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Full Paper

M. Rodriguez-Zubiri et al.

Rhodium Catalysis

Intermolecular Rhodium-Catalysed Hydroamination of Non-Activated Olefins: Effect of Olefin, Amine, Phosphine and Phosponium Salt

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The right combination: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3/n\text{Bu}_4\text{PI}/\text{I}_2$ led to the highest catalytic activity for the intermolecular hydroamination of ethylene, 1-butene, and 1-hexene with aniline-type amines. Excellent activities were also found using Rh^{I} Wilkinson's catalysts and the very efficient "in-situ generated" $\text{I}^{\text{M-}}$ from PPh_3/I_2 , which can substitute pre-synthesized $n\text{Bu}_4\text{PI}$ (see scheme; CE=catalytic efficiency).

halides

hydroamination

non-activated alkenes

phosphines

rhodium

The catalytic system $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} / 2\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3 / 65 n\text{Bu}_4\text{PI} / 2\text{I}_2$, which was discovered recently in our research group, allows the highest catalytic activity ever reported for the intermolecular hydroamination of ethylene, 1-butene, and 1-hexene with aniline-type amines (0.3 mol% catalytic precursor) to give the expected *N*-alkyl- (*N*-ethyl-, **1**) and *N,N*-dialkyl-anilines (*N,N*-diethyl-, **2**), along with 2-methyl quinolines (**3**) (in the case of ethylene). The effects of time and temperature, as well as the nature of the phosphonium salt, phosphine, and amine on the catalytic activity of this reaction have been studied. This system is particularly efficient for the hydroamination of ethylene with aniline in the presence of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ($\text{CE}^* = 460$) and tri(*p*-tolyl)phosphine ($\text{CE}^* = 520$). Good to excellent activities were also found by combining Wilkinson's catalysts (Rh^{I} complexes) with $n\text{Bu}_4\text{PI}$ and I_2 . The simple association of PPh_3 and I_2 has been shown to be a very efficient "in-situ generated" source of I^{M} promoters. *CE (catalytic efficiency) = $\text{TON}_1 + 2\text{TON}_2 + 2\text{TON}_3$.

Introduction

Amines are important chemicals used in industry and in everyday life.^[1,2] Chemists have developed many synthetic routes for the preparation of amines but most of them are not suitable for industrial purposes.^[3] Amines are mostly synthesised from alcohols by the process discovered in 1909 by Paul Sabatier.^[4,5] As alcohols are mainly obtained from alkenes either by hydration or by the hydroformylation/hydrogenation sequence,^[6,7] the overall synthesis of amines requires two steps----the last step also produces water, which is an expensive and polluting side-product to be removed (Scheme¹).

In this context, the direct transformation of olefins into amines (the hydroamination reaction; Scheme²) is obviously an interesting economic and ecologic alternative.

Nevertheless, this atom-economic reaction requires a catalytic process because such additions are characterised by a high activation barrier.^[8]

Great improvements have been reported on the design of catalytic systems for the intramolecular hydroamination of alkenes and for the intermolecular hydroamination of unsaturated substrates such as alkynes, vinylarenes, dienes, and allenes, which are more reactive than simple alkenes.^[9] Indeed, the intermolecular hydroamination of non-activated alkenes is particularly challenging and remains the main challenge.^[9,10]

A few years ago our research group reported the discovery of an original Pt^{II} system, PtBr₂/*n*Bu₄PBr, which involves the association of simple Pt^{II} salts with ionic liquids (phosphonium halides). It proved to be the first platinum-based system that allows the catalytic hydroamination of ethylene with anilines [Eq. (1)]. Furthermore, the above association permits the catalytic hydroamination of higher alkenes, such as 1-hexene (still a remarkable result) with a surprisingly high Markovnikov regioselectivity (>95%).^[11] A breakthrough in this area was the discovery of such platinum-based systems that were equally effective in water using common salts such as NaBr instead of *n*Bu₄PBr as the source of bromide ions.^[12]

<ZS>(1)

Aiming to improve the performance of this already efficient catalytic system, some mechanistic studies on the low-energy species of the catalytic cycle were carried out. The [Pt(C₂H₄)Br₃]^{<M>} complex was found to be the resting-state species.^[13]

In view of previous results on the platinum-based catalytic systems, we were prompted to examine the possible activating effect of *n*Bu₄PX derivatives on the rhodium(III)-catalysed hydroamination of ethylene with anilines.^[14] Literature data on rhodium-catalysed hydroamination reactions of ethylene and/or higher non-activated olefins are scarce and exemplify the challenges in achieving good catalytic activity for this reaction.

In 1971, Coulson first reported that RhCl₃·3H₂O catalyses the hydroamination of ethylene under high-temperature (180--200°C) and high-pressure (50--140 bar) conditions.^[15,16] Nevertheless, this reaction was restricted to ethylene and secondary amines

of high basicity and low steric bulk (e.g. piperidine, $pK_b=2.88$). In contrast, Diamond et al. reported that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, associated with PPh_3 (2^{equiv}), catalyses the hydroamination of ethylene with aniline ($pK_b=9.37$) at high temperatures.^[17,18] Although catalytic activity was quite low, the main interest of their study was to show that this reaction afforded 2-methylquinoline as a secondary, highly elaborated product. Later on, Taube et al. studied the Rh^{III} system reported by Coulson and concluded that it was limited because of decomposition of the active $[\text{RhCl}(\text{C}_2\text{H}_4)\text{pip}_2]$ (pip=piperidine) species to yield metallic rhodium species.^[19,20] Taube and co-workers conceived a cationic rhodium(I) complex, $[\text{Rh}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{Me}_2\text{CO})]\text{PF}_6$, which is active for the hydroamination of ethylene with piperidine at room temperature and at atmospheric pressure. Unfortunately, this system is completely deactivated within ten cycles.^[20,8b] These authors also reported relevant mechanistic investigations on a possible reaction pathway.^[21]

Taking into account the state-of-the-art mentioned above, our results in this area are particularly interesting. Indeed, the association of the usual " $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/2\text{PPh}_3$ " catalytic precursor (0.3^{mol%}) with $n\text{Bu}_4\text{PI}$ (65^{equiv} with respect to Rh) and iodine (2^{equiv} with respect to Rh) was found to be the most active catalytic system reported so far for the hydroamination of ethylene with aniline [Eq. (2)].^[14]

<ZS>(2)

This system proved particularly efficient for the hydroamination of ethylene with *N*-ethylaniline [Eq. (3); turnover number (TON)>260 after 24^h] and even more active, under comparable conditions, than the platinum systems ($\text{PtBr}_2/n\text{Bu}_4\text{PX}$) previously developed in our group.^[10-14]

<ZS>(3)

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. Indeed, control experiments indicated that in the absence of $n\text{Bu}_4\text{PI}$ and I_2 , the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/2\text{PPh}_3$ system allows only very low activity (TON<5) for the reaction of *N*-ethylaniline with ethylene, in agreement with observations reported by Diamond et al.^[17,18]

