1264 *Organometallics* **2004,** *23,* 1264−1268

The First Platinum-Catalyzed Hydroamination of Ethylene

Jean-Jacques Brunet,* Magali Cadena, Ngoc Chau Chu, Ousmane Diallo,
Kane Jacob, and Emmanuelle Mothes

*Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241, Liée par Conventions à
l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 Route de Narbonne,
31077 Toulouse Cedex 04, France*

Received September 18, 2003

The platinum-catalyzed hydroamination of ethylene with aniline is reported for the first time. Using $PtBr_2$ as a catalyst precursor in n-Bu_4PBr under 25 bar of ethylene pressure affords *N*-ethylaniline with 80 turnovers after 10 h at 150 °C. The reaction simultaneously produces 2-methylquinoline in ca. 10 cycles. The catalytic activity is slightly improved by increasing the reaction temperature or the ethylene pressure and strongly depends on the aniline/platinum ratio. The beneficial effects of added $P(OMe)_3$ (2 equiv/$PtBr_2$) or of a proton source (3 equiv/$PtBr_2$) have also been pointed out. A gradual poisoning by *N*-ethylaniline has been observed, which could be minimized by using biphasic systems. The best result for the hydroamination with aniline (TON = 145 after 10 h at 150 °C) has been obtained in a biphasic system (n-Bu_4PBr/decane) in the presence of $C_6H_5NH_3^+$ (3 equiv/$PtBr_2$). The basicity of the arylamine has been shown to play an important role: the lower the basicity, the higher the TON. Thus, the hydroamination of ethylene with the weakly basic 2-chloroaniline in the presence of the $PtBr_2/H^+$ catalytic system (0.3% mol) for 72 h at 150 °C yields *N*-ethyl-2-chloroaniline as the sole reaction product (70% yield based on the amine charged) with TON = 250. When conducted with 1% of the above catalytic system, the reaction resulted in nearly quantitative conversion of 2-chloroaniline.

Introduction

The catalytic hydroamination of alkenes (an atom-economic process) is a subject of current interest both for fundamental research and for the chemical industry.[1] Indeed, although significant improvements have been reported for the hydroamination of alkynes,[2] 1,3-dienes,[3] and styrenes,[4] as well as for the *intramolecular* hydroamination of alkenes,[5] the *intermolecular* hydroamination of nonfunctionalized alkenes is still a challenge for chemists. Since the first report by Coulson in 1971 on the Rh- or Ir-catalyzed hydroamination of ethylene with secondary amines,[6] only a few catalytic systems, based on rhodium or iridium, and very recently on organolanthanides, have been shown to exhibit some activity for such reactions.[7]

It has been known for a long time that alkenes coordinated to platinum(II) are susceptible to nucleophilic attack.[8] The case of amine nucleophiles has been particularly studied.[9−13] Stable zwitterionic complexes are formed by reaction of secondary amines, such as

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* Corresponding author. E-mail: brunet@lcc-toulouse.fr.

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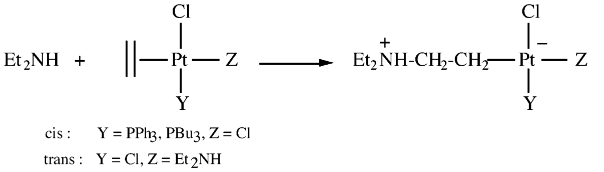
10.1021/om030605e CCC: $27.50

Table 1. Reaction of Aniline[a] with Ethylene[b] in Different Solvents

run	$PtBr_2$ (mmol)	solvent	reaction time (h)	PhNHEt (TON)[f]	$PhNEt_2$ (TON)[f]	2-Me-quinoline (TON)[f]	overall yield (%)[g]
1	0.13	*n*-Bu_4PBr[c]	10	80	~1	11	27
2	0.13	aniline[d]	10	23	~1	3	8
3	0.13	THF[e]	10	34	~1	4	11

[a] 45 mmol. [b] 25 bar, 150 °C. [c] 7.2 g. [d] 10 mL. [e] 7.5 mL. [f] TON = turnover number. [g] Based on charged aniline.

diethylamine, on coordinated ethylene in *cis*- or *trans*-$[Pt(C_2H_4)Cl_2L]$ (eq 1). These have been isolated and characterized by NMR spectroscopy[10,11] and in one case by single-crystal X-ray diffraction.[10d]



