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Mechanistic study of the $\text{Ru}_3(\text{CO})_{12}$ /chloride catalyzed carbonylation reactions of nitroarenes to carbamates and ureas; the role of the alkylammonium cation

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Abstract

The effect of the chloride counteranion on the mechanism of the $\text{Ru}_3(\text{CO})_{12}$ /chloride catalyzed carbonylation of nitroarenes to carbamates has been investigated. The reason for the higher activity and selectivity obtained with tetraethylammonium chloride with respect to $[\text{PPN}][\text{Cl}]$ is due to the higher hygroscopicity of the former (only when no aniline is added) and to its ability to decompose to yield triethylamine. The role of this last compound is twofold. On one hand, it accelerates the alcoholysis of the intermediately formed diarylurea. On the other, it favors a reaction pathway that consumes aniline together with nitrobenzene, thus converting a by-product into the desired product. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The carbonylation of organic nitro compounds is a process with a high synthetic potential and industrial interest since many products can be obtained from nitro compounds and CO, including isocyanates, carbamates and ureas [1]. Ureas and carbamates are important final products and intermediates in the synthesis of pesticides and fertilizers while mono- and diisocyanates are important intermediates

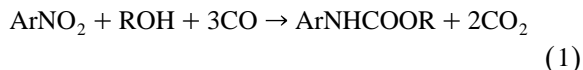
in the manufacturing of pesticides, polyurethane foams plastics, synthetic leather, adhesives, and coatings.

The classical method for the production of isocyanates requires the intermediate reduction of the nitro compound to amine, followed by reaction with phosgene. However, phosgene is a very toxic and corrosive material and an enormous effort has been applied to the development of phosgene-free routes to isocyanates. Among these, the carbonylation of nitro compounds, particularly of aromatic ones, represents one of the most interesting alternatives, but the direct carbonylation of nitro compounds to the corresponding isocyanates proved to be a difficult reaction. However, in the presence of an alcohol,

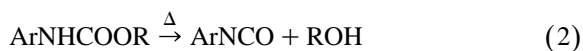
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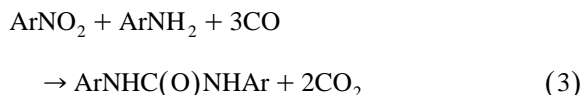
carbamates can be obtained more easily and with a high selectivity (Eq. (1)):



If the isocyanate is the desired product, this can be obtained by thermal cracking of the carbamate (Eq. (2)):



If the carbonylation reaction is conducted in the absence of an alcohol, but in the presence of at least a stoichiometric amount of aniline, diarylureas are formed (Eq. (3)):



Ureas are important products themselves, but can also be converted to the corresponding carbamates by reaction with an alcohol.

Some years ago, research in our group showed that $\text{Ru}_3(\text{CO})_{12}$, when activated by halides, especially chloride, is a very active catalyst for the carbonylation of nitroarenes in the presence of alcohols to afford the corresponding carbamates [2,3]. At the time, a mechanism was proposed for the catalytic cycle involving the formation of cluster species, and, with some additions, this mechanism has remained as a generally accepted reference for many years. However, we recently reinvestigated the mechanism of this catalytic cycle and found a completely different situation. Following are the data reported in a previous paper [4] and relevant to the present one.

–The active catalyst is $\text{Ru}(\text{CO})_5$. Cluster species play no role in the catalytic cycle.

–The main role of chloride is to accelerate the conversion of the starting $\text{Ru}_3(\text{CO})_{12}$ into $\text{Ru}(\text{CO})_5$, a reaction that otherwise would be slow even at the high temperature employed.

–A second role of chloride is to accelerate the reaction between $\text{Ru}(\text{CO})_5$ and the nitroarene, probably via an intermediate of the type $[\text{Ru}(\text{CO})_4(\text{COCl})]^-$ or $[\text{Ru}(\text{CO})_4(\text{Cl})]^-$. This acceleration is

not kinetically influent during most of the reaction course, since the kinetics is zero order in nitroarene, but may be important close to the end of the reaction, when a change in the kinetics is observed and the activation of the nitroarene becomes rate-determining.