Herein, we report a relevant study on the use of phosphorus ligands as co-catalysts for the rhodium-catalysed intermolecular hydroamination of ethylene and higher olefins such as 1-butene and 1-hexene with aniline ($pK_b=9.37$). This simple one-pot catalytic system does not need to operate under inert atmosphere and does not need laborious experimental procedures. The Rh^{III} /phosphine/ nBu_4PI catalytic system provides great possibilities for an asymmetric version of this reaction, an almost unexplored area of research to date.^[22,^23] Indeed, the only two literature reports on the asymmetric intermolecular hydroamination of non-activated alkenes are the unprecedented study reported by Widenhoefer and co-workers^[22] using chiral $[AuCl(phosphine)]$ pre-catalysts for ethylene and 1-alkene hydroamination with cyclic ureas ($pK_b=13.86--14.17$), and later on the study by Hultsch and co-workers^[23] involved chiral catalysts based on rare-earth metals for the stereoselective addition of basic amines (benzylamine, $pK_b=4.66$) to non-activated alkenes.

It is therefore important to note that our contribution concerns widely available amines, higher α -olefins, and low loading ($0.3^{mol\%}$) of a stable "one-pot" ready-to-use metal--ligand catalyst precursor. Furthermore, we were able to generate an "in situ" source of $I^{M->}$ promoters and to show that this catalytic system is also efficient using Rh^I complexes.

Results and Discussion

In this study, we were led to consider both the TON (moles of product formed by mole of catalyst used) and the catalytic efficiency (CE). The CE was calculated on the basis of the number of cycles needed by the catalyst to yield each product (two cycles for the product of double hydroamination, **2**, and for quinaldine, **3**)^[11a] [Eqs. (2) and (3)].

Hydroamination of ethylene by aniline: influence of the phosphine ligand

Our first experiments were aimed at investigating the effect of the relative amount of PPh_3 , an important parameter that was not extensively studied in our previous Communication^[14] where we intended to test the experimental and analytical conditions (experimental details as in ref. ^[17,^18]) with regards to those reported earlier by Diamond et al.^[17,^18] for the hydroamination of ethylene with aniline. Using 2^{equivalents} of PPh_3 , we supposed the active catalytic species to contain the

{RhI(PPh₃)₂} moiety necessary for either the coordination of the alkene followed by the external nucleophilic addition of the starting amine, or the N<C->H oxidative addition and subsequent insertion of the alkene moiety.^[8b]

Typically, catalytic runs conducted with variable amounts of PPh₃ (Table^{^1}, entries^{^1--6}) confirmed that, indeed, the best results are obtained with either a PPh₃/Rh ratio of 2 or 3. Either lower or higher amounts of phosphine resulted in a drop of the catalytic activity in part because of a lower conversion of **1** into **2**. These results suggest that the addition of PhNH₂ to ethylene is favoured in the presence of I₂ and is more sensitive to the PPh₃/Rh ratio than in the case of PhNH₂.

The influence of the nature of several phosphorus ligands was examined. Different types of phosphorus ligands containing alkyl, aryl, or alkoxy substituents were used and the results are listed in Table^{^2}. In contrast with previous results on the platinum(II)-catalysed reactions of aniline with ethylene,^[24] where phosphorus ligands (to the exception of trialkylphosphites) seemed to act as inhibitors, PPh₃ allows much better catalytic activity than trialkylphosphites (Table^{^2}, entries^{^3--7}). Aryloxy-substituted ligands (triaryl phosphites) and trialkylphosphines mediate the reaction but are inefficient co-catalysts (Table^{^2}, entries^{^1, 2, and 8--11}). In sharp contrast, the catalytic activity is partially recovered upon the introduction of phenyl groups as substituents of the phosphorus atoms as shown by the results obtained with mixed phosphorus ligands such as P(OMe)Ph₂ and dppe (1,2-bis(diphenylphosphino)ethane; Table^{^2}, entries^{^12 and 13}) where the P atom contains two phenyl substituents. Interestingly, excellent activities were obtained in the presence of binap (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; Table^{^2}, entries^{^14 and 15}), probably owing to the presence of three phenyl substituents on each P atom to create a quite similar electronic and steric environment when compared to PPh₃ (1^{^equiv} of binap corresponds to 2^{^equiv} of P, which is analogous to the use of 2^{^equiv} of PPh₃ with respect to Rh). Thus, it was concluded that the presence of phenyl groups in the structure of the phosphorus ligands is a key factor for achieving good catalytic activity.

Next, the electronic effects of the substituents on the phenyl groups of the triarylphosphines (Table^{^2}, entries^{^16--18}) were considered. We found that the

para substitution on the aryl ring with the strongly electron-withdrawing CF₃ group dramatically lowers the catalytic activity. In a minor way, the *p*-OMe group (mesomeric electron-donating and inductive electron-withdrawing) also causes a loss of activity. In sharp contrast, the *para* inductive electron-donating CH₃ substituent induces an important increase of the catalytic activity: this is in fact the best result ever reported for the intermolecular hydroamination of a non-activated olefin by aniline (CE=528; Table², entry¹⁷).

In any case, formation of quinaldine **3** seems favoured when production of **1** is not, thus suggesting, once more, that **1** is not an intermediate in the pathway leading to **3**.^[14] These results are of special importance when considering the enantioselective version of the intermolecular hydroamination of non-activated olefins (see introduction). These related studies are in progress within our group.

Hydroamination of ethylene by aniline: influence of the amine

To potentially widen the scope of this catalytic process, the addition of other primary and secondary amines to ethylene was studied. Hence, the efficiency for the hydroamination of ethylene with more basic amines was considered (Table³). Using *N*-ethylaniline, the catalytic system afforded *N,N*-diethylaniline as the only reaction product [Eq.⁽³⁾] with higher TON than when the reaction was performed with aniline (Table³, entries¹⁻³).

On the other hand, morpholine [Eq.⁽⁴⁾] and piperidine [Eq.⁽⁵⁾], two more-basic non-aromatic amines, afforded very low catalytic activities (Table³ entries⁵ and 6), possibly owing to strong coordination to the metal centre

<ZS>(4)

<ZS>(5)

Further experiments (Table 3, entry 4) showed an interesting result when performing the hydroamination of ethylene with benzylamine [Eq.⁽⁶⁾]. Indeed, as may be seen in Table³, the catalytic efficiency of this reaction does not depend on the p*K*_b value of the amine because morpholine and piperidine afford very low catalytic activities when compared to benzylamine, an amine with an intermediate p*K*_b value. Analogously, the amine

substitution does not seem to be a determining parameter by itself because aniline and benzylamine, two primary amines, allowed very different catalytic performance. The only structural factor that could somehow explain this result is perhaps, once more, related to the presence of an aryl group near to the nitrogen atom: for aniline and *N*-ethylaniline, the N atom is directly bonded to a Csp² atom and for the benzylamine, only one Csp³ atom separates the N atom from the aryl Csp² atom. Further studies (catalytic tests and theoretical calculations) are ongoing in our team to elucidate the parameters (nucleophilicity, basicity, and/or steric hindrance) that influence the catalytic performance as a function of the nature of the starting amine.

