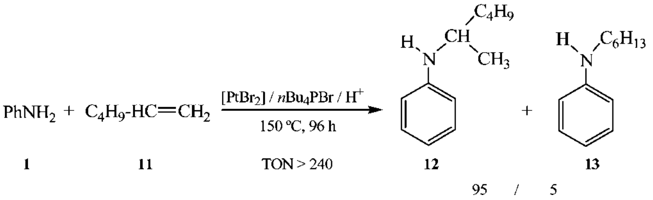
Equilibrium (c) represents the displacement of a halide ligand by aniline, similar to that involved in the formation of e.g. *trans*-$[PtCl_2(C_2H_4)(amine)]$ by reaction of $K[PtCl_3(C_2H_4)]$ with an amine.[64] This equilibrium may be shifted to the left in the presence of a very large excess of bromide ions.

Equilibrium (d) corresponds to the *external*[30c] nucleophilic attack of aniline on the neutral $[PtBr_2(C_2H_4)(C_6H_5NH_2)]$ complex to generate the corresponding zwitterionic complex. However, as indicated above, zwitterionic complexes derived from the attack of aniline have never been observed in detectable quantities (NMR spectroscopy), a failure attributed to the insufficient basicity of aniline. Nevertheless, from our work, the hydroamination of 1-hexene by aniline conducted at *150 °C* with $[PtBr_2]$ in the *absence* of nBu$_4$PBr afforded (**12** + **13**) in nearly stoichiometric amounts. This confirms that the attack of aniline on an alkene coordinated to $[PtBr_2]$ is possible, provided that the reaction is conducted at high temperature. This result may be due to a temperature-promoted evolution of the zwitterionic complex by a further proton-transfer step (vide infra).

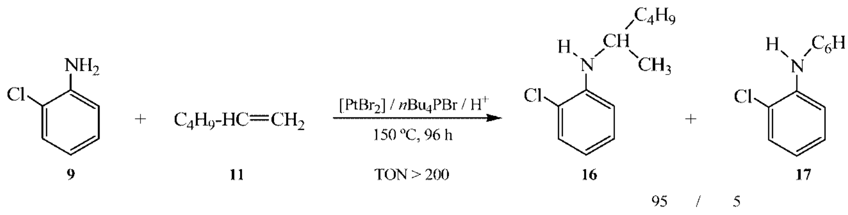
DFT calculations by Togni et al. strongly suggest that the platinum–carbon bond cleavage by protonolysis should be the determining step for the *catalytic* hydroamination of ethylene with ammonia.[49] In our opinion, this proton transfer should be facilitated by two parameters: the acidity of the N–H proton (ammonium part) and the basicity of the platinum center. The acidity of the proton is inversely related to the basicity of the aniline: the less basic the starting arylamine, the easier the proton transfer to the negative center. This hypothesis seems to be confirmed by our observation that the less basic aniline gave the highest TONs for the hydroamination of ethylene. For the basicity of the platinum center in the zwitterionic complex, the intervention of equilibrium (e) may possibly explain the promoting role of the bromide ions (generation of a platinum center bearing *formally* two negative charges). Note that the direct addition of aniline to $[PtBr_3(C_2H_4)]^-$ should lead to the same highly reactive zwitterionic complex [equilibrium (h)]. The liberation of the alkylated aniline proceeds either by direct protonolysis of the platinum–carbon bond [path (f)] or via a platinum hydride, followed by reductive elimination [path (g)].

Another point has to be considered. During the *catalytic* hydroamination of ethylene with aniline, a gradual poisoning effect was observed, which could be attributed to the reaction product *N*-ethylaniline. 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 (TON = 80). It is tentatively proposed that the poisoning effect by the alkylated aniline is attenuated by the presence of an 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 equilibria (a)–(c). A more complete study of the effect of the halide ions on hydroamination reactions has recently been carried out and is presented further on in this review.