–Nitrobenzene is intermediately reduced to aniline. This last compound is then carbonylated to diphenylurea and only at this point reaction of the alcohol with the urea affords the carbamate, regenerating one equivalent of aniline.

–The carbonylation of aniline is the slow step in the catalytic cycle, except, probably, for the very last part of the reaction, as mentioned above.

The reason for the differences observed when different counteranions for chloride are used was not explored in the previous paper and our results on this aspect of the catalytic cycle are reported in the following.

2. Results and discussion

In a previous paper we have identified the reason for which chloride increases the rate of the carbonylation reaction. However, during our catalytic studies [2,3], an influence of the identity of the chloride counteranion on both reaction rate and carbamate selectivity was also evidenced. The best results were obtained with Et_4N^+ and Bu_4N^+ , whereas Me_4N^+ and PPN^+ ($\text{PPN}^+ = (\text{PPh}_3)_2\text{N}^+$) afforded worse results and Et_3NH^+ was ineffective. Tetraethylammonium chloride was chosen for most of the following experiments. Other authors have then used this salt in related reactions [5,6] without questioning the reason for its higher efficiency, which has not yet been unveiled.

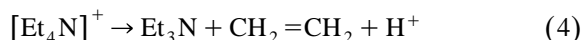
The lower activity of $[\text{Et}_3\text{NH}][\text{Cl}]$ as a co-catalyst may be due to its ability to form a hydrogen bond between the nitrogen-bond hydrogen atom and chloride, deactivating the latter from acting as a nucleophile. Indeed, by running an equilibration experiment between $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{CO})_5$ similar to the ones described in our previous paper [4], we could evidence that $[\text{Et}_3\text{NH}][\text{Cl}]$ does not accelerate to any detectable extent the formation of $\text{Ru}(\text{CO})_5$, thus explaining its ineffectiveness.

However, the reason why PPN⁺ and Me₄N⁺ gave lower conversions and even lower selectivities than Et₄N⁺ and Bu₄N⁺ cannot be explained by the same token.

The first feature that is easily identified is the different amount of moisture present in the co-catalysts. As stated in the Introduction, aniline is necessary for the reaction to proceed. If no aniline is added since the beginning, some must be formed before the carbonylation can start. Alcohol dehydrogenation can afford the required hydrogen atoms, but the presence of water (together with CO) is much more effective [7]. Indeed, Ru₃(CO)₁₂ can also be used as a precatalyst for the reduction of nitroarenes by CO/H₂O and this last reaction is usually much faster than the corresponding carbonylation reactions to afford carbamates [8]. At the time of our earlier experiments, the importance of the presence of aniline had not yet been realized and none was added to the reaction mixture. The presence of moisture can then become an important factor in allowing the carbonylation reaction to start in a short time and both tetraethylammonium and tetrabutylammonium chlorides are very hygroscopic, whereas [PPN][Cl] is not.

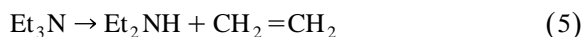
Although the aforementioned effect is surely operating in the absence of added aniline, its importance should become negligible when some aniline is added since the beginning to the reaction solution. On the other hand, as shown by the results reported below, a significant enhancement in selectivity is still observed even in this last case when tetraethylammonium chloride is used as co-catalyst instead of [PPN][Cl], although, depending on the experimental conditions, the rate of the reaction may even be higher in this second case.