<ZS>(6)

Hydroamination of ethylene by aniline: influence of the phosphonium salt

On the basis of the excellent catalytic results obtained with the association of *n*Bu₄PI with PPh₃, we were prompted to evaluate the influence of the nature of the cation of the ionic salts, as we had done previously with the anion.^[14] For this purpose, catalytic runs were conducted in the presence of Ph₄PI, a phosphonium salt containing phenyl substituents on the P atom as in the case of the efficient PPh₃ ligand, and *n*Bu₄NI, an ammonium salt with the same *n*Bu groups as our previous phosphonium candidate (Table⁴). Surprisingly, association of the RhCl₃·3H₂O catalyst with Ph₄PI inhibited the efficiency of the reaction even in the presence of PPh₃ (Table⁴, entries¹⁻⁴), showing that the PPh₄⁺ counter cation must also have a role on the reactivity. Physical properties of this salt, such as its high melting point (338°C), are not, a priori, responsible for its catalytic behaviour because Ph₄PI is soluble in aniline even at room temperature and thus able to react under the catalytic conditions (150°C).

In the same way, *n*Bu₄NI, strongly decreased the catalytic activity (Table⁴, entry⁵) in the presence of PPh₃ and I₂, thus confirming our previously stated hypothesis on the relevance of the cation moiety of the promoter salt used.

Hydroamination of ethylene by aniline: "in-situ generated" source of I^{M-} promoters

The rhodium-catalysed hydroamination reaction was tested in the presence of PPh₃ and I₂ (Table⁵). Our aim was to form "in situ" an ionic liquid similar to the one used previously (*n*Bu₄PI), and to avoid in this way its synthesis, purification, and conditioning (see the Experimental Section). This idea was based on literature data that have proved the formation of the corresponding phosphonium salts when reacting a phosphine with X₂ (Scheme³).^[25]

Good results were obtained when using stoichiometric quantities of PPh₃ and I₂, with an optimum at 10^{equiv} of each (Table⁵, entries²⁻⁴ and 6). Moreover, only 5^{equiv} of each (Table⁵, entry²), PPh₃ and I₂, afforded a better catalytic performance than the use of 20^{equiv} of *n*Bu₄PI (TON₁=73, TON₂=6, TON₃=0, CE=85).^[14]

Hydroamination of ethylene by aniline: influence of temperature and reaction time

Studies on the rhodium(III)-based catalytic systems were initially conducted at 150^{°C} because previous studies on the platinum(II)-catalysed addition of PhNH₂ to ethylene had shown that this temperature seemed a good compromise between activity and energetic input.^[26] We wished then to explore the performance of this catalytic reaction under "milder" conditions to determine whether the catalytic efficiency could remain reasonably high in view of chiral processes. As may be seen in Table⁶, catalytic activity drops dramatically when the temperature of the reaction was decreased from 150^{°C} to 125^{°C} or 100^{°C}. As already stated,^[11c] a possible explanation for this phenomena is as follows: because the reaction of aniline with ethylene coordinated to a transition-metal complex is disfavoured by the low nucleophilicity of aniline, the catalytic hydroamination is possible under high-temperature conditions to allow the zwitterionic addition complex (Scheme⁴) to experience a temperature-promoted cleavage of the carbon--metal bond, and thus displacing all the steps of the reaction to the formation of *N*-ethylaniline.^[11b]

In the same way, it was observed that an increase of the ethylene pressure from 25^{bar} to 45^{bar} has a negative effect on the TON of the reaction. This outcome is in contrast with previous results on the optimisation of the platinum(II)-catalysed

hydroamination of ethylene by aniline where catalytic activity was promoted in the presence of higher amounts of either of the substrates (aniline/Pt and/or ethylene/Pt).^[26]

Another important parameter to be studied was the evolution of the reaction with time. Hence, various experiments were carried out under the usual conditions for 10^h and 93^h. The results are collected in Table⁷. As may be seen, after 10^h of reaction (Table⁷, entry¹), the three hydroamination products were formed, although only small amounts of **2** and **3** were observed. The proportions are 19:2:1 for **1/2/3**. On the other hand, after 93^h of reaction (Table⁷, entry²), the main product was **2**, small amounts of **1** were detected compared to **2**, and the amount of **3** did not increase after 10^h of reaction. This outcome is consistent with the idea that *N,N*-diethylaniline is the product of a second hydroamination cycle where *N*-ethylaniline is added to ethylene. Thus, along the course of the reaction, the amount of **1** increase and, at the same time, **1** is transformed into **2**. The proportions are 9:75:1 for **1/2/3** after 93^h of reaction.

As shown by the results stated in Table⁷, as the reaction evolves, amounts of **2** increase whereas **1** is consumed thus suggesting that hydroamination of ethylene by more basic anilines such as **1**, is favoured. Amounts of the quinoline derivative **3** remained unchanged after more than 80^h, thereby confirming once more that **1** is probably not an intermediate in the pathway leading to **3**.

Hydroamination of higher α -olefins by aniline

The next step in our study was to use the Rh^{III} precursors to explore the intermolecular hydroamination of higher non-activated α -olefins such as 1-butene and 1-hexene. The products resulting from these reactions are of great relevance in industry and the reaction of higher α -olefins is itself an important scientific challenge.^[15,18,27] Literature on the intermolecular hydroamination of 1-butene and higher α -olefins by simple amines is scarce, and only recently reported. Although catalytic activities were quite low when using organolanthanide complexes, Marks and co-workers^[28,29] successfully achieved the hydroamination of 1-pentene with *n*-propylamine, under anaerobic conditions, at 60^{°C}, using 20^{mol%} of the metal catalyst. These authors reported to deal with a challenging reaction, the *intermolecular* hydroamination of *non-activated* alkenes, in comparison to *intramolecular*

hydroamination, 350x faster, and alkyne hydroamination, 1400x faster. In 2006, He and co-workers studied the addition of TsNH₂ to 1-octene with 5^{mol%} of [AuCl(PPh₃)] /AgOTf in toluene at 85^{°C}.^[29a] In 2007, Loh and co-workers studied the same reaction in the presence of InBr₃ (20^{mol%}) in toluene at 120^{°C}.^[29b] Both research groups obtained the desired Markovnikov hydroamination product along with another Markovnikov isomer resulting from the hydroamination of an internal alkene formed by isomerisation of the initial terminal double bond.^[29] Later on, Loh and Yin found that lanthanide salts in ionic solvents (2^{mol%} of Pr(OTf)₃ + *n*Bu₄PI + I₂) catalysed the hydroamination of 1-heptene and 1-octene with aniline, at 160^{°C}, with up to 95% of the Markovnikov addition products.^[30] They reported the use of phosphonium salts as we had previously described in two unprecedented reports on the hydroamination of 1-hexene by aniline in the presence of a ligandless, inexpensive, and non-toxic PtBr₂/*n*Bu₄PBr/H⁺ catalyst, at 150^{°C}, leading to 95% of the Markovnikov product without alkene isomerisation and with TON up to 200.^[11c,31] In 2010, Hultsch and co-workers^[23] succeeded in the use of sensitive rare-earth-metal asymmetric complexes (5^{mol%}) in toluene for the addition of simple amines to 1-alkenes at 150^{°C}, with good conversions and moderate *ee* values. Finally, Michon, Agbossou-Niedercorn, and co-workers succeeded in the combined use of a copper halide (5^{mol%}) and a silver salt (5--10^{mol%}) for the hydroamination of 1-hexene by TsNH₂ at 100^{°C} to yield the Markovnikov isomers (*N*-2- and *N*-3-hexylamines) in a ratio 4:6.^[32]