(1)

Although similar zwitterionic complexes have been observed with varied amines, the reaction is limited to amines of sufficient basicity ($pK_a > 5$). For instance, *aniline* failed to give an observable addition compound when reacted with *trans*-$[Pt(C_2H_4)(Et_2NH)Cl_2]$.[10b,d,11]

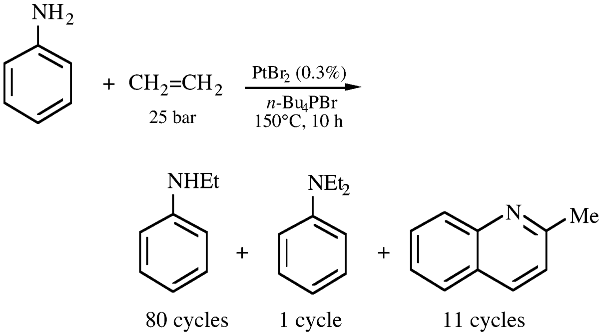
Liberation of the alkylated amine by cleavage of the platinum−carbon bond of the above zwitterionic complexes occurs *only* by treatment with HCl or $NaBH_4$.[10] The overall result is thus a *stoichiometric* hydroamination of ethylene.[14]

We recently reported the beneficial use of selected ionic liquids[15] for the hydroamination of norbornene with aniline using rhodium(III) complexes as catalysts.[16] We also mentioned for the first time that platinum salts or complexes were active catalyst precursors for the hydroamination of norbornene in *n*-Bu_4PBr.

We now wish to report the first example of a platinum-catalyzed hydroamination of ethylene. Interestingly, the reaction occurs *catalytically* with aniline and other arylamines.

Results and Discussion

The first runs were performed in *n*-Bu_4PBr (mp = 103 °C). In a typical experiment the reaction of aniline (45 mmol) with ethylene (25 bar at RT) in *n*-Bu_4PBr (7.2 g) for 10 h at 150 °C in the presence of $PtBr_2$ (0.13 mmol) reproducibly afforded (GC−MS and quantitative GC analysis) three products: *N*-ethylaniline (80 cycles), 2-methylquinoline (11 cycles), and *N*,*N*-diethylaniline (1 cycle). Some other organic compounds were detected in trace amounts (<0.5%), among which 1,2,3,4-tetrahydro-2-methylquinoline could be identified on the basis of GC−MS analysis.



(2)

The formation of *N*-ethylaniline with TON = 80 is the first example of a *platinum*-catalyzed hydroamination of ethylene. Note that the selectivity of mono- versus dialkylation of aniline is high. With regards to catalysis of reaction 2 by other transition metals, the only precedent is the reaction of aniline with ethylene in the presence of $RhCl_3/2PPh_3$.[7a] However, the rhodium system was less active (*N*-ethylaniline: 30 cycles; 2-methylquinoline: 10 cycles) under more forcing conditions (100 bar, 200°C) and with a longer reaction time (72 h).

The catalytic formation of 2-methylquinoline is also noteworthy since it involves an *ortho*-C−H activation of aniline as the first step of a complex catalytic cycle.[7b] Such catalytic C−H activation on aniline derivatives has very few precedents,[7a,17,18] but has already been observed in our group for both the Rh- and Pt-catalyzed hydroamination of aniline with norbornene, producing 2-norbornylaniline.[16,19] In reaction 2, no traces of 2-ethylaniline or *N*-ethyl-2-ethylaniline could be detected.

Analysis of the remaining gases after reaction 2 (see Experimental Section) indicated the presence of significant amounts of ethane (not quantified) and the absence of any ethylene oligomer, in contrast with what has been found for the $RhCl_3$-based system.[7a] The formation of ethane is tentatively proposed to occur by a platinum-catalyzed transfer hydrogenation of ethylene from 1,2,3,4-tetrahydro-2-methylquinoline, which is believed to be a reaction intermediate.[7a] Such transfer hydrogenations from tetrahydroquinoline are known to occur in the presence of rhodium(III) salts at 170−190 °C.[20]

Control experiments (Table 1) indicated that reaction 2 also occurs using THF or aniline as solvent, although in these solvents the reaction rate was much lower than in *n*-Bu_4PBr, as previously found for the hydroamination of norbornene.[16]

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Table 2. Reaction of Aniline[a] with Ethylene:[b,c] Influence of the Reaction Temperature

run	$PtBr_2$ (mmol)	reaction time (h)	reaction temp (°C)	PhNHEt (TON)[d]	$PhNEt_2$ (TON)[d]	2-Me-quinoline (TON)[d]	overall yield (%)[e]
4	0.13	10	120	43	∼1	8	15
1	0.13	10	150	80	∼1	11	27
5	0.13	10	180	89	∼2	15	31

[a] 45 mmol. [b] 25 bar, 150 °C. [c] In n-Bu_4PBr: 7.2 g. [d] TON = turnover number. [e] Based on charge aniline.