Finally, the role of an added catalytic source of protons was examined. Reactions performed under standard conditions, except for the additional presence of anilinium sulfate (3 equiv. per mol of the Pt species), allowed the formation of (**12** + **13**) with 70 cycles for a reaction time of 10 h, 180 cycles after 48 h, and finally 243 cycles after 96 h [Equation (12)] (70% yield based on aniline). Interestingly,



(12)



(13)

under the above conditions, the formation of the side-products **14** and **15** is limited to only traces (TON < 1).

Control experiments showed that, in the *absence* of $n\mathrm{Bu_4PBr}$, the $[\mathrm{PtBr_2}]/\mathrm{H^+}$ system allowed the formation of (**12** + **13**) with a TON of about 10, thus evidencing that the major activation is induced by $n\mathrm{Bu_4PBr}$. Furthermore, in the absence of $[\mathrm{PtBr_2}]$, the $n\mathrm{Bu_4PBr/H^+}$ system yielded (**12** + **13**) with a TON of 2 (vs. $\mathrm{H^+}$ catalyst), which indicates that simple Brønsted catalysis is not significant.

Lastly, the hydroamination of 1-hexene with 2-chloroaniline, catalyzed by the $[\mathrm{PtBr_2}]/n\mathrm{Bu_4PBr/CF_3SO_3H}$ system, afforded the expected alkylated chloroanilines (**16** + **17**) with TON = 200 and a 95% Markovnikov selectivity [Equation (13)].

From a practical point of view, it is very important to note that the above *Pt^{II}-catalyzed hydroamination reactions can be conducted under aerobic conditions without loss in yield*. To the best of our knowledge, the ligandless, cheap and nontoxic $[\mathrm{PtBr_2}]/n\mathrm{Bu_4PBr/H^+}$ system is the most efficient ever reported (up to the end of 2006) for the catalytic *intermolecular* hydroamination of an α-olefin such as 1-hexene.

2.4. Platinum-Catalyzed Transformation of Anilines into 2-Alkylquinolines

During the above studies, some unexpected observations involving the formation of quinoline derivatives were noticed. These have been examined in more detail, which allows the very interesting properties of $\mathrm{Pt^{II}}$-based catalysts for different C–H activation processes to be highlighted.[65] Although these studies are beyond the scope of this paper, we have evidenced, for the first time, that 2-alkylquinolines are formed by a multistep, platinum(II)-catalyzed, in situ transformation of *N*-alkylanilines (Scheme 4).[66] In other words, quinoline derivatives originate from the primary hydroamination products. This new, platinum(II)-catalyzed transformation is strongly favored by the presence of an alkene (hydrogen acceptor) and compares favorably with the recently reported ruthenium-catalyzed formation of 2-alkylquinoline from aniline and trialkylamines.[67]

2.5. The Promoting Effect of Halide Ions for the Pt^{II}-Catalyzed Hydroamination of Alkenes

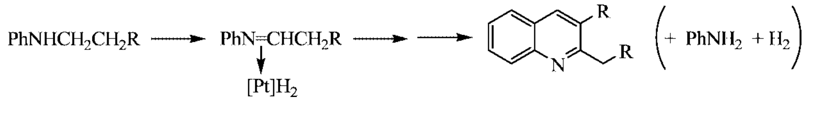
In the early stages of this work, ionic liquids and molten salts were first considered as solvents. The beneficial effect of some of them, especially $n\mathrm{Bu_4PBr}$, was identified for the hydroamination of norbornene and ethylene. However, for the hydroamination of 1-hexene, it was pointed out that the catalytic efficiency depended upon both the $n\mathrm{Bu_4PX}/[\mathrm{PtBr_2}]$ ratio and the nature of the anion ($\mathrm{Br^-} >> \mathrm{Cl^-}$). This is obviously the heart of the matter since, under classical conditions, the reaction of amines with $\mathrm{Pt^{II}}$–alkene complexes leads to stable zwitterionic species.[30d]

In order to deepen our understanding, we investigated the influence of the $n\mathrm{Bu_4PX}/[\mathrm{PtBr_2}]$ ratio as well as that of the nature of the associated halide anion $\mathrm{X^-}$ on the hydroamination of ethylene with aniline. For this study, experiments were conducted without the $\mathrm{H^+}$ cocatalyst in order to better observe, if possible, the influence of the phosphonium halides.