No studies have been reported using rhodium-based catalytic systems---a fact that led us to test our RhCl₃·3H₂O/*n*Bu₄PI/PPh₃/I₂ system, which has turned out to be the best to date for the hydroamination of ethylene by simple amines. Thus, the addition of aniline to 1-butene (Scheme⁵) first, and to 1-hexene next (Scheme⁶) were studied.

Our results in this area are particularly promising. In fact, this system is also an efficient catalyst for the hydroamination of 1-butene with up to 150^{TON} (Table⁸, entry⁶), and similar effects to the case of ethylene. Actually, the reaction of aniline with 1-butene in the presence of the above rhodium(III)-based catalyst afforded the expected hydroamination butylanilines products, with a single Markovnikov isomer being highly predominant (99%). Thus, the regioselectivity of this reaction appears even higher than for

the $\text{PtBr}_2/n\text{Bu}_4\text{PBr}$ system, for which a 95:5 Markovnikov/anti-Markovnikov ratio (M/AM) was observed.^[11b] This is a significant result when thinking about applying this catalytic system to the enantioselective version of this reaction.

As no dibutylaniline compounds were detected after the reaction, it seems that, under our experimental conditions, a second hydroamination reaction of 1-butene by *N*-sec-butylaniline does not proceed, possibly owing to steric effects. In the same way, no quinoline product from an aromatic C<C>-H activation was observed. An overview of the results stated in Table⁸ reveals that for the addition of aniline to 1-butene, the precursor $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is not active by itself (Table⁸, entry¹), thus confirming the work done by Coulson on the hydroamination reactions catalysed by the same precursor, where the catalyst showed activity only for the reaction of ethylene with basic amines.^[15,16] In the presence of the phosphonium salts, moderate activities were observed (Table⁸, entries² and 3), especially with the $n\text{Bu}_4\text{PI}$ salt as was the case for the hydroamination of ethylene.^[14] Additionally, PPh_3 and I_2 , in the absence of phosphonium salts, led to low activity (Table⁸, entry⁴), with a higher promoting effect than $n\text{Bu}_4\text{PBr}$, but lower than the effect of $n\text{Bu}_4\text{PI}$. An increase of the activity is once more observed when both promoters, $n\text{Bu}_4\text{PI}$ and PPh_3 , are present (Table⁸, entry⁵), as was reported for the ethylene hydroamination with the same catalytic system.^[14] Results are improved by the addition of molecular iodine (Table⁸, entries⁶ and 7), with an optimum at 65^{equiv} of $n\text{Bu}_4\text{PI}$.

The results in Table⁸ show that the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/n\text{Bu}_4\text{PI}/\text{PPh}_3/\text{I}_2$ system appears to be a highly selective catalyst for the hydroamination of higher olefins such as 1-butene by anilines, thus affording approximately a quarter of the catalytic activity reached for the same process with ethylene.

Concerning the hydroamination of 1-hexene (Scheme⁶), preliminary results using the optimised conditions obtained for the reactions of ethylene and 1-butene in the presence of the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/n\text{Bu}_4\text{PI}/\text{PPh}_3/\text{I}_2$ catalytic system, have shown (Table⁹) the catalyst to achieve only one catalytic cycle in the absence of phosphonium salt (Table⁹, entry³). Nevertheless, the catalytic activity is recovered in the presence of $n\text{Bu}_4\text{PI}$ (150^{equiv}; Table⁹, entry²). More importantly, the very high regioselectivity obtained, 100% for the

Markovnikov product, **8**, with neither traces of the anti-Markovnikov isomer, **10**, nor of quinoline derivatives. This is an important feature when compared to literature data where a great difference of regioselectivity between the (stoichiometric) hydroamination of propene (100% Markovnikov) and 1-hexene (46% Markovnikov, 54% anti-Markovnikov) was reported using $[cis-PtCl_2(PR_3)(olefin)]$ catalysts.^[33]

On the other hand, a significant amount of a secondary Markovnikov isomer (*N*-3-hexylaniline, **9**) resulting from the addition of aniline to 2-hexene (the isomerisation product of 1-hexene), was also obtained along with the expected Markovnikov isomer (*N*-2-hexylaniline, **8**). The ratio of the isomers **8** and **9** is approximately 50:50 (Scheme⁶). This outcome is obviously a consequence of the recognised nature of many rhodium-based catalytic precursors as being good catalysts for olefin isomerisation. This was certainly not observed during the above-described hydroamination of 1-butene because the 2-butene isomer yields the same Markovnikov addition product as 1-butene.

Compared to our results with the $PtBr_2/nBu_4PBr$ system (a non-olefin isomerisation catalyst), the rhodium(III)-based catalyst induces a higher M/AM regioselectivity with no other side products (quinoline) except the Markovnikov addition product; nevertheless it readily promotes olefin isomerisation and subsequent hydroamination at the 3-position.

Hydroamination of ethylene by aniline in the presence of Rh^I precursors

Finally, we decided to explore the hydroamination of ethylene by aniline in the presence of Rh^I precursors (Table¹⁰). This is an idea based on the hypothesis that the active species in the catalytic cycle of the rhodium-catalysed hydroamination are Rh^I species.^[15,17a,18] In view of the extremely important role played by phosphorus ligands in this reaction, especially aromatic phosphines such as PPh_3 , we were prompted to test the catalytic performance of both Wilkinson's catalysts: $[RhCl(PPh_3)_3]$ and the corresponding dimer $[\{RhCl(PPh_3)_2\}_2]$, which were directly synthesised from $RhCl_3 \cdot 3H_2O$ and PPh_3 precursors used in this study.^[34]

Wilkinson and co-workers studied a series of relevant chemical processes involving the Rh^I complexes, which could be partially applied to the hydroamination mechanism, or at

least, to provide an insight on relative equilibria.^[34] In fact, $[\text{RhCl}(\text{PPh}_3)_2]$, which is formed from Rh^{I} species reacts quickly with ethylene and slower with higher olefins. Furthermore, the formation of the olefin complex is favoured, as in our case, by the presence of $\text{I}^{\langle\text{M}\rangle}$ rather than $\text{Br}^{\langle\text{M}\rangle}$ or $\text{Cl}^{\langle\text{M}\rangle}$ as a consequence of the *trans* effect of $\text{X}^{\langle\text{M}\rangle}$ when in the position *trans* to ethylene.^[34]

As expected, Wilkinson's catalyst allows very high catalytic activities when performing the hydroamination of ethylene by aniline under optimised experimental conditions, using $n\text{Bu}_4\text{PI}$ and I_2 promoters. Under similar conditions the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/n\text{Bu}_4\text{PI}/\text{PPh}_3/\text{I}_2$ catalytic system afforded slightly higher TON ($\text{TON}_1=28$, $\text{TON}_2=225$, $\text{TON}_3=3$, $\text{CE}=484$) mainly because it seems to better promote the formation of **2** from **1**, and thus the hydroamination by more basic amines.

