

Intermolecular hydroamination of non-activated alkenes catalyzed by Pt(II) or Pt(IV)-*n*-Bu₄PX (X = Cl, Br, I) systems: Key effect of the halide anion

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Abstract

Ionic liquids such as *n*-Bu₄PX salts (X = Cl⁻, Br⁻, I⁻) have a strong promoting effect for the Pt(II)-catalyzed hydroamination of ethylene and 1-hexene with aniline. In the case of ethylene, *n*-Bu₄PBr is the most efficient activator, whereas *n*-Bu₄PI is even more efficient in the case of 1-hexene. A special effect of molecular iodine has also been pointed out. Most notably, Pt(IV) precursors are also shown to be active for the hydroamination of ethylene. As for Pt(II) precursors, Pt(IV)-*n*-Bu₄PX associations exhibit enhanced catalytic activities.
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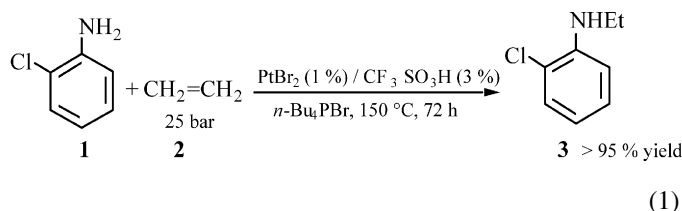
Keywords: Hydroamination; Platinum catalysts; Phosphonium halide; Promotors

1. Introduction

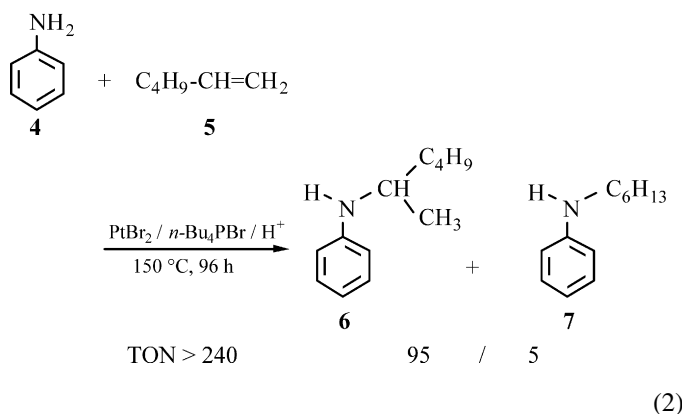
The catalytic hydroamination of alkenes (an atom-economic process) is a subject of current interest for both fundamental research and chemical industry [1]. Indeed, although significant improvements have been reported for the hydroamination of styrenes [2] and 1,3-dienes [3], as well as for the *intramolecular*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

We have recently reported a new and very efficient catalytic system for the intermolecular hydroamination of non-activated alkenes with aromatic amines [7–10]. This phosphine-free system results from the association of PtBr₂ with tetrabutylphosphonium bromide. The PtBr₂-*n*-Bu₄PBr system is the most efficient reported so far for the hydroamination of ethylene (Eq.

(1)) [8,11],



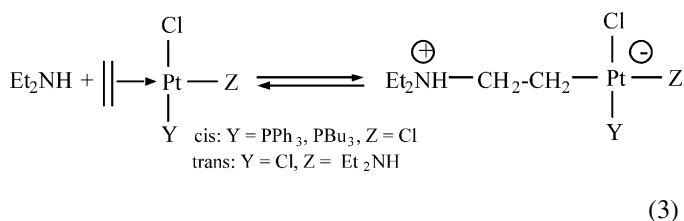
but also for that of 1-hexene (Eq. (2)) [9], affording the hydroamination products with an unprecedented regioselectivity (95% Markovnikov) [1a].



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It is also noteworthy that this system proved to be as efficient when runs were performed under aerobic conditions [9].

It has long been known that the reaction of amines with alkenes coordinated to Pt(II) lead to stable zwitterionic complexes (Eq. (3)) [12–18].



Cleavage of the carbon–Pt bond in these zwitterionic complexes (to liberate the alkylated amine) occurs only by further treatment (e.g. with HCl), so that these reactions are only *stoichiometric* [19].