An examination of the structure of the cations employed is evidence that the two most effective counteranions have hydrogen atoms in the β position with respect to the nitrogen atom, whereas the other two do not. Hydrogen atoms in the β position may allow for a Hofmann degradation (Eq. (4)) [9]:



In this context, it is also interesting to recall that a related reaction, the decomposition of triethylamine

into diethylamine, has been reported to be catalyzed by Ru₃(CO)₁₂ (Eq. (5)) [10]:



By analyzing the products at the end of the catalytic reactions to which tetraethylammonium chloride had been added, it was indeed possible to evidence by CG and GC–MS the presence of triethylamine, even though it was not possible to quantify it in a consistent manner because it apparently tends to react after the end of the reaction quite quickly, and it is usually possible to detect it in relevant amounts only if the solution for the gas chromatographic analysis is prepared and injected immediately. However, it appears that approximately half of the starting ammonium salt is converted into triethylamine. We have not yet succeeded in identifying the cause of this decomposition. However, addition to the catalytic solution of a base like proton sponge resulted in only a small increase of the peak of triethylamine. Thus, the disappearance of triethylamine is not due to a simple protonation.

The decomposition of tetraethylammonium cation was also observed when its chloride was reacted under usual catalytic conditions, but in the absence of the metal, nitrobenzene and aniline. The extent of decomposition was lower in this case (about 3%). The addition of aniline doubled this value, whereas the addition of Ru₃(CO)₁₂ was apparently not influential, even when the CO pressure was decreased to 10 bar to disfavor the equilibration of Ru₃(CO)₁₂ into Ru(CO)₅. As the study of the degradation of the tetraethylammonium cation was outside the scope of this study, we did not investigate it any further. Anyway, the fact that its decomposition is apparently faster during the catalytic reactions than in the model experiments indicates that the process may be catalyzed by some species, possibly a ruthenium-containing one, formed during the reaction but not in the absence of all of the reagents.

Independent of the exact amount of triethylamine present in solution, it is necessary to understand what its role may be. From several pieces of evidence and from data from the literature [5,7,11–13], it is clear, as previously said, that the reaction proceeds through the intermediate formation of diphenylurea, which is only later alcoholized to carbamate, regenerating the aniline necessary for the proceeding of the reaction.

Table 1
Urea alcoholysis^a

Catalyst	Alcoholysis, %
none	49.5
[Et ₄ N][Cl]	33.0
Et ₃ N	62.5
[Et ₃ NH][Cl]	47.8

^a Experimental conditions: Diphenylurea = 4.8 mmol, Catalyst = 1.1 mmol, PhNO₂ = 16.4 mmol, in toluene (23 ml) + MeOH (4 ml), P_{CO} = 15 bar, T = 160°C, t = 45 min.

Such alcoholysis is analogous to a transesterification reaction and is expected to be base-catalyzed. A series of experiments of urea alcoholysis under typical catalytic reaction conditions and in the presence of several possible promoters is reported in Table 1.

From the obtained data, it is clear, in agreement with what was reported in the literature [5,7,11–13], that alcoholysis occurs even in the absence of any promoter. Also in accord with our expectations, triethylamine appreciably increases the rate of the reaction whereas, quite unexpectedly, [Et₄N][Cl] retards it (as we were at first surprised by this effect, the experiment was repeated several times by two different persons at different periods, but the results were reproducible at the percent). The only plausible explanation is that in the same way as methanol deactivates chloride by hydrogen bonding to it [14], chloride should deactivate methanol. Since methanol is present in a large excess with respect to chloride, a sensible activity is still observed anyway. Trieth-

ylammonium chloride apparently hydrogen bonds to itself (vide supra) and influences little the reaction.

One reason for the higher activity of the tetraethyl- and tetrabutylammonium salts is thus to be found in their ability to decompose during the catalytic reaction, affording the right species at the right moment. Indeed, at the beginning of the reaction the counteraction has no active role, but must leave chloride completely free, so that it can catalyze the transformation of Ru₃(CO)₁₂ into Ru(CO)₅. All of the counteractions employed fulfill this requirement, except for [Et₃NH][Cl] which is indeed the least effective. As the reaction proceeds, chloride becomes completely useless [4], but diphenylurea starts to accumulate and needs to be alcoholized. At this point, the presence of a base is beneficial and tetraethyl- and tetrabutylammonium can provide it, whereas tetramethylammonium and PPN cannot.

