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Communications

Rhodium-Catalyzed Hydroamination of Ethylene. Highly Promoting Effect of Iodide Ions

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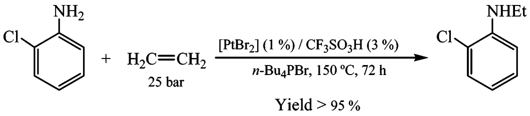
Summary: Association of the usual "$RhCl_3-3H_2O-2PPh_3$" catalytic precursor (0.3%) with n-Bu_4PI (65 equiv/Rh) and iodine (2 equiv/Rh) generates the most active catalytic system reported so far for the hydroamination of ethylene with aniline to give mixtures of N-ethyl- and N,N-diethylanilines. This system proved particularly efficient for the hydroamination of ethylene with N-ethylaniline (TON > 260 after 24 h).

The direct addition of an amine N−H bond on carbon−carbon double bonds (hydroamination, an atom economical process) to produce amines has long been recognized as a challenge for chemists. During the last 20 years, intense efforts have been devoted to research and develop catalysts that efficiently perform such reactions.[1,2] In the last 10 years, several exhaustive reviews[3,4] and recent papers have been published that show great success for intramolecular reactions,[5] as well as for the intermolecular hydroamination of activated alkenes such as vinylarenes.[6] The main unsolved problem remains the intermolecular hydroamination of nonactivated alkenes such as ethylene.[3,4,7]

We have recently reported the discovery of an original Pt(II) system that consists in an association of Pt(II) salts with ionic liquids, especially the $PtBr_2-n\text{-}Bu_4PBr$ combination. The latter proved to be the first platinum-based system that allows the *catalytic* hydroamination of ethylene with anilines (eq 1).[8]



(1)

Furthermore, the above association allows the catalytic hydroamination of higher alkenes, such as 1-hexene (a still more remarkable result) with a surprisingly high Markovnikov regioselectivity (>95%).[9]

This platinum-based system, without phosphorus ligand, works under aerobic conditions and appears as the most efficient system reported for the intermolecular hydroamination of nonactivated alkenes with anilines.[9] The key activating effect of the halide ions associated with the phosphonium moiety has recently been studied in some detail, and the special role of iodides has been pointed out.[10]

At the beginning of the above study, the beneficial effect of ionic liquids (especially $n\text{-}Bu_4PBr$) had been pointed out for both Pt(II) and Rh(III) catalyst precursors.[8] Although the reaction mechanisms could be different with either metal precursor, we obviously were prompted to examine the possible activating effect of $n\text{-}Bu_4PX$ derivatives on the Rh(III)-catalyzed hydroamination of ethylene with anilines.

Coulson first reported that $RhCl_3-3H_2O$ catalyzes the hydroamination of ethylene under high temperature (180−200 °C) and pressure (50−140 bar).[11,12] This reaction was clearly shown to be restricted to ethylene and to secondary amines of high basicity and low steric bulk (e.g., piperidine, $pK_a = 11.12$). In contrast, Diamond et al. later reported that $RhCl_3-3H_2O$, associated with PPh_3 (2 equiv), catalyzes the hydroamination of ethylene with aniline ($pK_a = 4.63$) at high temperatures.[13,14] Although catalytic activities were quite low, it was shown that the reaction afforded 2-methylquinoline as a secondary, highly elaborated product. Later on, Taube et al. demonstrated that the $RhCl_3-3H_2O$-catalyzed hydroamination of ethylene with piperidine (pip) was limited because of decomposition of active

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(1) Gasc, M. B.; Lattes, A.; Perié, J.-J. Tetrahedron Report 144. *Tetrahedron* **1983**, *39*, 703−731.

(2) Brunet, J.-J.; Neibecker, D.; Niedercorn, F. *J. Mol. Catal.* **1989**, *49*, 235−259.

(3) (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675−703. (b) Müller, T. E.; Beller, M. In *Transition Metals for Organic Synthesis*, Vol. 2; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; pp 316−330. (c) Beller, M.; Seyad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398.