In a previous report, it was briefly pointed out that the catalytic efficiency for the hydroamination of 1-hexene (Eq. (2)) depended upon both the *n*-Bu₄PX/PtBr₂ ratio and the nature of the anion (Br[−] ≫ Cl[−]) [9]. Thus, the presence of halide ions is obviously the key point of the catalytic system. In order to confirm and generalize our observations, it was decided to investigate the influence of the *n*-Bu₄PX/PtBr₂ ratio as well as that of the nature of the associated halide anion X[−] for the hydroamination of *ethylene* with aniline. For this study, experiments were conducted without H⁺ cocatalyst in order to better observe, if possible, the role of the phosphonium halides. Note that in our previous study, for the same reaction [8], the phosphonium bromide was considered only as an ionic solvent (mp = 100–103 °C), although the importance of the bromide anions (versus Cl[−] or PF₆[−]) had already been briefly noted in the case of the hydroamination of norbornene with aniline [7].

2. Experimental

2.1. Instrumentation

GC analyses were performed on a Hewlett-Packard HP 4890 (FID) chromatograph (HP 3395 integrator) equipped with a 30 m HP1 capillary column. GC–MS analyses were performed on a Hewlett-Packard HP 6890 apparatus equipped with a HP 5973 M ion detector. NMR analyses were performed on Bruker AM 250 or AC 200 machines. Catalytic experiments were conducted in a 100 mL stainless steel thermoregulated (electric oven) autoclave with a glass liner and a magnetic stirring bar.

2.2. Methods and materials

Tetra(*n*-butyl)phosphonium bromide (Aldrich) was stored in a dessicator under vacuum. Tetra(*n*-butyl)phosphonium chloride (Fluka) was heated at 110 °C for 12 h under vacuum and stored under argon. Tetra(*n*-butyl)phosphonium iodide was prepared from *n*-Bu₃P and *n*-BuI (see below), stored under argon and protected from light. Tetra(*n*-butyl)phosphonium hexafluorophosphate was prepared from *n*-Bu₄PBr and KPF₆ (see below) and stored in a dessicator under vacuum.

N,N-dibutylaniline (Aldrich), tri(*n*-butyl)phosphine (Aldrich), 1-iodobutane (Jansen Chimica), platinum salts (PtBr₂ and PtCl₄, Strem; PtBr₄, Alfa) and potassium hexafluorophosphate (Alfa) were used as received. Molecular iodine was purchased from Acros. Aniline (Fluka) and 1-hexene (Aldrich) were distilled before use. Ethylene (N25) was purchased from Air Liquide.

2.3. Preparation of tetra(*n*-butyl)phosphonium iodide

Tri(*n*-butyl)phosphine (38 mL, 0.15 mol) was slowly added to 1-iodobutane (40 mL, 0.35 mol) under argon. The mixture was stirred for 1 h at RT and then at 100 °C for 20 h. After cooling, the resulting precipitate was washed with diethylether (4 × 50 mL) until a white solid was obtained. Evaporation of residual solvent under vacuum overnight afforded pure *n*-Bu₄PI as a white powder (96% yield). mp = 95–96 °C. Anal. calcd. for: C₁₆H₃₆IP: C, 49.74; H, 9.39; found: C, 49.75; H, 9.57. NMR (acetone-*d*₆): ¹H (250 MHz): δ (ppm) = 0.96 (t, 3H); 1.55 (m, 2H); 0.96 (t, *J* = 3H); 1.70 (m, 2H); 2.54 (m, 2H); ³¹P: δ (ppm) = 33.52 (s).

2.4. Preparation of tetra(*n*-butyl)phosphonium hexafluorophosphate

n-Bu₄PBr (16.7 g, 49 mmol) was dissolved in distilled water (90 mL) and added to potassium hexafluorophosphate (10 g, 54 mmol). A white precipitate formed on heating. After cooling to RT, the precipitate was separated by filtration, dissolved in the minimum amount of ethyl acetate and washed with distilled water (3 × 200 mL). Evaporation of the solvent, and drying under vacuum, afforded pure tetra(*n*-butyl)phosphonium hexafluorophosphate as a white solid (96% yield). mp = 219 °C. Anal. calcd. for: C₁₆H₃₆F₆P₂: C, 47.52; H, 8.97; found: C, 47.67; H, 9.19. NMR (acetone-*d*₆): ¹H (200.13 MHz): δ (ppm) = 0.99 (t, *J* = 6 Hz, 3H); 1.54 (m, 4H); 2.16 (m, 2H); ³¹P (81.00 MHz): δ (ppm) = −93.21 (sept, *J* = 700 Hz); 84.06 (s); ¹⁹F (188.31 MHz): δ (ppm) = −72.5 (d, *J* = 700 Hz).