A closer examination of the differences between the outcome of reactions run employing [Et₄N][Cl] or [PPN][Cl] (even in the presence of Et₃N) as co-catalysts, however, evidences another effect (Table 2).

When a reaction is run for 1.5 h in the presence even of aniline (mol ratio PhNH₂/Ru₃(CO)₁₂ = 50), [PPN][Cl] (mol ratio [PPN][Cl]/Ru₃(CO)₁₂ = 10), and triethylamine (mol ratio Et₃N/Ru₃(CO)₁₂ = 10), the nitrobenzene conversion is approximately halved with respect to the conversion obtained by using [PPN][Cl] alone under the same conditions (Table 2, runs 1 and 2). How-

Table 2
Comparison of PPN⁺ and Et₄N⁺ with respect to the selectivity in carbamate and the aniline consumption^a

Run	Cation	Et ₃ N/Ru ₃ (CO) ₁₂ mol ratio	t (h)	PhNO ₂ conv., % ^b	PhNH ₂ conv., % ^c	Carbamate select. /PhNO ₂ , % ^d	Carbamate select. /PhNO ₂ + PhNH ₂ , % ^e	Urea select., % ^e
1	PPN ⁺	–	1.5	37.5	7.6	50.9	48.9	30.7
2	PPN ⁺	10	1.5	14.5	67.2	114.3	59.1	29.2
3	Et ₄ N ⁺	–	1.5	30.1	16.1	66.4	59.9	30.5
4	PPN ⁺	–	6	91.9	– ^f	76.3	–	20.4
5	Et ₄ N ⁺	–	6	90.3	7.3	84.1	82.8	14.2

^a Experimental conditions: Ru₃(CO)₁₂ = 0.10 mmol, PhNO₂ = 25.0 mmol, PhNH₂ = 5.0 mmol, [Et₄N][Cl] or [PPN][Cl] = 1.0 mmol, in toluene (23 ml) + MeOH (4 ml), P_{CO} = 60 bar, T = 160°C.

^b Calculated with respect to the starting PhNO₂.

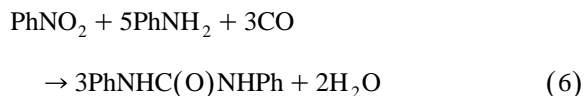
^c Calculated with respect to the starting PhNH₂.

^d Calculated with respect to the reacted PhNO₂.

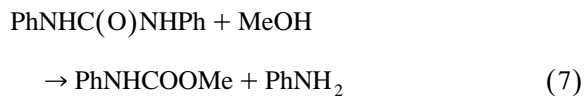
^e Calculated with respect to the sum of reacted PhNO₂ and PhNH₂.

^f 0.54 mmol of aniline (2.3% selectivity with respect to the reacted nitroarene) were formed.

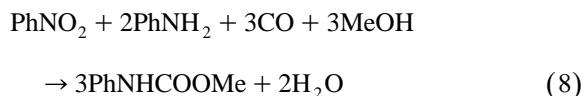
ever, the aniline conversion increases from as much as 7.6% to 67.2% and the selectivity in carbamate with respect to the reacted nitrobenzene reaches the absurd value of 114.3%, the selectivity in urea remaining essentially constant. Such a result cannot be explained by any mechanism if the stoichiometry in Eq. (1) is considered as the only one responsible for carbamate formation (independent of the *intermediate* role of aniline). However, we recall that another stoichiometry has been evidenced for the formation of ureas from nitroarenes and anilines (Eq. (6)):



This equation can be coupled with urea alcoholysis (Eq. (7)):



to yield the stoichiometry (Eq. (8)):

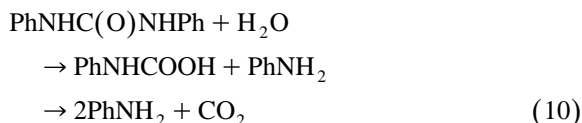
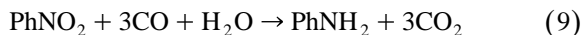