Table 3. Reaction of Aniline[a] with Ethylene:[b] Influence of the Ethylene Pressure

run	$PtBr_2$ (mmol)	pressure (bar)	reaction time (h)	PhNHEt (TON)[c]	$PhNEt_2$ (TON)[c]	2-Me-quinoline (TON)[c]	overall yield (%)[d]
6	0.13	10	10	73	∼1	8	24
1	0.13	25	10	80	∼1	11	27
7	0.13	35	10	83	∼1	18	30
8	0.13	50	10	90	∼1	20	32

[a] 45 mmol. [b] 150 °C in n-Bu_4PBr: 7.2 g. [c] TON = turnover number. [d] Based on charged aniline.

Table 4. Reaction of Aniline with Ethylene:[a,b] Influence of the Pt/Aniline Ratio

run	$PtBr_2$ (mmol)	aniline (mmol)	reaction time (h)	PhNHEt (TON)[c]	$PhNEt_2$ (TON)[c]	2-Me-quinoline (TON)[c]	overall yield §%)[d]
9	0.13	90	10	99	∼1	15	16
1	0.13	45	10	80	∼1	11	27
10	0.13	22	10	58	∼1	7	39
11	0.13	9	10	30	∼1	4	51

[a] 25 bar, 150 °C. [b] In n-Bu_4PBr: 7.2 g. [c] TON = turnover number. [d] Based on charged aniline.

Table 5. Reaction of Aniline with Ethylene:[a,b] Influence of the Reaction Time

run	$PtBr_2$ (mmol)	aniline (mmol)	reaction time (h)	PhNHEt (TON)[c]	$PhNEt_2$ (TON)[c]	2-Me-quinoline (TON)[c]	overall yield (%)[d]
1	0.13	45	10	80	∼1	11	27
12	0.13	45	5	72	∼1	11	24
13	0.13	45	2.5	64	∼1	10	22
14	0.13	45	1	37	∼1	5	12

[a] 25 bar, 150 °C. [b] In n-Bu_4PBr: 7.2 g. [c] TON = turnover number. [d] Based on charged aniline.

On the basis of the above results, and owing to the easy separation of reaction products (and potential recycling of the catalytic system), further experiments were conducted in n-Bu_4PBr. We examined the influence of the main reaction parameters, being successively the reaction temperature, the ethylene pressure, the platinum/aniline ratio, and the reaction time.

As may be seen from Table 2, increasing the reaction temperature from 120 to 150 °C nearly doubles the TON in *N*-ethylaniline. However, the temperature effect between 150 and 180 °C is less important. So, for experimental convenience, further experiments were carried out at 150 °C.

The influence of the ethylene pressure was examined in the range 10−50 bar. As indicated in Table 3, increasing the ethylene pressure slightly increases the TON for *N*-ethylaniline, but has a more pronounced effect on the formation of 2-methylquinoline (TON from 8 to 20).

Interestingly, the amine/platinum ratio has a strong influence on the formation of both *N*-ethylaniline and 2-methylquinoline. Results in Table 4 indicate that increasing the aniline concentration (while keeping the platinum amount constant) increases the TON, both for the formation of *N*-ethylaniline (× 3.3) and for the formation of 2-methylquinoline (× 4.3). Nevertheless, this decreases the overall yield (calculated on charged aniline).

These results clearly confirm the beneficial effect of the phosphonium salt. Indeed, run 9 (Table 4) conducted with 90 mmol of aniline in the presence of n-Bu_4PBr gave a much higher TON (99) than run 2 (Table 1) (TON = 23) conducted with nearly the same amount of aniline (110 mmol), but in the absence of the phosphonium salt.