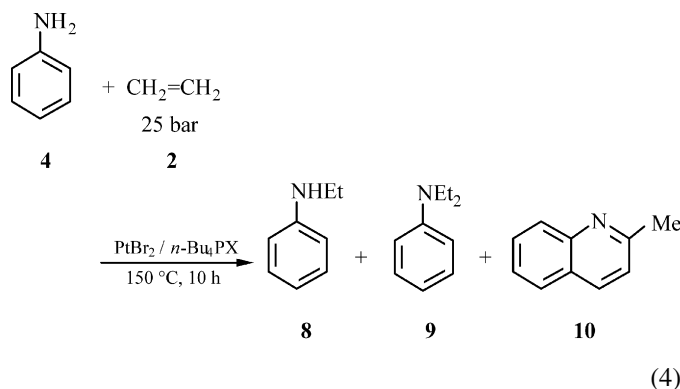
2.5. Reactions

Hydroamination of ethylene: typical procedure. The autoclave was charged with PtBr₂ (46.2 mg, 0.13 mmol) and *n*-Bu₄PBr (7.2 g, 8.45 mmol), closed and submitted to several 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 (ca. 100 mmol). 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 poured into 120 mL of diethylether, stirred for 2 h, and then filtered. The external standard (*N,N*-di(*n*-butyl)aniline, ca. 0.15 g) was added to the collected ethereal phases and the solution analyzed by GC and GC–MS.

3. Results and discussion

At first, it must be recalled that, in the absence of PtBr₂, no reaction occurs between aniline (45 mmol) and ethylene (25 bar, c.a. 100 mmol) for 96 h at 150 °C [8]. For these control

experiments, the presence of *n*-Bu₄PBr (ca. 7 g) has no effect. In contrast, PtBr₂-based systems exhibit catalytic activity for the formation of hydroamination products. For the present study, two parameters have been considered: the nature of the halide anion X⁻ associated with the phosphonium salt *n*-Bu₄PX, and the *n*-Bu₄PX/PtBr₂ ratio. According to previous studies, the selected reaction time was 10 h [8]. The most general reaction is represented by Eq. (4).



Compounds **8** and **9** are direct hydroamination products. The formation of **10** has been shown to occur in situ from 2 equiv. of **8** with elimination of PhNH₂ [10] and H₂ (3 equiv.) which is consumed in the ethylene hydrogenation process, as already stated [6a,8]. Thus, the activity of the catalytic system is best represented by the TON calculated on the amount of **8**, **9** and **10**. The selectivity for each product is given in mol.% of the total amount of reaction products. The main results are summarized in Table 1 (traces of unidentified side products (<1%), either light or heavy, were detected in most cases by GC analysis).

The first comment concerns the result of run 2 which confirms that PtBr₂ alone catalyzes the hydroamination of ethylene (TON = 20) [8]. Up to when we first reported this observation in 2004 [8], no platinum-catalyzed hydroamination had been reported [19], despite many studies are available on the reactivity of amines towards ethylene–platinum complexes [12–18]. Furthermore, no zwitterionic complex (Eq. (3)) resulting from the reaction of *aniline* (pK_a = 4.63) with a Pt–olefin complex

Table 2

Hydroamination of 1-hexene with aniline catalyzed by PtBr₂-*n*-Bu₄PX combinations^a

Run	Catalytic system	TON (6+7)	Regioselectivity (6/7)
14	PtBr ₂	1	nd
15	PtBr ₂ - <i>n</i> -Bu ₄ PPF ₆	3	nd
16	PtBr ₂ - <i>n</i> -Bu ₄ PCl	5	nd
17	PtBr ₂ - <i>n</i> -Bu ₄ PBr	57	95/5
18	PtBr ₂ - <i>n</i> -Bu ₄ PI	70	95/5
19	PtBr ₂ - <i>n</i> -Bu ₄ PBr-I ₂ ^b	115	95/5
20	PtBr ₂ - <i>n</i> -Bu ₄ PBr-I ₂ ^c	92	95/5

^a Aniline, 45 mmol; 1-hexene, 90 mmol; PtBr₂, 0.13 mmol; *n*-Bu₄PX, 8.45 mmol, 150 °C, 10 h.