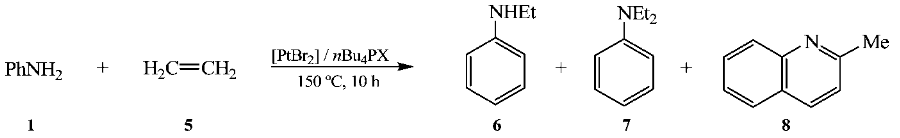
At first, it was verified that in the absence of $[\mathrm{PtBr_2}]$ no reaction occurred between aniline (45 mmol) and ethylene (25 bar, ca. 100 mmol) over 96 h at 150 °C. For these control experiments, the presence of $n\mathrm{Bu_4PBr}$ (ca. 7 g) had no effect. In contrast, $[\mathrm{PtBr_2}]$-based systems exhibited catalytic activity for the formation of hydroamination products. Two parameters have been considered: the nature of the halide anion $\mathrm{X^-}$ associated with the phosphonium salt $n\mathrm{Bu_4PX}$ and the $n\mathrm{Bu_4PX}/[\mathrm{PtBr_2}]$ ratio. The most general reaction is represented by [Equation (14)].

Compounds **6** and **7** are direct hydroamination products. Since the formation of **8** was shown to occur in situ from 2 equiv. of **6** (vide supra), the activity of the catalytic system is best represented by the total TON calculated for the amount of **6** initially formed (Table 6, see footnote [b]).[68]

As shown in Table 6, the three phosphonium halides enhance the catalytic activity. For $n\mathrm{Bu_4PCl}$, the maximum activity was obtained using 65 equiv. of phosphonium halide, whereas for both $n\mathrm{Bu_4PBr}$ and $n\mathrm{Bu_4PI}$, the maximum catalytic activity was reached with a $n\mathrm{Bu_4PX}/[\mathrm{PtBr_2}]$ ratio of approximately 10. It is quite clear that these phosphonium halides, first intended to play the role of ionic solvents,[50,53]



Scheme 4. Formation of 2-alkylquinolines from *N*-alkylanilines.



(14)

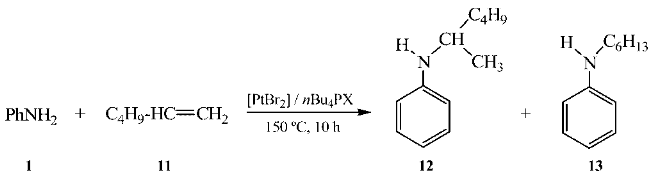
Table 6. Hydroamination of ethylene with aniline catalyzed by $[PtBr_2]/nBu_4PX$ systems.[a]

Run	nBu_4PX (equiv. per mol Pt)	$[PtBr_2]$ [mmol]	Total TON[b]	Reaction products: % **6**	**7**	**8**
23	–	–	–	–	–	–
24	–	0.13	20	100	–	–
25	nBu_4PCl (10)	0.13	50	91	–	9
26	nBu_4PCl (65)	0.13	105	92	2	6
27	nBu_4PCl (150)	0.13	80	95	1	3
28	nBu_4PBr (5)	0.13	140	88	4	7
29	nBu_4PBr (10)	0.13	150	89	3	8
30	nBu_4PBr (65)	0.13	130	87	2	11
31	nBu_4PBr (150)	0.13	88	86	1	11
32	nBu_4PI (5)	0.13	110	93	2	4
33	nBu_4PI (10)	0.13	135	90	2	7
34	nBu_4PI (65)	0.13	100	80	1	17
35	nBu_4PI (150)	0.13	5	100	–	–

[a] Aniline: 45 mmol, ethylene: 25 bar at room temperature (ca. 100 mmol), 150 °C, 10 h. [b] Turnover number, TON calculated as $TON_{\mathbf{6}} + TON_{\mathbf{7}} + 2\,TON_{\mathbf{8}}$.

must rather be considered as promoters or cocatalysts. However, very large quantities of these "promoters" decrease their positive effect, so that their role is difficult to rationalize. The "promoting" order of the nBu_4PX salts for the hydroamination of ethylene seems to be $Br^- > I^- > Cl^-$.