The overall turnover rate observed for the formation of *N*-ethylaniline in reaction 2 is of 8 h^{-1}. To appreciate the evolution of the reaction with time, further experiments were performed using shorter reaction times. As may be seen from Table 5, a turnover rate of 37 h^{-1} was observed during the first hour for the production of *N*-ethylaniline (run 14). For longer reaction times, the overall turnover rate decreased, suggesting a gradual poisoning of the catalyst.

To address the possible poisoning by either of the two main reaction products, new runs were performed under the conditions of eq 2, but in the presence of added 2-methylquinoline (1.5 mmol) or *N*-ethylaniline (15 mmol). After 10 h at 150 °C, the first reaction showed no significant difference with run 1, whereas the reaction conducted in the presence of added *N*-ethylaniline indicated a further formation of *N*-ethylaniline corresponding to less than 40 cycles. Still more convincing is the observation that pretreatment of a mixture $PtBr_2$/aniline/*N*-ethylaniline (1/350/100 mmol) for 10 h at 150 °C before addition of ethylene resulted in a relatively inactive system for the production of *N*-ethylaniline, but still active for the formation of 2-methylquinoline (9 cycles after 10 h). These results confirm that in reaction 2 the increase of *N*-ethylaniline concentration results

Table 6. Reaction of Aniline[a] with Ethylene[a] in a Biphasic System (n-Bu_4PBr[c] + decane[d])

run	$PtBr_2$ (mmol)	reaction time (h)	PhNHEt (TON)[e]	$PhNEt_2$ (TON)[e]	2-Me-quinoline (TON)[e]	overall yield (%)[f]
15	0.13	10	115	2	17	38
16	0.13	5	100	~1	13	33
17	0.13	2.5	75	~1	10	25
18	0.13	1	45	~1	8	16

[a] 45 mmol. [b] 25 bar, 150 °C. [c] 7.2 g. [d] 4.5 mL. [e] TON = turnover number. [f] Based on charged aniline.

Table 7. Reaction of Aniline[a] with Ethylene[b] in the Presence of Phosphorus Ligands

run	$PtBr_2$ (mmol)	ligand (mmol)	PhNHEt (TON)[c]	$PhNEt_2$ (TON)[c]	2-Me-quinoline (TON)[c]	overall yield (%)[d]
19	0.13	PEt_3 (0.26)	2	~1	2	1
20	0.13	PPh_3 (0.26)	6	~1	13	6
21	0.13	$P(OMe)_3$ (0.26)	110	~1	13	36

[a] 45 mmol, in n-Bu_4PBr: 7.2 g. [b] 25 bar, 150 °C, 10 h. [c] TON = turnover number. [d] Based on charged aniline.

Table 8. Hydroamination of Ethylene:[a,b] Influence of the Basicity of Arylamines[c]

run	$ArNH_2$ (Ar =)	pK_a	ArNHEt (TON)[d]	$ArNEt_2$ (TON)[d]	"quinoline derivative" (TON)[d]	overall yield (%)[e]
22	4-$MeOC_6H_4$	5.34	22	~1	11	9
23	4-MeC_6H_4	5.08	55	~1	17	21
1	C_6H_5	4.63	80	~1	11	27
24	2-MeC_6H_4	4.44	85	~1	11	27
25	4-ClC_6H_4	4.15	93	~1	11	31
26	2-ClC_6H_4	2.65	110	0	0	32

[a] $PtBr_2$: 0.13 mmol, n-Bu_4PBr (7.2 g). [b] 25 bar for 10 h at 150 °C. [c] 45 mmol. [d] TON = turnover number. [e] Based on the charged $ArNH_2$.

in a gradual poisoning of the catalyst and therefore in a decrease of the reaction rate with time.

On the basis of these observations, it was decided to perform catalytic runs in a biphasic medium consisting of n-Bu_4PBr and a high-boiling (>170 °C), *nonmiscible* hydrocarbon, to lower the *N*-ethylaniline concentration in the catalyst phase.

Performing run 15 (Table 6) under the conditions of run 1 (Table 1) but in the presence of decane (4.5 mL for 7.2 g of phosphonium salt) effectively allowed the achievement of higher TONs (*N*-ethylaniline: 115 cycles; *N*,*N*-diethylaniline: 2 cycles; 2-methylquinoline: 17 cycles).