In the same way, Wilkinson's dimer appeared to be a good hydroamination catalyst although the selectivity of the reaction is different because less *N,N*-diethylaniline is formed either because the formation of **2** is less favoured than in the case of the corresponding monomer, or simply because the reaction is slower. It is important to note that no quinoline was observed when using either of the Wilkinson's complexes.

Our study on the performance of rhodium(I)-phosphine precursors, in the presence of phosphonium salts, could provide important access to a new and large family of asymmetric catalytic systems for the enantioselective intermolecular hydroamination of non-activated olefins by simple amines.

Conclusion

In summary, the association of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/2\text{PPh}_3/n\text{Bu}_4\text{PI}/\text{I}_2$ has been shown to afford excellent catalytic activities for the hydroamination of ethylene and higher non-activated α -olefins with aniline. Even more important is to note the very high regioselectivity of this rhodium-based catalytic system towards Markovnikov addition products (up to 100% for the reaction of 1-hexene with aniline). It is also an excellent catalytic system for the addition of more basic anilines, such as *N*-ethylaniline, to non-activated olefins.

From a practical point of view, this system offers several advantages because it involves simple starting materials and tolerates the presence of common aromatic phosphines as potential chiral vectors for the enantioselective version of this reaction. Furthermore, good to excellent activities were achieved by "one-pot" addition of PPh₃ and I₂, a source of an "in-situ" generated halide promoter, in the absence of *n*Bu₄PI.

Research is now in progress to elucidate the nature and the energy of the intermediates of the catalytic cycle of this reaction and to take advantage of these promoting effects to explore the enantioselective intermolecular hydroamination of non-activated alkenes by simple amines in the presence of racemic and chiral Rh^I-based N-heterocyclic carbene--phosphine precursors.

Experimental Section

Instrumentation

The GC analyses were performed on a Hewlett--Packard HP⁴4890 (FID) chromatograph (HP³3395 integrator) equipped with a 30^m HP1 capillary column. The GC-MS analyses were performed on a Hewlett--Packard HP⁶6890 apparatus equipped with a HP⁵5973 M ion detector. The NMR analyses were performed on Bruker AM²250 machine. Catalytic experiments were conducted in a 100^{mL} stainless-steel thermoregulated (electric oven) autoclave with a glass liner and a magnetic stirring bar.

Methods and Materials

Tetra-*n*-butylphosphonium iodide was prepared from *n*Bu₃P and *n*BuI (see below), stored under argon, in a freezer, and protected from light. Tetra-*n*-butylphosphonium bromide (Aldrich, 98%), tetraphenylphosphonium iodide (Alfa Aesar, >98%), tetra-*n*-butylammonium iodide (Fluka, >99%), 1-iodobutane (Alfa Aesar, 99%), tri-*n*-butylphosphine (Acros Organics, 95%), triphenylphosphine (Aldrich, 99%), triphenylphosphite (Acros, 99%), trimethylphosphite (Strem, 97%), methyldiphenylphosphinite (Acros, 99%), tri(4-methoxyphenyl)phosphine (Alfa Aesar, 98%), tri((4-trifluoromethyl)phenyl)phosphine (Avocado, 98%), tri(*p*-tolyl)phosphine (Fluka, >97%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (Aldrich, 97%), 1,2-bis(diphenylphosphino)ethane (Strem, 99%), and rhodium trichloride trihydrate (Johnson Matthey,

41.92%) were used as received. Molecular iodine was purchased from Acros. Aniline (Acros Organics, 99% for analysis ACS), *N*-ethylaniline (Acros Organics, 98%), morpholine (Fluka, 99%), piperidine (Acros Organics, 99%), benzylamine (Aldrich, >99.5%), *N,N*-di-*n*-butylaniline (Aldrich, 97%), 4-*n*-octylaniline (TCI, >95%), 1-hexene (Aldrich, 97%) and triethylphosphite (Aldrich, 98%) were distilled before use and stored under argon. Ethylene (N25) and 1-butene were purchased from Air Liquide. Tricyclohexylphosphine was recrystallised from toluene/methanol. $[\text{RhCl}(\text{PPh}_3)_3]$, $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$ were prepared according to established methods.^[34]

Preparation of tetra-*n*-butylphosphonium iodide

Tri-*n*-butylphosphine (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. The solution was heated with a heat gun for approximately 15 min. After cooling, the resulting precipitate was washed with diethyl ether (4 × 50 mL) until a white solid was obtained. Evaporation of residual solvent was carried out under vacuum overnight to afford pure *n*Bu₄PI as a white powder (96% yield). m.p. 95--96 °C; ¹H NMR (250 MHz, [D₆]acetone): δ = 0.96 (t, 3H, *J* = 3 Hz), 1.55 (m, 2H), 1.70 (m, 2H), 2.54 ppm (m, 2H); ³¹P NMR (250 MHz, [D₆]acetone): δ = 33.52 ppm (s); elemental analysis calcd (%) for C₁₆H₃₆IP: C 49.74, H 9.39; found: C 49.75, H 9.57.

Typical hydroamination reactions

Hydroamination of ethylene: The autoclave was charged with RhCl₃·3H₂O (34.0 mg, 0.13 mmol), I₂ (2 equiv with respect to Rh, 66.0 mg, 0.26 mmol), PPh₃ (2 equiv with respect to Rh, 68.0 mg, 0.26 mmol), and *n*Bu₄PI (3.3 g, 8.45 mmol). The autoclave was closed and submitted to several argon-vacuum cycles. Distilled and degassed aniline (4.1 mL, 45 mmol) was then syringed into the autoclave. The ethylene pipe was connected to the autoclave, purged, and the ethylene pressure was adjusted to 25 bar at RT (ca. 100 mmol). The temperature was then raised to 150 °C. After 96 h, the autoclave was cooled to RT and slowly vented in a fume cupboard. The reaction mixture was poured into diethyl ether (120 mL), stirred for 2 h, and then filtered. The external standard (*N,N*-di-*n*-butylaniline, ca. 0.15 g) was added to the collected ethereal phases and the solution was analysed by GC and GCMS.