If the process described by Eqs. (6) or (8) is operative, aniline is not simply acting as a catalytic intermediate, but is irreversibly consumed. The importance of such a process in related palladium-catalyzed reactions is well documented [15–18], but, to the best of our knowledge, this is the first time the existence of this process is observed in a ruthenium-catalyzed reaction. The lower nitrobenzene conversion in the presence of triethylamine is clearly due to the faster consumption of aniline, which is surely involved in the r.d.s. of the principal catalytic cycle (as shown in our previous paper [4]) and is probably so even for the catalytic cycle obeying Eq. (8), by analogy with the palladium-catalyzed reactions [17]. The reaction run in the presence of $[\text{Et}_4\text{N}][\text{Cl}]$ (Table 2, run 3) gives an intermediate result, in accord with the expectation that a lower amount of Et_3N will be formed and only slowly during the reaction. Note that the selectivity in urea is virtually the same in all

of these three reactions. Although this may seem to contradict the previous observation that triethylamine should accelerate urea alcoholysis, it must be considered that the amount of carbamate formed in the three reactions indicates that an increasing amount of urea has alcoholized in the series run 2 > run 3 > run 1, in accord with the increasing amount of Et_3N present in these reactions. Also interesting is the comparison between reactions conducted for 6 h (runs 4,5). In this case the conversion of the nitrobenzene is within experimental error the same if PPN^+ or Et_4N^+ is used as a counteranion, but, in the case of PPN^+ , more aniline is present at the end of the reaction than was added at the beginning. On the other hand, in the case of Et_4N^+ , some aniline is consumed. However, if we take into consideration the aniline that may be liberated from the formed urea by alcoholysis, the total amount of aniline present at the end is almost indistinguishable from the starting one. This means that, if we were not aware of the presence of a process associated with the stoichiometry in Eq. (6), we may easily mistake the second catalytic reaction for a *very selective* reaction obeying the stoichiometry in Eq. (1) and wonder why tetraethylammonium has the ability to completely inhibit aniline formation. As a matter of fact, this incorrect explanation of the observed selectivities is the one that has been generally accepted up to now. On the other hand, it is now evident that the *accumulation* of aniline, which is associated with alcohol dehydrogenation, is probably not significantly altered if Et_4N^+ is substituted for PPN^+ ; but in the former case the formation of Et_3N allows for a consumption of the accumulated aniline to afford the desired product, whereas accumulation of aniline is irreversible in the absence of a base. Note that, on the longer time scale of runs 4 and 5, urea alcoholysis is clearly more efficient when Et_4N^+ is used as counteranion.

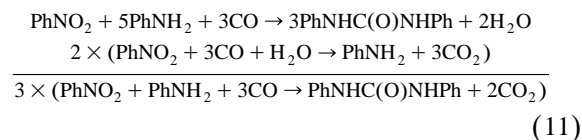
We now turn to the reason for which the stoichiometry in Eq. (6) is operating in the presence of a base. First of all, it must be noted that this reaction produces water. This may reenter the catalytic cycle in two ways: it may react with nitrobenzene and CO to afford aniline (Eq. (9)), or react with urea in place of methanol, to initially afford an equivalent of aniline and one of phenylcarbamic acid, which then decomposes by CO_2 loss to afford another equiva-

lent of aniline. N-substituted carbamic acid are known to decompose very easily to afford amines and CO₂ (Eq. (10)) [19]:



The process in Eq. (9) is a very fast reaction that is known to be catalyzed with a high efficiency by ruthenium carbonyls [8] and is faster than the corresponding carbonylation reaction involving methanol. Concerning the second reaction, we have observed it when studying urea alcoholysis if undried methanol was employed.