As a control experiment, using decane (7 mL) in the absence of n-Bu_4PBr for 10 h at 150 °C gave *N*-ethylaniline (20 cycles) and 2-methylquinoline (5 cycles). However, even under biphasic conditions, a gradual reduction in rate was observed (Table 6). Nevertheless, this biphasic system allows TONs unprecedented for *intermolecular* hydroamination reactions to be obtained.[1] In particular, the above system is more efficient than the rhodium-based system $RhCl_3/2PPh_3$ (vide supra).[7b]

The possible influence of phosphorus ligands (2 equiv/$PtBr_2$) was also examined. As may be seen from Table 7, in the presence of PEt_3 the formation of both *N*-ethylaniline and 2-methylquinoline is dramatically inhibited. In the presence of PPh_3, only the formation of *N*-ethylaniline is inhibited. In contrast, in the presence of $P(OMe)_3$ (run 21), the TON for the formation of *N*-ethylaniline is increased up to 110 cycles (vs 80 for $PtBr_2$ alone, run 1, Table 1), whereas the formation of 2-methylquinoline is practically unchanged.

It must be noted that the detrimental effect of PPh_3 (run 20) is in sharp contrast with what has been reported for the $RhCl_3$-catalyzed hydroamination of ethylene with aniline.[7b] Indeed, in the case of $RhCl_3$, the presence of PPh_3 dramatically increased the catalytic activity for the production of *N*-ethylaniline (from 12.6 cycles in 7 days to 30 cycles in 2 days).[7b]

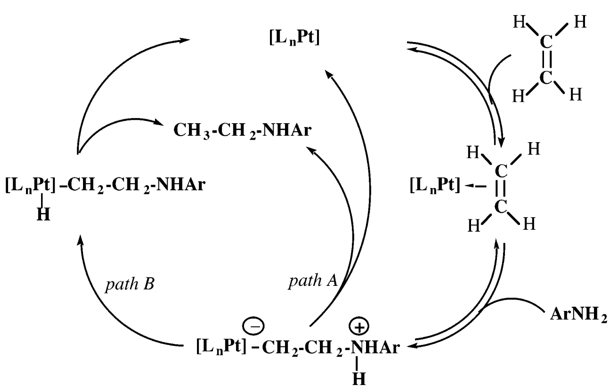
The possible influence of a proton source was also tested. Performing reaction 2 in the presence of anilinium sulfate (3 equiv/$PtBr_2$) effectively increased the TON from 80 to 130 (using larger amounts of anilinium sulfate did not significantly improve the TON). Under biphasic conditions (n-Bu_4PBr/decane), the presence of anilinium sulfate increased the TON from 115 (run 15, Table 6) to 145, the highest TON observed in the current work for the hydroamination of ethylene with aniline. Similar results were obtained when using CF_3SO_3H (3 equiv/$PtBr_2$) instead of anilinium sulfate.

As indicated in the Introduction, the reaction of amines with coordinated ethylene in $Pt(C_2H_4)Cl_2L$ complexes is only stoichiometric and furthermore limited to amines of sufficient basicity (pK_a > 5). We have now pointed out that the weakly basic aniline (pK_a = 4.63) can be made to react catalytically with ethylene in the presence of $PtBr_2$ in n-Bu_4PBr. However, it seemed interesting to examine further the scope of the reaction with regards to the basicity of the arylamine. Thus, anilines bearing different substituents were reacted with ethylene under the conditions of eq 2. Results are reported in Table 8.

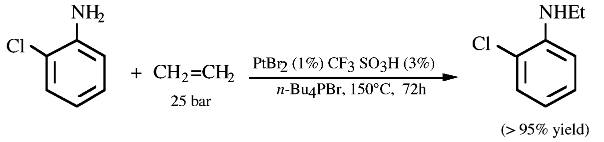
As may be seen, the lower the basicity of the arylamine, the higher the turnover number for the formation of the ArNHEt derivative. This result is in contrast with what has been reported for the *stoichiometric* reaction of amines with ethylene coordinated to platinum(II) centers (vide supra, eq 1). 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 the reactivity of the expected zwitterionic intermediate (vide infra), but also a reduction of the poisoning ability of the resulting ArNHEt derivative (the less basic the $ArNH_2$, the less poisoning the ArNHEt). It must also be noted that in the case of 2-chloroaniline no quinoline-type derivative could be detected.