<+>**Hydroamination of 1-butene:** The autoclave was charged with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (34.0[^]mg, 0.13[^]mmol), I_2 (2[^]equiv with respect to Rh, 66.0[^]mg, 0.26[^]mmol), PPh_3 (2[^]equiv with respect to Rh, 68.0[^]mg, 0.26[^]mmol) and $n\text{Bu}_4\text{PI}$ (3.3[^]g, 8.45[^]mmol). The autoclave was closed and submitted to several argon-vacuum cycles. Distilled and degassed aniline (4.1[^]mL, 45[^]mmol) was then syringed into the autoclave. Pre-cooled 1-butene (8.9[^]mL, 100[^]mmol) was then transferred from a Schlenk flask to the previously cooled (in a liquid nitrogen bath) autoclave by a cannula. The whole system was warmed to RT and then the temperature was raised to 150[^]°C. After 96[^]h, the autoclave was cooled to RT and slowly vented in a fume cupboard. The reaction mixture was poured into diethyl ether (120[^]mL), stirred for 2[^]h, and then filtered. The external standard (4-*n*-octylaniline, ca.[^]0.15[^]g) was added to the collected ethereal phases and the solution was analysed by GC and GCMS.

<+>**Hydroamination of 1-hexene:** The autoclave was charged with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (34.0[^]mg, 0.13[^]mmol), I_2 (2[^]equiv with respect to Rh, 66.0[^]mg, 0.26[^]mmol), PPh_3 (2[^]equiv with respect to Rh, 68.0[^]mg, 0.26[^]mmol) and $n\text{Bu}_4\text{PI}$ (3.3[^]g, 8.45[^]mmol). The autoclave was closed and submitted to several argon-vacuum cycles. Distilled and degassed aniline (4.1[^]mL, 45[^]mmol) and 1-hexene (11.3[^]mL, 91[^]mmol) were then sequentially syringed into the autoclave. The temperature was then raised to 150[^]°C. After 96[^]h, the autoclave was cooled to RT and slowly vented in a fume cupboard. The reaction mixture was then poured into diethyl ether (120[^]mL), and stirred for 2[^]h, then filtered. The external standard (*N,N*-di-*n*-butylaniline, ca.[^]0.15[^]g) was added to the collected ethereal phases and the solution was analysed by GC and GCMS.

<+>Taking into account the liquid nature of both substrates (aniline and 1-hexene), the hydroamination of 1-hexene by aniline could analogously be carried out using Schlenk glassware techniques.

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Scheme[^]1 Industrial synthesis of amines by hydroformylation/hydrogenation sequence and by hydration.^[4--7]

Scheme[^]2 Addition of an N<C->H bond across a double bond: hydroamination of olefins. M=metal.

Scheme[^]3 Reaction of phosphorus (III) derivatives with molecular halides.

Scheme[^]4 Formation of a zwitterionic complex by addition of aniline to ethylene coordinated to a Pt^{II} complex and further elimination of the hydroamination product.

Scheme[^]5 Products formed in the RhCl₃·3H₂O-catalysed hydroamination of 1-butene by aniline.

Scheme[^]6 Products formed in the RhCl₃·3H₂O-catalysed hydroamination of 1-hexene by aniline.

Table[^]1 <w=1>Effect of the amount of PPh₃ on the RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline.^[a]

| Entry | PPh ₃ [^] [equiv] | I ₂ [^] [equiv] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | CE ^[c] |
|-------|---------------------------------------|-------------------------------------|----------------------|----------------------|----------------------|-------------------|
| 1 | 1 | 2 | 49<dp> | 192<dp> | 5 | 442<dp> |
| 2 | 2 | 2 | 21<dp> | 230<dp> | 3 | 487<dp> |
| 3 | 2 | -- | 114<dp> | 114<dp> | 7 | 355<dp> |
| 4 | 3 | -- | 148<dp> | 101<dp> | 3 | 356<dp> |
| 5 | 5 | -- | 129<dp> | 40<dp> | 2 | 213<dp> |

| | | | | | | |
|---|----|----|--------|-------|---|--------|
| 6 | 10 | -- | 31<dp> | 1<dp> | 1 | 36<dp> |
|---|----|----|--------|-------|---|--------|

[a][^]Reaction conditions: RhCl₃·3H₂O (34.2[^]mg, 0.13[^]mmol), PPh₃, *n*Bu₄PI (3.3[^]g, 8.45[^]mmol, 65[^]equiv), I₂ (0.066[^]g, 0.26[^]mmol, 2[^]equiv), PhNH₂ (4.1[^]mL, 45.5[^]mmol, 350[^]equiv), C₂H₄ (25[^]bar, ca.[^]100[^]mmol, 770[^]equiv), 150[^]°C, 96[^]h.
[b][^]*N*-ethylaniline (**1**), *N,N*-diethylaniline (**2**), 2-methyl-quinoline (**3**). [c][^]TON₁ + 2TON₂ + 2TON₃.

Table[^]2 <w=1>Effect of the nature of the phosphorus ligand on the RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline in the presence of I₂.^[a]

| Entry | Ligand [^] [equiv] | <i>t</i> [^] [h] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | CE ^[c] |
|-------|--------------------------------|---------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------|
| 1 | P(OPh) ₃ (1) | 24 | 13<dp> | 1<dp> | 7<dp> | 29<dp> |
| 2 | P(OPh) ₃ (2) | 24 | 19<dp> | --<dp> | 3<dp> | 25<dp> |
| 3 | P(OMe) ₃ (1) | 24 | 11<dp> | 2<dp> | 8<dp> | 31<dp> |
| 4 | P(OMe) ₃ (2) | 24 | 11<dp> | 2<dp> | 11<dp> | 37<dp> |
| 5 | P(OMe) ₃ (2) | 96 | 12<dp> | 3<dp> | 7<dp> | 32<dp> |
| 6 | P(OEt) ₃ (1) | 24 | 12<dp> | --<dp> | 9<dp> | 30<dp> |
| 7 | P(OEt) ₃ (2) | 24 | 13<dp> | --<dp> | 10<dp> | 33<dp> |
| 8 | <i>n</i> Bu ₃ P (1) | 24 | 10<dp> | 2<dp> | 9<dp> | 32<dp> |
| 9 | <i>n</i> Bu ₃ P (2) | 24 | 9<dp> | 1<dp> | 8<dp> | 27<dp> |
| 10 | <i>n</i> Bu ₃ P (2) | 96 | 14<dp> | 5<dp> | 11<dp> | 46<dp> |
| 11 | PCy ₃ (2) | 96 | 26<dp> | 0<dp> | 12<dp> | 50<dp> ^[d] |
| 12 | P(OMe)Ph ₂ (2) | 96 | 104<dp> | 13<dp> | 8<dp> | 147<dp> |

| | | | | | | |
|----|---|----|---------|---------|--------|---------|
| 13 | dppe (1) | 24 | 106<dp> | 16<dp> | 8<dp> | 154<dp> |
| 14 | binap (1) | 24 | 119<dp> | 50<dp> | 4<dp> | 227<dp> |
| 15 | binap (1) | 96 | 53<dp> | 203<dp> | --<dp> | 459<dp> |
| 16 | P(<i>p</i> -CF ₃ C ₆ H ₄) ₃ (2) | 96 | 46<dp> | 4<dp> | --<dp> | 54<dp> |
| 17 | P(<i>p</i> -CH ₃ C ₆ H ₄) ₃ (2) | 96 | 22<dp> | 250<dp> | 3<dp> | 528<dp> |
| 18 | P(<i>p</i> -OCH ₃ C ₆ H ₄) ₃ (2) | 96 | 143<dp> | 64<dp> | --<dp> | 271<dp> |