(4) (a) Brunet, J.-J.; Neibecker, D. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; VCH: Weinheim, 2001; pp 91−141. (b) Beller, M.; Breindl, C.; Eichberger, M.; Hartung, C.-G.; Seayad, J.; Thiel, O.-R.; Tillack, A.; Trauthwein, H. *Synlett* **2002**, 1579−1594.

(5) (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686. (b) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748−3759, and references therein.

(6) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828−1839, and references therein.

(7) The base-catalyzed hydroamination of ethylene with diethylamine has been recently revisited: Khedkar, V.; Tillack, A.; Benisch, C.; Melder, J.-P.; Beller, M. *J. Mol. Catal. A: Chem.* **2005**, *241*, 175−183.

(8) (a) Brunet, J.-J.; Chu, N. C.; Diallo, O.; Mothes, E. *J. Mol. Catal. A: Chem.* **2003**, *198*, 107−110. (b) Brunet, J.-J.; Cadena, M.; Chu, N. C.; Diallo, O.; Jacob, K.; Mothes, E. *Organometallics* **2004**, *23*, 1264−1268.

(9) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104−3110.

(10) Rodriguez-Zubiri, M.; Brunet, J.-J.; Anguille, S. *J. Mol. Catal. A: Chem.* **2007**, *271*, 146−151.

(11) Coulson, D. R. *Tetrahedron Lett.* **1971**, 429−430.

(12) Coulson, D. R. (E. I. du Pont de Nemours and Co.) US 3,758,586, 1973.

(13) (a) Diamond, S. E.; Szalkiewicz, A.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 490−49. (b) Diamond, E.; Mares, F. (Allied Chemical Corp.) US 4,215,218, 1980.

(14) Diamond, S. E.; Szalkiewicz, A.; Mares, F. *Fund. Res. Homogeneous Catal.* **1979**, *3*, 345−358.

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Table 1. Catalytic Hydroamination of Ethylene by Aniline with $RhCl_3-3H_2O-$ Based Systems[a]

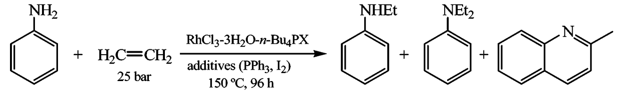
run	PPh_3 (equiv/Rh)	n-Bu_4PX X = (equiv/Rh)	additive (equiv/Rh)	**3** TON[b]	**4** TON[b]	**5** TON[b]	catalytic efficiency[c]
1				11		7	25
2	PPh_3 (1)			12	1	4	22
3	PPh_3 (2)			20	2	2	28
4		Cl (65)		22	3	4	36
5		Cl (150)		22	2		26
6		Br (10)		34		6	46
7		Br (65)		20	2	10	44
8		Br (150)		18		7	32
9		I (10)		7		2	11
10		I (65)		17	2	9	39
11		I (150)		13	3	10	39
12	PPh_3 (2)	Cl (65)		9			9
13	PPh_3 (2)	Br (10)		34	3	6	52
14	PPh_3 (2)	Br (65)		16			16
15	PPh_3 (2)	Br (150)		11			11
16	PPh_3 (2)	I (10)		47	3		53
17	PPh_3 (2)	I (20)		73	6		79
18	PPh_3 (2)	I (65)		130	93	4	324
19	PPh_3 (2)	I (150)		102	120	5	352
20	PPh_3 (2)	I (10)	I_2 (2)	152	25		202
21	PPh_3 (2)	I (65)	I_2 (2)	28	225	3	484
22	PPh_3 (2)	I (150)	I_2 (2)	21	230	3	487
23	PPh_3 (2)	I (65)	I_2 (5)	8	9	13	52
24	PPh_3 (2)		I_2 (2)	39	1	2	45

[a] 25 bar of ethylene at RT, 0.13 mmol of $RhCl_3-3H_2O$, 45 mmol of aniline, 150 °C, 96 h. [b] Calculated as mol product/mol Rh. [c] Calculated as $TON_{(3)} + 2\ TON_{(4)} + 2\ TON_{(5)}$.