If we consider that all water reenters the catalytic cycle by one of the two possible aforementioned ways, then we obtain the same stoichiometry of Eq. (3) (or Eq. (1), if urea alcoholysis is included) (Eq. (11), the same result is obtained if Eq. (10) or any linear combination of Eqs. (9) and (10) is employed instead of Eq. (9)):

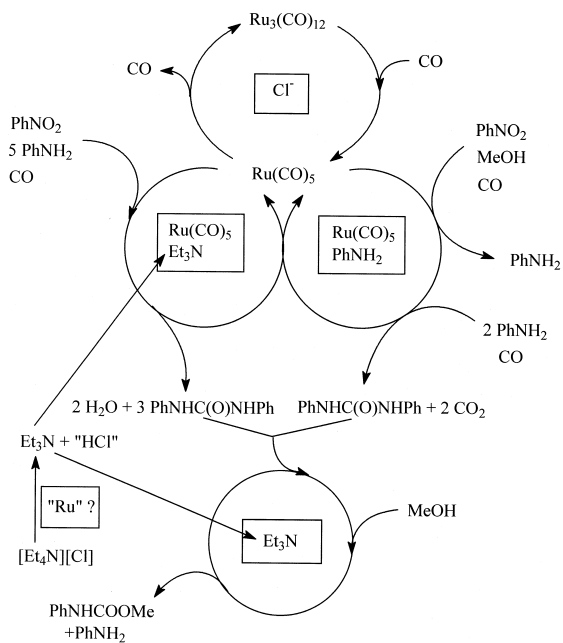


To explain the observed selectivities in the catalytic reactions, we can either suppose that the small amount of water formed does not effectively compete with the present methanol, or that a reaction is present that irreversibly consumes water. Indeed, Ru₃(CO)₁₂ has been reported to be a catalyst for the water gas shift reaction, and the reaction is faster in the presence of a base [20–22]! Notably, Et₃N and aniline are among the bases that have been shown to be effective [23], although their promoting effect is quite low, at least under mild conditions. However, the hydrogen content in the gas phase after the reactions in Table 2 was found to be even lower than the one initially present in the CO gas as an impurity. Thus, it is clear that the role of Et₃N is not to simply eliminate water from the solution by accelerating the WGS reaction, but it directly accelerates a catalytic cycle obeying the stoichiometry in Eq. (8). How this occurs is not known at the present and will require an additional study.

3. Conclusions

A simplified reaction scheme for the catalytic reaction examined in this paper, evidencing the aspects discussed here, is reported in Scheme 1. Species acting as *catalysts* for the individual cycles have been highlighted in frames.

The actual catalytic cycle is composed of at least four independent catalytic cycles (the decomposition of the tetraethylammonium cation may also be a catalytic process), each of which is catalyzed by a different species, which, in some cases, is formed in one of the others. As a first step, chloride *catalyzes* the transformation of the precatalyst Ru₃(CO)₁₂ into the active catalyst Ru(CO)₅. This in turns catalyzes the transformation of the nitroarene into diarylurea. This reaction, which represents the core of the whole catalytic reaction, can occur following two different stoichiometries. In the absence of bases, the stoichiometry consuming one equivalent of nitroarene and one of aniline to afford one equivalent of urea and two of CO₂ is strongly favored (Eq. (3)), if not exclusive (right hand cycle in the scheme). In the presence of a base, another stoichiometry, consuming five equivalents of aniline per equivalent of



Scheme 1.

nitroarene and producing water instead of CO_2 (Eq. (6)), also operates (left hand side of the scheme). Aniline is surely intermediately formed in the first cycle and is probably so even in the second one, but a firm evidence for this is not available at the moment. Independent of the reaction pathway followed up to the formation of the urea, this product is then alcoholized by methanol to yield carbamate and aniline, a reaction which is *catalyzed* by Et_3N . This in turn is formed by the decomposition of the tetraethylammonium cation, a reaction which may be *catalyzed* by some ruthenium complex formed during the reaction. Unfortunately, the pathway consuming more aniline than nitroarene always occurs only as a secondary reaction and little information on it could be gained. However, the existence of this secondary pathway is very helpful in increasing the selectivity of the total carbonylation reaction, as a by-product of the main catalytic cycle (aniline) becomes a reagent of this secondary cycle, thus “re-covering” some lost product into the desired compound.