^b I₂: 0.13 mmol.

^c I₂: 0.65 mmol.

has ever been detected, so that the formation of such addition complexes was considered to be limited to amines with pK_a > 5 [14b,d,15]. We tentatively propose that, although the reaction of aniline with ethylene coordinated to a platinum complex is disfavored by the low nucleophilicity of aniline, the zwitterionic addition complex (Eq. (3)) experiences temperature-promoted cleavage of the carbon–platinum bond, thus displacing the reaction to *N*-ethylaniline.

As may be seen from Table 1, the three phosphonium halides exhibit a promoting effect on the catalytic activity of PtBr₂ (with the exception of *n*-Bu₄PI used in large quantity, run 13). For *n*-Bu₄PCl, the maximum activity is obtained using 65 equiv. of phosphonium halide (run 4), whereas for both *n*-Bu₄PBr and *n*-Bu₄PI, the maximum catalytic activity is reached with a *n*-Bu₄PX/PtBr₂ ratio near 10 (runs 7 and 11). It is thus clear that these phosphonium halides, first intended to play the role of ionic solvents [7,8], must rather be considered as promoters or co-catalysts. However, too large quantities of these “promoters” decrease their beneficial effect, so that their role is difficult to rationalize at the present time. The selectivity for the formation of *N*-ethylaniline is nearly the same, whatever the phosphonium halide, especially when they are used in the most favorable ratios

Table 1

Hydroamination of ethylene with aniline catalyzed by *n*-Bu₄PX/PtBr₂^a

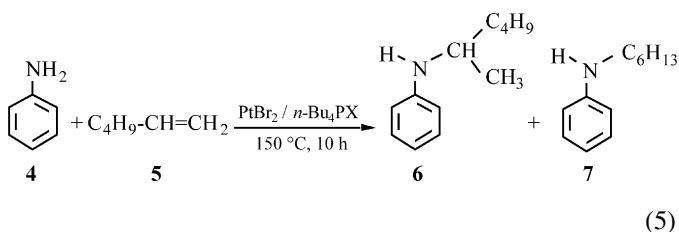
Run	<i>n</i> -Bu ₄ PX (equiv./Pt)	PtBr ₂ (mmol)	TON (8 + 9 + 10) ^b	8 (%)	9 (%)	10 (%)
1	–	–	–	–	–	–
2	–	0.13	20	100	–	–
3	<i>n</i> -Bu ₄ PCl (10)	0.13	50	91	9	–
4	<i>n</i> -Bu ₄ PCl (65)	0.13	105	92	2	6
5	<i>n</i> -Bu ₄ PCl (150)	0.13	80	95	1	4
6	<i>n</i> -Bu ₄ PBr (5)	0.13	140	87	4	8
7	<i>n</i> -Bu ₄ PBr (10)	0.13	150	89	3	8
8	<i>n</i> -Bu ₄ PBr (65)	0.13	130	87	2	11
9	<i>n</i> -Bu ₄ PBr (150)	0.13	88	86	1	12
10	<i>n</i> -Bu ₄ PI (5)	0.13	110	93	2	5
11	<i>n</i> -Bu ₄ PI (10)	0.13	135	91	2	7
12	<i>n</i> -Bu ₄ PI (65)	0.13	100	80	1	17
13	<i>n</i> -Bu ₄ PI (150)	0.13	5	100	–	–

^a Aniline, 45 mmol; ethylene, 25 bar at RT (c.a. 100 mmol); PtBr₂, 0.13 mmol, 150 °C, 10 h.

^b TON calculated as TON₈ + TON₉ + 2TON₁₀.

(runs 4, 7 and 11). The “promoting” effect of the *n*-Bu₄PX salts varies in the order Br⁻ > I⁻ > Cl⁻.

As mentioned in the Introduction, the PtBr₂-*n*-Bu₄Br association is the only efficient catalyst reported so far for the hydroamination of 1-hexene with aniline. In this case, the best *n*-Bu₄PBr/PtBr₂ ratio has been determined to be 65 for reactions conducted for 10 h at 150 °C [9]. Since this reaction (Eq. (2)) occurs with a particularly promising regioselectivity (95% Markovnikov), it was interesting to compare the activating capability of several *n*-Bu₄PX salts associated with PtBr₂ (1/65 equiv.) and their possible influence on the regioselectivity (Eq. (5)). The most significant results are summarized in Table 2.