[RhCl(ethylene)pip$_2$] species to metallic rhodium.[15,16] Taube et al. conceived a cationic rhodium (I) complex, [Rh(PPh_3)$_2$-(ethylene)acetone]PF_6, that is active for the hydroamination of ethylene with piperidine at RT and atmospheric pressure! Unfortunately, this system is completely deactivated within 10 cycles.[16,17] Mechanistic investigations on possible reaction mechanisms were also reported.[18]

We report below the first results of our successful study on the possible activating effect of n-Bu_4PX for $RhCl_3-3H_2O$ and $RhCl_3-3H_2O-PPh_3$ associations as catalytic precursors for the hydroamination of ethylene.

Our first experiments were aimed at testing our experimental and analytical conditions (experimental details as in ref 10) with regards to those reported earlier by Diamond et al.[13,14] for the hydroamination of ethylene with aniline (eq 2).



1 **2** **3** **4** **5** (2)

In this work, we were led to consider both the TON (moles of product formed by moles of catalyst) and the catalyst efficiency, a number that takes into account that N,N-diethylaniline (**4**) results from two successive hydroamination steps and that 2-methylquinoline (**5**) is formed from two N-ethylaniline (**3**) molecules.[19]

Typically, catalytic runs conducted for 96 h at 150 °C under 25 bar of ethylene pressure (runs 1−3, Table 1) afforded results in agreement with those previously reported under slightly different conditions.[13,14] These results suggest that the presence of PPh_3 somewhat inhibits the formation of 2-methylquinoline (which likely originates from N-ethylaniline).[19] In most experiments, traces of 2-methyl-1,2,3,4-tetrahydoquinoline could be detected by GC-MS analysis. This compound is the precursor of **5** (transfer hydrogenation of ethylene), as already shown during the hydroamination of ethylene by aniline with either platinum or rhodium catalysts.[8,13]

Further experiments conducted in the presence of $RhCl_3-3H_2O$ associated with tetra-n-butylphosphonium halides (runs 4−11) indicated that the presence of the phosphonium halide has no significant effect on the catalyst efficiency, whatever the nature of the halide ion (X = Cl, Br, I) and the n-Bu_4PX/Rh ratio (10, 65, 150). This is in contrast with our previous results on the activating effect of n-Bu_4PBr for the Pt(II)-catalyzed reactions (*vide supra*).[10]

In the same way, association of the $RhCl_3-3H_2O-2PPh_3$ catalyst with n-Bu_4PCl or n-Bu_4PBr (runs 12−15) either inhibited or did not improve the efficiency of the reaction.

In sharp contrast, association of the $RhCl_3-3H_2O-2PPh_3$ catalyst with n-Bu_4PI induces a strong increase of the catalytic efficiency (runs 16−19) when increasing the amount of n-Bu_4PI from 10 to 150 equiv with an optimum at 65 equiv for the formation of **3** and at 150 equiv for the formation of **4**. This system affords a much higher TON for the formation of **3**, but also, unexpectedly, for N,N-diethylaniline (**4**), which results from *in situ* hydroamination of ethylene with **3** (all runs were repeated at least twice). The TON for the formation of **5** is not changed significantly. The reaction product **4** was easily isolated (by column chromatography) from the reaction mixture (run 22) and fully characterized by spectroscopic analyses in order not to confuse it with any of the (o, m, or p)-ethyl-N-ethylanilines.

It is important to note that the high activity increase is observed only when both the phosphine (PPh_3) and the iodide source (n-Bu_4PI) are present (compare runs 3, 11, and 19).

On the basis of previous results for the platinum-catalyzed hydroamination of alkenes (in the absence of phosphine ligand),[10] the possible role of molecular iodine was also

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(15) Steinborn, D.; Taube, R. *Z. Chem.* **1986**, *26*, 349−359.

(16) Krukowka, E.; Taube, R.; Steinborn, D. (Technische Hochschule Leuna) DD 296,909, 1991.

