Mechanistic Study of the Ru₃(CO)₁₂/Tetraalkylammonium Chloride Catalyzed Carbonylation Reactions of Nitroarenes to Carbamates and Ureas: A Completely Revised Picture

Fabio Ragaini,* Alessandro Ghitti, and Sergio Cenini

*Dipartimento di Chimica Inorganica, Metallorganica e Analitica and CNR Center,
V. G. Venezian 21, 20133 Milano, Italy*

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The mechanism of the $Ru_3(CO)_{12}$/tetraalkylammonium halide catalyzed carbonylation of nitroarenes to carbamates has been investigated. A completely revised picture has emerged with respect to what was earlier believed. The carbonylation reaction of nitroarenes catalyzed by $Ru_3(CO)_{12}$ proceeds through the intermediate formation of aniline. Moreover, the active species is mononuclear and not a cluster. The effect of chloride is to accelerate the formation of $Ru(CO)_5$. This last complex forms an adduct with chloride that reacts with nitroarenes at a much higher rate than $Ru(CO)_5$ itself, but this acceleration is not kinetically relevant during most of the reaction, as the initial nitroarene activation is not rate determining. Only toward the end of the reaction is a change in rds observed and the formation of the chloride adduct may become important. $[PPN][Ru_3(CO)_{11}(Cl)]$ also reacts with nitroarenes much more easily than $Ru_3(CO)_{12}$.

Introduction

The carbonylation of organic nitro compounds is a process with a high potential synthetic and industrial interest, since many products can be obtained from nitro compounds and CO, including isocyanates, carbamates, and ureas.[1] Some years ago, research in our group showed that $Ru_3(CO)_{12}$, when activated by a tetralkyl-ammonium halide, is a very active catalyst for the carbonylation of nitroarenes in the presence of alcohols to afford the corresponding carbamates (eq 1).[2]

$$ArNO_2 + ROH + 3CO \xrightarrow[\text{toluene}]{Ru_3(CO)_{12}/[Et_4N]Cl} ArNHCOOR + 2CO_2 \quad (1)$$
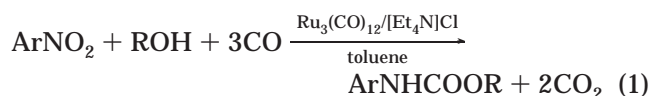
A catalytic cycle was tentatively proposed that included the formation of $Ru_3(CO)_{10}(\mu_3\text{-NPh})$[3] (Scheme 1).

In the following years, research in Geoffroy's group supported some of the intermediate steps proposed and added additional details.[4−6] Moreover, it was found that the addition of [PPN][X] (PPN⁺ = (PPh₃)₂N⁺, X = Cl, Br, I) strongly accelerates the reaction between $Ru_3(CO)_{12}$ and nitrosobenzene, to afford an imido cluster in which

Scheme 1
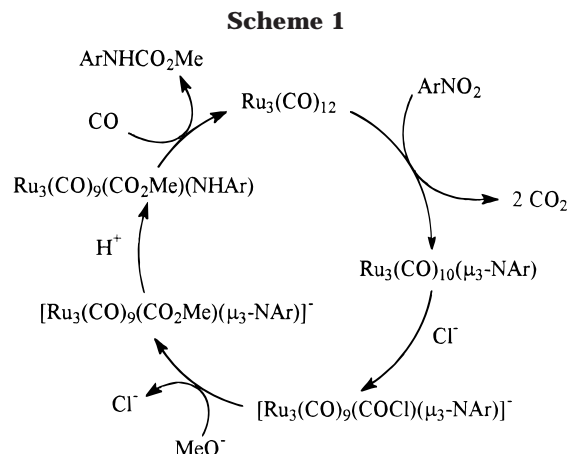
the halide ion is bound in a terminal position, and these clusters react with CO under very mild conditions to afford phenylisocyanate.[5] The order of efficiency of the halides (Cl > Br > I) in this reaction is the same as found in our catalytic reactions. The promoting role of halides in the isocyanate-producing reaction was ascribed to their ability to assume a bridging position in the cluster, likely weakening at the same time one of the N−Ru bonds and rendering the imido fragment more prone to attack a coordinated CO. The occurrence of such reactions was indeed confirmed by later studies on related osmium clusters,[6] for which several intermediates could be isolated.

Some model reactions on related trinuclear ruthenium clusters, especially related to the reduction reactions of nitrobenzene to aniline, have also been reported by Bhaduri and co-workers,[7] and several papers have also been published by different groups on related reactions of ruthenium and osmium clusters containing imido,

* Corresponding author. E-mail: ragaini@csmtbo.mi.cnr.it.

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amido, or isocyanate fragments,[8] although the latter were not intended as models for catalytic reactions. A high-pressure infrared study of the catalytic reaction has also been published.[9]

Although in all of Geoffroy's papers it was always remarked that no firm evidence existed that the reactions reported were of any relevance at all to the actual catalytic cycle, this prudential statement is not always found in other authors' papers and appears anyway to have been overlooked by many readers, so that the involvement of imido clusters as intermediates in the catalytic carbonylation reactions of nitroarenes catalyzed by $Ru_3(CO)_{12}$ appears now to be given for granted by many researchers in the field.