In contrast to what has been observed in the case of ethylene (vide supra), PtBr₂ alone does not catalyze the hydroamination of 1-hexene with aniline (run 14). In the same way, association of PtBr₂ with either *n*-Bu₄PPF₆ or *n*-Bu₄PCl (runs 15, 16) resulted in very low activities. In contrast, as already reported [9], association with *n*-Bu₄PBr promotes a significant catalytic activity (TON = 57, run 17). An even higher activation has now been obtained with the PtBr₂-*n*-Bu₄PI system (run 18). For the above reaction (Eq. (5)), the “promoting” effect of the phosphonium halides varies as I⁻ > Br⁻ ≫ Cl⁻, a different trend than in the case of ethylene. The nature of the halide anion has no significant effect on the regioselectivity.

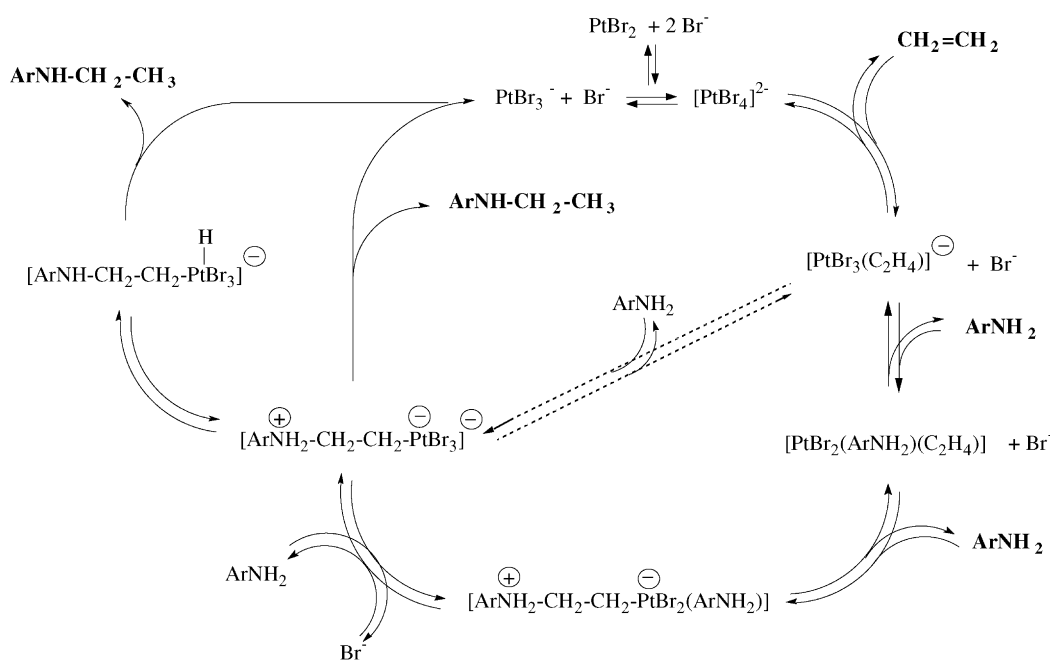
Iodide effects in transition metal catalyzed reactions are well known and have, in some cases, been rationalized [20]. The beneficial effect of molecular iodine has also been observed in some transition metal catalyzed reactions (iodine is generally used in large amounts, e.g. 20 equiv. versus the catalyst precursor) [21]. This also proved to be the case for the platinum(II)-catalyzed hydroamination of 1-hexene. Using the new PtBr₂-*n*-Bu₄PBr-I₂ association (1/65/1 ratio) allowed to reach an even higher activity (TON = 115, run 19) than that obtained with the PtBr₂-*n*-Bu₄PBr system (TON = 57, run 17). Using higher amounts of iodine (versus PtBr₂) has no beneficial effect on the TON (run 20).

The catalytic cycle already proposed [9] for these hydroamination reactions is represented in Scheme 1 in a simplified way in the case of ethylene and *n*-Bu₄PBr as promoter.

The role of the activating bromide anion was considered to increase the “basicity” of the platinum center in the zwitterionic intermediate, thus favoring the proton transfer from the ammonium site to generate a transient Pt(IV) hydride [22]. The results reported in this paper are consistent with such hypothesis, but suggest that the halide anions also play a role in other step(s) of the catalytic cycle, such as the alkene coordination, the aniline attack on the coordinated alkene, or even by postponing poisoning effects [8].