[a][^]Reaction conditions: RhCl₃·3H₂O (34.2[^]mg, 0.13[^]mmol), phosphine ligand, I₂ (0.066[^]g, 0.26[^]mmol, 2[^]equiv), *n*Bu₄PI (3.3[^]g, 8.45[^]mmol, 65[^]equiv), PhNH₂ (4.1[^]mL, 45.5[^]mmol, 350[^]equiv), C₂H₄ (25[^]bar, ca.100[^]mmol, 770[^]equiv), 150[^]°C.
[b][^]*N*-ethylaniline (**1**), *N,N*-diethylaniline (**2**), 2-methyl-quinoline (**3**). [c][^]TON₁ + 2TON₂ + 2TON₃. [d][^]Without I₂. Cy=cyclohexyl

Table[^]3 <w=1>Effects of the nature of the starting amine on the RhCl₃·3H₂O-catalysed hydroamination of ethylene.^[a]

| Entry | Amine | p <i>K</i> _b | <i>t</i> [^] [h] | Product(s) ^[b] | TON | CE ^[c] |
|-------|------------------------|-------------------------|---------------------------|----------------------------------|----------------------------|-------------------|
| 1 | aniline | 9.42 | 24 | 1 2 3 | 84<dp> 147<dp> 2<dp> | 383<dp> |
| 2 | <i>N</i> -ethylaniline | 8.88 | 10 | 2 | 187<dp> | 187<dp> |
| 3 | <i>N</i> -ethylaniline | 8.88 | 24 | 2 | 267<dp> | 267<dp> |
| 4 | benzylamine | 4.67 | 96 | 6 7 | 23<dp> 13<dp> | 49<dp> |

| | | | | | | |
|---|------------|------|----|----------|-------|-------|
| 5 | morpholine | 5.64 | 24 | 4 | 4<dp> | 4<dp> |
| 6 | piperidine | 2.89 | 24 | 5 | 4<dp> | 4<dp> |

[a]^{Reaction conditions:} RhCl₃·3H₂O (34.2^{mg}, 0.13^{mmol}, 1^{equiv}), PPh₃ (68.2^{mg}, 0.26^{mmol}, 2^{equiv}), *n*Bu₄PI (3.3^g, 8.45^{mmol}, 65^{equiv}), I₂ (0.066^g, 0.26^{mmol}, 2^{equiv}), amine (45.5^{mmol}, 350^{equiv}), C₂H₄ (25^{bar}, ca. 100^{mmol}, 770^{equiv}), 150^{°C}. [b]^{*N*-ethylaniline (1), *N,N*-diethylaniline (2), 2-methyl-quinoline (3), *N*-ethylmorpholine (4), *N*-ethylpiperidine (5), *N*-ethylbenzylamine (6), *N,N*-diethylbenzylamine (7).} [c]^{TON_{1 or 4 or 5 or 6} + 2TON_{2 or 7} + 2TON₃.}

Table⁴ <w=1>Effect of the nature of the cation from the ionic liquid on the RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline.^[a]

| Entry | Ionic liquid ^[equiv] | Ligand ^[equiv] | I ₂ ^[equiv] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | CE ^[c] |
|-------|----------------------------------|---------------------------|-----------------------------------|----------------------|----------------------|----------------------|-------------------|
| 1 | Ph ₄ PI (20) | -- | -- | 10 | 0 | 2 | 14 |
| 2 | Ph ₄ PI (65) | -- | -- | 16 | 0 | 0 | 16 |
| 3 | Ph ₄ PI (20) | PPh ₃ (2) | -- | 26 | 0 | 1 | 28 |
| 4 | Ph ₄ PI (65) | PPh ₃ (2) | -- | 27 | 0 | 0 | 27 |
| 5 | <i>n</i> Bu ₄ NI (65) | PPh ₃ (2) | 2 | 47 | 0 | 0 | 47 |

[a]^{Reaction conditions:} RhCl₃·3H₂O (34.2^{mg}, 0.13^{mmol}, 1^{equiv}), PPh₃ (68.2^{mg}, 0.26^{mmol}, 2^{equiv}), I₂ (0.066^g, 0.26^{mmol}, 2^{equiv}), aniline (4.1^{mL}, 45.5^{mmol}, 350^{equiv}), C₂H₄ (25^{bar}, ca. 100^{mmol}, 770^{equiv}), 96^h, 150^{°C}. [b]^{*N*-ethylaniline (1), *N,N*-diethylaniline (2), 2-methyl-quinoline (3).} [c]^{TON₁ + 2TON₂ + 2TON₃.}

Table⁵ <w=1>RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline in the presence of an "in-situ" generated ionic liquid by one-pot addition of PPh₃ and I₂.^[a]

| Entry | PPh ₃ ^[equiv] | I ₂ ^[equiv] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | CE ^[c] |
|-------|-------------------------------------|-----------------------------------|----------------------|----------------------|----------------------|-------------------|
| 1 | 2<dp> | 20<dp> | 25<dp> | --<dp> | 6<dp> | 37<dp> |
| 2 | 5<dp> | 5<dp> | 94<dp> | 6<dp> | --<dp> | 106<dp> |
| 3 | 7<dp>.5 | 7<dp>.5 | 134<dp> | 30<dp> | --<dp> | 194<dp> |
| 4 | 10<dp> | 10<dp> | 21<dp> | 189<dp> | --<dp> | 399<dp> |
| 5 | 12<dp> | 10<dp> | 65<dp> | 96<dp> | --<dp> | 257<dp> |
| 6 | 20<dp> | 20<dp> | 23<dp> | 139<dp> | --<dp> | 301<dp> |
| 7 | 20<dp> | 22<dp> | 46<dp> | 63<dp> | --<dp> | 172<dp> |

[a][^]Reaction conditions: RhCl₃·3H₂O (34.2[^]mg, 0.13[^]mmol, 1[^]equiv), PPh₃, I₂, aniline (4.1[^]mL, 45.5[^]mmol, 350[^]equiv), C₂H₄ (25[^]bar, ca.[^]100[^]mmol, 770[^]equiv), 96[^]h, 150[^]°C. [b][^]N-ethylaniline (**1**), N,N-diethylaniline (**2**), 2-methyl-quinoline (**3**). [c][^]TON₁ + 2 TON₂ + 2 TON₃.