The $[PtBr_2]/nBu_4Br$ system is the only efficient catalyst reported so far for the hydroamination of 1-hexene with aniline. Since this reaction occurs with a particularly promising regioselectivity (95% Markovnikov), it was interesting to compare the activating ability of several nBu_4PX salts associated with $[PtBr_2]$ with their possible influence on the regioselectivity [Equation (15)]. The most significant results are summarized in Table 7.[68]



(15)

As may be seen from Table 7,[68] $[PtBr_2]$ alone did not catalyze the hydroamination of 1-hexene with aniline (run 36). In the same way, association of $[PtBr_2]$ with either nBu_4PPF_6 or nBu_4PCl (runs 37 and 38) resulted in very low TONs. In contrast, as already found, association with nBu_4PBr promoted a significant catalytic activity (TON = 57, run 39). An even higher activity was obtained with the $[PtBr_2]/nBu_4PI$ system, for which a TON of 83 was reached (run 40). For Equation (15), the "promoting" effect of the phosphonium halides varies as $I^- > Br^- >> Cl^-$. The nature of the halide anion has no effect on the regioselectivity.

Table 7. Hydroamination of 1-hexene with aniline catalyzed by $[PtBr_2]/nBu_4PX$ systems.[a]

Run	Catalytic system	Total TON (**12** + **13**)	Regioselectivity (**12**/**13**)
36	$[PtBr_2]$	1	n.d.
37	$[PtBr_2]/nBu_4PPF_6$	3	n.d.
38	$[PtBr_2]/nBu_4PCl$	5	n.d.
39	$[PtBr_2]/nBu_4PBr$	57	95:5
40	$[PtBr_2]/nBu_4PI$	83	95:5
41	$[PtBr_2]/nBu_4PBr/I_2$[b]	115	95:5

[a] Aniline: 45 mmol, 1-hexene: 90 mmol, $[PtBr_2]$: 0.13 mmol, nBu_4PX: 8.45 mmol, 150 °C, 10 h. [b] I_2: 0.13 mmol.

Iodide effects in transition-metal-catalyzed reactions are well known, and in some cases their role has been rationalized.[62] The beneficial effect of molecular iodine (generally used in large amounts) has also been observed in some transition-metal-catalyzed reactions.[69] This proved to be the case also for the Pt^{II}-catalyzed hydroamination of 1-hexene. With the new $[PtBr_2]/nBu_4PBr/I_2$ system (1:65:1 ratio), an even higher activity (TON = 115, run 41) than that obtained with the $[PtBr_2]/nBu_4PBr$ system (TON = 57, run 39) was reached. The use of higher amounts of iodine (vs. $[PtBr_2]$) had no beneficial effect on the TON.

These results agree with the general mechanism proposed (see Scheme 3), but suggest that the halide anions also play a role in other step(s) of the catalytic cycle, such as the coordination of the alkene and the attack of aniline on the coordinated alkene, or even by postponing poisoning effects.

Drent et al. recently reported a detailed study of the halide-anion-promoted palladium-catalyzed hydroformylation of internal alkenes to linear alcohols.[70] In the case of the $[(bcope)Pd(OTf)_2]$ complex [bcope = bis(cyclooctyl)phosphinoethane], they found that the use of substoichiometric amounts (vs. Pd) of added halide anions strongly promoted the reaction rate. Most of their observations were rationalized in a qualitative way. However, it is clear that the halide-anion-promoting effect pointed out in the present work is different (no phosphorus ligand), and further detailed studies are required to gain a complete insight into these phenomena.