Finally, on the basis of the observed beneficial effect of a proton source (vide supra), the hydroamination of ethylene with 2-chloroaniline was performed using a $PtBr_2/3CF_3SO_3H$ catalytic system. Under the usual

Scheme 1



conditions (150 °C, 25 bar ethylene), the reaction *selectively* afforded *N*-ethyl-2-chloroaniline with a TON of 250 after 72 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 ($PtBr_2/H^+$) for 72 h at 150 °C (eq 3).



(3)

As far as the reaction mechanisms are concerned, it would be premature to speculate about the exact nature of the active species. Nevertheless, concerning the formation of the *N*-ethylated arylamines, our results seem in good agreement with a catalytic cycle (Scheme 1) involving a zwitterionic intermediate (as in eq 1) formed by nucleophilic attack of the arylamine on ethylene coordinated to a platinum(II) center.

The formation of a zwitterionic complex in the case of arylamines (never observed in previously reported stoichiometric reactions, vide supra) should be favored by the highly polar ionic solvent,[15] even if this were a reversible reaction. As suggested by ab initio DFT studies of the hydroamination of alkenes by activation of the alkene,[21] the rate-determining step of such a catalytic cycle would be the cleavage of the platinum–carbon bond (either by acidolysis, path A, or by formation of a platinum hydride, followed by reductive elimination, path B). This could occur intramolecularly and is therefore facilitated by the greater acidity of the ammonium proton (in fact by the lower basicity of the arylamine nucleophile). The observed effect of the basicity of the arylamine on the TON supports, at least in part, this hypothesis. The cleavage of the platinum–carbon bond can also occur intermolecularly by reaction with an external source of protons. The beneficial effect of an added catalytic source of protons also supports this hypothesis.

Conclusion

The results reported in this paper show for the first time that the *platinum*-catalyzed hydroamination of ethylene by aniline is possible. Some important features have been pointed out, such as the beneficial effect of the ionic solvent, the gradual poisoning of the catalyst by the *N*-alkylated aniline, and the strong effect of the basicity of the arylamine on the course of the hydroamination process. It has been shown that using biphasic reaction media or performing reactions in the presence of a proton source allows for an increase in the turnover number. The best results in terms of TON have been obtained for the hydroamination of ethylene with 2-chloroaniline obtained using a $PtBr_2/3CF_3SO_3H$ system as catalyst, allowing a TON of 250 in 72 h to be reached. These novel hydroamination systems merit a more thorough investigation to determine their scope and limitations, especially for the hydroamination of substituted alkenes. Work is in progress in this area.

Experimental Section

Methods and Materials. Tetra(*n*-butyl)phosphonium bromide (Janssen), *N*,*N*-dibutylaniline (Acros), phosphanes (Acros), and platinum salts (Strem) were used as received. Arylamines (Fluka or Acros) were distilled before use. Ethylene (N25) was purchased from L'Air Liquide. All sample manipulations of transition metal complexes were carried out under argon using standard Schlenk tube and vacuum line techniques.

Instumentation. 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 apparatus. Catalytic experiments were conducted in a 100 mL stainless steel autoclave with a glass liner and a magnetic stirring bar.

Reactions. Hydroamination of Ethylene: Typical Procedure. The autoclave was charged with $PtBr_2$ (46.2 mg, 0.13 mmol) and $n\text{-}Bu_4PBr$ (7.2 g), closed, and submitted to argon-vacuum cycles. Degassed aniline (4.1 mL, 45 mmol) was then syringed into the autoclave and the ethylene pressure adjusted to 25 bar at RT. The temperature was then raised to 150 °C. After 10 h, the autoclave was allowed to cool to room temperature and slowly vented. 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.

Analysis of Gases. At the end of the reaction, the autoclave was allowed to cool to room temperature and the gases were quenched by slowly bubbling into $CDCl_3$ at ca. 200 K. The solution was then transferred in a NMR tube and analyzed by NMR at 218 K, indicating the presence of ethylene and ethane exclusively: ^1H NMR δ 0.85 (s) (ethane) and 5.4 (s) (ethylene); ^{13}C NMR δ 11.2 (q) (ethane) and 123.5 (t) (ethylene).

Acknowledgment. The Centre National de la Recherche Scientifique (France) is acknowledged for financial support. It is a pleasure for the authors to gratefully acknowledge J. Tumpane for his help in editing the English of the manuscript.

OM030605E

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