Table[^]6 <w=1>Effect of reaction temperature and ethylene pressure on the RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline.^[a]

| Entry | T [^] [°C] | P [^] [bar] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | CE ^[c] |
|-------|---------------------|----------------------|----------------------|----------------------|----------------------|-------------------|
| 1 | 150 | 25 | 114<dp> | 114<dp> | 7<dp> | 355<dp> |
| 2 | 100 | 25 | 56<dp> | 8<dp> | --<dp> | 72<dp> |
| 3 | 100 | 45 | 30<dp> | 2<dp> | 3<dp> | 40<dp> |
| 4 | 125 | 45 | 46<dp> | 4<dp> | 4<dp> | 62<dp> |

[a][^]Reaction conditions: RhCl₃·3H₂O (34.2[^]mg, 0.13[^]mmol), PPh₃ (68.2[^]mg, 0.26[^]mmol, 2[^]equiv), nBu₄PI (3.3[^]g, 8.45[^]mmol, 65[^]equiv), PhNH₂ (4.1[^]mL,

45.5^{mmol}, 350^{equiv}), C₂H₄, 96^h. [b]^N-ethylaniline (**1**), *N,N*-diethylaniline (**2**), 2-methyl-quinoline (**3**). [c]^{TON₁ + 2TON₂ + 2TON₃}.

Table⁷ <w=1>Effect of reaction time on the RhCl₃·3H₂O-catalysed hydroamination of ethylene by aniline.^[a]

| Entry | <i>t</i> ^[h] | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | EC ^[c] |
|-------|-------------------------|-----------------------------|-----------------------------|-----------------------------|-------------------|
| 1 | 10 | 56 | 5<dp> | 3 | 72<dp> |
| 2 | 93 | 28 | 225<dp> | 3 | 484<dp> |

[a]^{Reaction conditions:} RhCl₃·3H₂O (34.2^{mg}, 0.13^{mmol}), PPh₃ (68.2^{mg}, 0.26^{mmol}, 2^{equiv}), I₂ (0.066^g, 0.26^{mmol}, 2^{equiv}), *n*Bu₄PI (3.3^g, 8.45^{mmol}, 65^{equiv}), PhNH₂ (4.1^{mL}, 45.5^{mmol}, 350^{equiv}), C₂H₄ (25^{bar}, ca.¹⁰⁰^{mmol}, 770^{equiv}), 150^{°C}. [b]^N-ethylaniline (**1**), *N,N*-diethylaniline (**2**), 2-methyl-quinoline (**3**). [c]^{TON₁ + 2TON₂ + 2TON₃}.

Table⁸ <w=1>Hydroamination of 1-butene by aniline catalysed by the RhCl₃·3H₂O/PPh₃ system.^[a]

| Entry | Ligand | Salt ^[equiv] | I ₂ ^[equiv] | TON | M/AM ^[b] |
|-------|------------------|-----------------------------------|-----------------------------------|---------|---------------------|
| 1 | -- | -- | --<dp> | 1<dp> | n.d. |
| 2 | -- | <i>n</i> Bu ₄ PBr (65) | --<dp> | 18<dp> | 99:1 |
| 3 | -- | <i>n</i> Bu ₄ PI (65) | --<dp> | 74<dp> | 99:1 |
| 4 | PPh ₃ | -- | 2<dp> | 23<dp> | 99:1 |
| 5 | PPh ₃ | <i>n</i> Bu ₄ PI (65) | --<dp> | 86<dp> | 99:1 |
| 6 | PPh ₃ | <i>n</i> Bu ₄ PI (65) | 2<dp> | 153<dp> | 99:1 |
| 7 | PPh ₃ | <i>n</i> Bu ₄ PI (150) | 2<dp> | 133<dp> | 99:1 |

[a]^{Reaction conditions: RhCl₃·3H₂O (34.2 mg, 0.13 mmol), PPh₃ (68.2 mg, 0.26 mmol, 2 equiv), *n*Bu₄PBr or *n*Bu₄PI, PhNH₂ (4.1 mL, 45.5 mmol, 350 equiv), I₂, 1-butene (8.9 mL, 100 mmol, ca. 770 equiv), 150 °C, 96 h. [b]^{Ratio of Markovnikov (M) and anti-Markovnikov (AM) isomers. n.d.=not determined.}}

Table 9 <w=1>Hydroamination of 1-hexene by aniline catalysed by RhCl₃·3H₂O/PPh₃.^[a]

| Entry | Catalyst | Salt ^[equiv] | Ligand ^[equiv] | <i>t</i> ^[h] | TON | M/AM ^[b] |
|-------|--------------------------------------|-----------------------------------|---------------------------|-------------------------|--------|---------------------|
| 1 | PtBr ₂ | <i>n</i> Bu ₄ PI (65) | -- | 10 | 6<dp> | 95<dp>:5 |
| 2 | RhCl ₃ ·3H ₂ O | <i>n</i> Bu ₄ PI (150) | PPh ₃ (2) | 96 | 56<dp> | 100<dp>:0 |
| 3 | RhCl ₃ ·3H ₂ O | -- | PPh ₃ (2) | 96 | 1<dp> | 100<dp>:0 |

[a]^{Reaction conditions: RhCl₃·3H₂O (34.2 mg, 0.13 mmol), PPh₃ (68.2 mg, 0.26 mmol, 2 equiv), *n*Bu₄PI, PhNH₂ (4.1 mL, 45.5 mmol, 350 equiv), 1-hexene (11.3 mL, 91 mmol, ca. 770 equiv), 150 °C. [b]^{Ratio of Markovnikov (M) and anti-Markovnikov (AM) isomers.}}

Table 10 <w=1>Hydroamination of ethylene by aniline catalysed by Rh^I complexes.^[a]

| Entry | Catalyst | TON 1 ^[b] | TON 2 ^[b] | TON 3 ^[b] | EC ^[c] |
|-------|--|----------------------|----------------------|----------------------|-------------------|
| 1 | [RhCl(PPh ₃) ₃] | 122 | 126<dp> | -- | 374 |
| 2 | [RhCl(PPh ₃) ₂] ₂ | 129 | 73<dp> | -- | 275 |

[a]^{Reaction conditions: Rh^I (0.13 mmol), I₂ (0.066 g, 0.26 mmol, 2 equiv), *n*Bu₄PI (3.3 g, 8.45 mmol, 65 equiv), PhNH₂ (4.1 mL, 45.5 mmol, 350 equiv), C₂H₄ (25 bar, ca. 100 mmol, 770 equiv), 150 °C, 96 h. [b]^{*N*-ethylaniline (1), *N,N*-diethylaniline (2), 2-methyl-quinoline (3). [c]^{TON₁ + 2TON₂ + 2TON₃.}}}