The observed positive role of the I₂ additive led us to consider platinum(IV) salts as catalyst precursors. To the best of our knowledge, no hydroamination reaction, neither stoichiometric nor catalytic, has ever been reported using Pt(IV) salts [1,12]. The first results of this study are summarized in Table 3 for the hydroamination of ethylene. Both Pt(IV) salts and Pt(IV)-*n*-Bu₄X associations (1/65 ratio) have been considered.

The most important feature that emerges from Table 3 is that Pt(IV) bromide and chloride are shown for the first time to cat-



Scheme 1.

Table 3
Hydroamination of ethylene with aniline catalyzed by Pt(IV)-based systems^a

Run	Pt(IV) system	<i>n</i> -Bu ₄ PX/PtBr ₂ ratio	TON (8 + 9 + 10) ^b	8 (%)	9 (%)	10 (%)
21	PtBr ₄	–	50	89	4	7
22	PtBr ₄ - <i>n</i> -Bu ₄ PCl	65	75	84	14	2
23	PtBr ₄ - <i>n</i> -Bu ₄ PBr	65	135	85	6	7
24	PtBr ₄ - <i>n</i> -Bu ₄ PI	65	110	84	2	13
25	PtCl ₄	–	15	100	–	–
26	PtCl ₄ - <i>n</i> -Bu ₄ PCl	65	45	98	2	–
27	PtCl ₄ - <i>n</i> -Bu ₄ PBr	65	120	90	3	7
28	PtCl ₄ - <i>n</i> -Bu ₄ PI	65	110	86	2	11

^a Aniline, 45 mmol; ethylene, 25 bar at RT (c.a. 100 mmol); PtX₂, 0.13 mmol, 150 °C, 10 h.

^b TON calculated as TON₈ + TON₉ + 2TON₁₀.

alyze the hydroamination reaction: PtBr₄ (run 21) is even more active than PtBr₂ (run 2; Table 1) [23]. Secondly, association of these Pt(IV) precursors with *n*-Bu₄PX derivatives promotes a significant increase of the catalytic activity, thus confirming the promoting effect pointed out with Pt(II) catalytic precursors. Although the role of the *n*-Bu₄X/Pt(IV) ratio has not yet been studied, the most efficient “promoter” seems to be *n*-Bu₄PBr, as was the case for Pt(II) systems (vide supra). For both Pt(II) and Pt(IV) catalytic precursors, the efficiency order exhibited by the phosphonium halide is Br[−] > I[−] > Cl[−]. Although it is premature to speculate about the exact role of these “promoters”, this unusual order again suggests that these anions play a role in different steps of the catalytic cycle by the formation of different anionic species.

Drent and co-workers recently reported a detailed study of the halide anion-promoted palladium-catalyzed hydroformylation of internal alkenes to linear alcohols [24]. In the case of the [(bcope)Pd(OTf)₂] complex (bcope = bis(cyclooctyl)phosphinoethane), they found that using *substoichiometric* amounts (versus Pd) of added halide anions strongly promoted the reaction rate and improved the chemo- and regioselectivity (the observed effects strongly depend upon the nature of the phosphorus ligand). In particular, volcano-shape promotion curves were observed (X[−]/Pd from 0 to 1) with a maximum reaction rate near 0.5 for each halide ion (Cl[−] ~ Br[−] > I[−]). 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 mechanistic studies are required to gain full insight into these phenomena.

4. Conclusions

We have compared different *n*-Bu₄PX salts (X = Cl[−], Br[−], I[−]) in terms of their promoting effect for the Pt(II)-catalyzed hydroamination of ethylene and 1-hexene with aniline. In the case of ethylene, *n*-Bu₄PBr is the most efficient promoter, whereas *n*-Bu₄PI is more efficient than *n*-Bu₄PBr in the case of 1-hexene. A special effect of molecular iodine has also been pointed out. Most notably, it has been shown for the first time that Pt(IV) precursors are also active for the hydroamination of ethylene. As for Pt(II) precursors, Pt(IV)-*n*-Bu₄PX associations exhibit enhanced catalytic activities. Work is now in progress

to elucidate the mechanistic details of this reaction and to take advantage of these promoting effects for other hydroamination reactions.

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