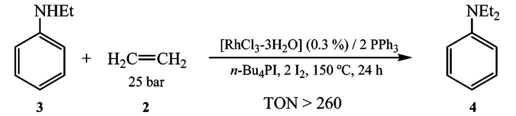
(17) Taube, R. In *Applied Homogeneous Catalysis with Organometallic Complexes*, Vol. 2; Cornils, B., Herrmann, W., Eds.; VCH: Weinheim, 1996; pp 507−521.

(18) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, 435−440, and references therein.

(19) Anguille, S.; Brunet, J.-J.; Chu, N. C.; Diallo, O.; Pages, C.; Vincendeau, S. *Organometallics* **2006**, *25*, 2943−2948.

considered despite the presence of PPh_3. The high efficiency observed for the rhodium-catalyzed *in situ* hydroamination of ethylene with *N*-ethylaniline (runs 18, 19) is again somewhat enhanced in the presence of molecular iodine (2 equiv/Rh) as additive (runs 21 and 22). Higher amounts of iodine have a detrimental effect on the catalytic activity (run 23). The presence of iodine apparently increases the efficiency of the catalyst for the transformation **3** → **4**, that is, the hydroamination of ethylene with the more basic amine present in the reaction medium (pK_a aniline = 4.63; pK_a *N*-ethylaniline = 5.12).[20] Last, control experiments performed in the presence of molecular iodine but in the absence of the phosphorus iodide activator (run 24) confirm the independent intervention of both iodide ions and molecular iodine.

The efficiency of the hydroamination of ethylene with *in situ* formed *N*-ethylaniline was confirmed by a separate experiment using commercial *N*-ethylaniline. As expected, the catalytic system $RhCl_3-3H_2O-2PPh_3-n\text{-}Bu_4PI-I_2$ (1/2/65/2 mole ratio) afforded *N*,*N*-diethylaniline as the only reaction product (no heterocyclic compound was formed) with high TONs (135 after 10 h, 267 after 24 h) (eq 3).



(3)

The above results (eq 3) confirm the remarkable activating effect of $n\text{-}Bu_4PI$ (and I_2) on the catalytic activity of the $RhCl_3-3H_2O-2PPh_3$ system. Indeed, control experiments indicated that in the absence of $n\text{-}Bu_4PI$ and I_2, the $RhCl_3-3H_2O-2PPh_3$ system results in only very low activity (TON < 5) for the reaction of *N*-ethylaniline with ethylene, in agreement with observations reported by Diamond et al.[13,14]

To the best of our knowledge, this is by far the most active catalytic system ever reported for the hydroamination of ethylene.[1−4,7] It is even more active, under comparable conditions, than the platinum systems $PtBr_2-n\text{-}Bu_4PX$ recently developed in this lab.[7−10] In both cases, the halide ions (especially iodides for the rhodium catalyst) associated with the phosphonium salt promote a dramatic increase of the catalytic activity. In both cases too, molecular iodine has been shown to play a role, which is not understood at the present time. A possible rationalization of the role of bromine and iodide ions has been proposed in the case of the Pt(II)-catalyzed hydroamination reactions.[9,10] At the present time, the mechanism involved for the rhodium-catalyzed hydroamination of ethylene is far from clear,[21] and hypotheses on the role of iodide ions and molecular iodine would be premature (similar iodide effects have already been reported and rationalized in some cases).[22,23]

Further investigation of the scope and limitations of these highly active hydroamination catalysts is in progress.

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(20) *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986−1987; p D159.

(21) A theoretical (static and dynamic *ab initio* DFT) study of the rhodium-catalyzed hydroamination via alkene activation has been reported: Senn, H. M.; Blöchl, P. E.; Togni, A. *J. Am. Chem. Soc.* **2000**, *122*, 4098−4107.

(22) Maitlis, P. M.; Haynes, A.; James, B. R.; Catellani, M.; Chiusoli, G. P. *Dalton Trans.* **2004**, 3409−3419, and references therein.

(23) See, for example: (a) Wang, X.; Lu, S.-M.; Yang, P.-Y.; Han, X.-W.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2003**, *125*, 10536−10537. (b) Xiao, D.; Zhang, X. *Angew. Chem., Int. Ed.* **2001**, *40*, 3425−3428.