We have nevertheless shown that nBu_4PX salts ($X = Cl^-$, Br^-, I^-) have a strong promoting effect on the Pt^{II}-catalyzed hydroamination of ethylene and 1-hexene with aniline. In the case of ethylene, nBu_4PBr is the most efficient activator, whereas nBu_4PI is more efficient than nBu_4PBr in the case of 1-hexene. A special effect of molecular iodine has also been pointed out.[68]

2.6. Pt^{IV} Salts Also Allow the Hydroamination Reaction!

In the course of the above studies, we examined the properties of Pt^{IV} salts as catalytic precursors for the hydroamination of ethylene with aniline [see Equation (14)]. To the best of our knowledge, no hydroamination reaction, neither stoichiometric nor catalytic, has ever been reported by using Pt^{IV} precursors.[21,29] The first results of this study are summarized in Table 8. Both Pt^{IV} salts and Pt^{IV}/nBu_4X systems (1:65 ratio) have been considered.

Table 8. Hydroamination of ethylene with aniline catalyzed by Pt^{IV}-based systems.[a]

Run	Pt^{IV} system	$nBu_4PX/[PtBr_2]$ ratio	Total TON[b]	Reaction products: % **6**	**7**	**8**
42	$[PtBr_4]$	–	50	89	4	7
43	$[PtBr_4]/nBu_4PCl$	65	75	84	14	2
44	$[PtBr_4]/nBu_4PBr$	65	135	85	6	7
45	$[PtBr_4]/nBu_4PI$	65	110	84	2	13
46	$[PtCl_4]$	–	15	100	–	–
47	$[PtCl_4]/nBu_4PCl$	65	45	98	2	–
48	$[PtCl_4]/nBu_4PBr$	65	120	90	3	7
49	$[PtCl_4]/nBu_4PI$	65	110	86	2	11

[a] Aniline: 45.5 mmol, ethylene: 25 bar at room temperature (ca. 100 mmol), $[PtX_4]$: 0.13 mmol, 150 °C, 10 h. [b] Turnover number, TON calculated as $TON_{\mathbf{6}} + TON_{\mathbf{7}} + 2\ TON_{\mathbf{8}}$.

The first and most important feature that emerges from Table 8 is that Pt^{IV} bromide and chloride are shown for the first time to exhibit a catalytic activity for the hydroamination reaction: $[PtBr_4]$ (run 42) is even more active than $[PtBr_2]$ (run 24, Table 6).[71] Secondly, association of nBu_4PX with these catalytic precursors promotes a significant increase in the catalytic activity. Although the role of the nBu_4PX/Pt^{IV} ratio has not yet been studied, the most efficient "promoter" seems to be nBu_4PBr, as was the case for the Pt^{II} systems (see above). For both Pt^{II} and Pt^{IV} catalytic precursors, the promoting ability exhibited by the phosphonium halide seems to follow the order $Br^- > I^- >> Cl^-$. It is again tentatively suggested that this unusual order is indicative that these halide anions play a role in different steps of the catalytic cycle.

Conclusions

In the previous sections, we have described our progress in the study of the catalytic hydroamination of *nonactivated* alkenes with arylamines. Starting from the idea that molten salts or ionic liquids may be used as solvents for such reactions, we managed to show that tetraalkylphosphonium halides, in fact, play the role of "promoters", especially nBu_4PBr and nBu_4PI. It has been clearly evidenced that the promoting effect of these "cocatalysts" depends only upon their anionic moiety. The role of these anions is difficult to rationalize at the present time. Nevertheless, we succeeded in designing catalytic Pt^{II}- and Pt^{IV}/nBu_4PX systems that are the most active catalysts reported to date for the hydroamination of ethylene with amines, especially weakly basic amines such as anilines. The Pt^{II}/nBu_4PBr combination exhibits an unprecedented catalytic activity for the hydroamination of a higher alkene such as 1-hexene. In addition, the hydroamination of α-olefins has been found to occur with a very high regioselectivity (> 95%, Markovnikov), which opens the possibility to study an enantioselective version of this reaction. The interest in these promising catalytic systems for possible applications is heightened by the fact that the reactions can be conducted under aerobic conditions without loss of yield.

Acknowledgments

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