The chloride counteraction plays an important role in orienting the global reaction. At the beginning of the reaction, it just helps the solubilization of chloride and it is essential that strong ionic couples between the two ions are avoided. In case aniline is not added as a reagent, the presence of moisture in hygroscopic salts is beneficial in accelerating its formation. As the reaction proceeds, the presence of a base becomes beneficial in order to accelerate the alcoholysis of the formed urea and to switch on a catalytic cycle consuming some of the aniline that has accumulated in the meanwhile. Adding triethylamine since the beginning does not afford the same effect, as aniline will be consumed too early in the reaction, with the effect of slowing down the main catalytic cycle, whose rate is dependent on the aniline concentration.

It is instructive to realize that the postulation of a wrong mechanism can lead to a search for the wrong promoters. Indeed, based on the old mechanism, in which aniline is only a by-product, one would be led to consider that the ideal co-catalyst should be stable and non-hygroscopic, whereas it turned out, in accord with the new mechanism, that the best co-catalysts are those that are very hygroscopic and which decompose during the reaction.

4. Experimental

4.1. General procedure

Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring. Solvents were dried and distilled by standard procedures and stored under dinitrogen. Nitrobenzene was purified by shaking with 10% H_2SO_4 , washing with water, and drying with Na_2SO_4 , followed by distillation under dinitrogen and storage under an inert atmosphere. Aniline was treated with KOH , distilled and stored under dinitrogen. Diphenylurea was synthesized by reaction of freshly distilled phenylisocyanate with aniline. $\text{Ru}_3(\text{CO})_{12}$ [24] was synthesized by the method reported in the literature. $[\text{Et}_4\text{N}][\text{Cl}]$ and $[\text{PPN}][\text{Cl}]$ were dried by heating in vacuo and stored under dinitrogen. All other compounds were commercial products and were used as received. Gas chromatographic analyses were performed on a Perkin Elmer 8420 capillary gas chromatograph equipped with a PS 255 column. R_i values (R_i = response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of known concentrations of the compounds (the same holds for HPLC analyses). GC–MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph, equipped with a 5971A mass selective detector. The H_2/CO ratio in the gaseous reagents after the catalytic reactions was determined by use of a Carlo Erba HRGC 5300 Mega Series gas chromatograph, equipped with a molecular sieves column. HPLC analyses were performed on a Hewlett-Packard 1050 chromatograph equipped with a Purosphere RP-18 e column ($\text{CH}_3\text{CN}/\text{water}$ as eluent). Catalytic reactions were performed as previously described [4]. The urea alcoholysis experiments were performed similarly to the catalytic reactions, except for the absence of $\text{Ru}_3(\text{CO})_{12}$.

4.2. Decomposition of $[\text{Et}_4\text{N}]^+$

To a glass liner was added $[\text{Et}_4\text{N}][\text{Cl}]$ (180 mg, 1.09 mmol), toluene (23 ml), methanol (4 ml) and, if required $\text{Ru}_3(\text{CO})_{12}$ (80 mg, 0.125 mmol) or aniline

(782 mg, 8.40 mmol). The liner was placed inside an autoclave with a procedure analogous to the one previously described for the catalytic reactions [4] and the reaction was run at 160°C and under 60 bar CO (the experiment in the presence of Ru₃(CO)₁₂ was also repeated under 10 bars CO), for 45 min. The solution was analyzed by GC as previously described. In the absence of catalysts, the detected Et₃N accounted for 2.7% of the charged Et₄N⁺. In the presence of Ru₃(CO)₁₂ it accounted for 3.2% (60 bar) and 4.5% (10 bar), respectively, and in the presence of aniline for 5.8%.

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