However, some results apparently in contrast with the above-mentioned scenario have been reported in a series of patents by Grate and co-workers.[10] It was reported that the addition of aniline strongly accelerates the carbonylation reaction. If no aniline is added, as in the case of our early experiments, some is generated by reduction of nitrobenzene, the necessary hydrogen atoms coming from the dehydrogenation of the alcohol present in the reaction mixture.[10,11] The rate enhancement was said to be "proportional" to the amount of aniline. If no alcohol was added, but in the presence of added aniline, diphenylurea was obtained at comparable initial rates. If an aniline was added bearing different substituents with respect to the nitroarene employed, mixtures of ureas were obtained, but it should be noted that, at the temperature employed in this experiment (160 °C), exchange of the ArNH− groups in the urea with external aniline is an easy process. It was proposed that the nitroarene is intermediately reduced to aniline, and this last compound is only subsequently carbonylated to diarylurea. If an alcohol is present, the urea is then alcoholyzed to afford 1 equiv of carbamate and 1 equiv of aniline, which reenters the catalytic cycle. Urea

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Table 1. Carbonylation of 3,5-(or 3,4-)Dichloronitrobenzene and Aniline to Afford a Mixture of Diphenylurea and 3,5-(or 3,4-)$Cl_2C_6H_3NHC(O)NHPh$[a]

reaction	nitroarene	$Ru_3(CO)_{12}$ (mg)	nitroarene conv. %[b]	mixed urea (% in mol)
1	3,5-$Cl_2C_6H_3NO_2$	12.5	38.2	0.8
2	3,5-$Cl_2C_6H_3NO_2$	100	98.6	2.4
3	3,4-$Cl_2C_6H_3NO_2$	12.5	36.0	2.9
4	3,4-$Cl_2C_6H_3NO_2$	25	58.8	5.0
5	3,4-$Cl_2C_6H_3NO_2$	50	78.7	7.3
6	3,4-$Cl_2C_6H_3NO_2$	100	97.8	8.4
7[c]	3,4-$Cl_2C_6H_3NO_2$	12.5	54.6	5.0
8[c]	3,4-$Cl_2C_6H_3NO_2$	25	77.5	6.3
9[d]	3,4-$Cl_2C_6H_3NO_2$	50	65.8	6.0
10[e]	3,4-$Cl_2C_6H_3NO_2$	50	22.7	2.8

[a] 3,5-(or 3,4-)$Cl_2C_6H_3NO_2$ = 3.81 mmol, $PhNH_2$ = 15.50 mmol, $[Bu_4N][Cl]$ = 0.52 mmol, in toluene (8 mL), P_{CO} = 60 bar, T = 120 °C, t = 3 h. [b] Calculated with respect to the starting nitroarene. [c] t = 6 h. [d] P_{CO} = 30 bar. [e] Without $[Bu_4N]Cl$.

alcoholysis was independently tested and is a spontaneous reaction at high temperature, which requires no metal catalyst. We recall that a pathway in which aniline is an intermediate would be analogous to the one later investigated by Gladfelter and his group for the related carbonylation reactions catalyzed by $Ru(CO)_3$-$(DPPE)$[12] ($DPPE$ = 1,2-bis(diphenylphosphinoethane)). In this case, a key intermediate is a bis(carbalkoxy) complex $Ru(CO)_2(DPPE)(COOMe)_2$.

At this point, the traditionally accepted mechanism required some reinvestigation in order to get some insight into the real processes involved. In this paper we report the results of our mechanistic study, which show that the previously discovered reactions are not relevant to the actual catalytic cycle, while a new mechanistic picture emerges.

Results and Discussion

Aniline as an Intermediate. In this work, we found that the catalytic reaction follows a zero-order kinetics with respect to nitrobenzene (Table 2, runs 3, 6, 7). The dependence of the rate of the reaction on the aniline concentration is complex and will be the focus of a future work. However, an increase in rate when increasing the initial aniline amount has been clearly observed in several experiments, which is inconsistent with the reaction pathway reported in Scheme 1 and indicates that aniline must be involved in the reaction.

For some years, a typical test to determine if aniline was an intermediate in a catalytic carbonylation of a nitroarene to carbamate was to run the carbonylation reaction of a nitroarene in the presence of an aniline bearing on the aromatic ring different substituents with respect to the ones on the nitroarene. If aniline is not an intermediate, only the carbamate deriving from the

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Table 2. Effect of the Ru$_3$(CO)$_{12}$ and PhNO$_2$ Amounts on the Rate of the Carbonylation Reaction to Yield Methyl Phenylcarbamate[a]

reaction	Ru$_3$(CO)$_{12}$ (mg)	TOF (h^{-1})
1	15	60.6
2	30	61.0
3	50	61.6
4	70	59.4
5	90	57.7
6[b]	50	58.0
7[c]	50	60.0

[a] PhNO$_2$ = 32.80 mmol, PhNH$_2$ = 8.40 mmol, [Et$_4$N][Cl] = 1.06 mmol, in toluene (23 mL) + MeOH (4 mL), P_{CO} = 60 bar, T = 160 °C, t = 1.5 h. [b] PhNO$_2$ = 16.40 mmol. [c] PhNO$_2$ = 24.6 mmol.

Scheme 2
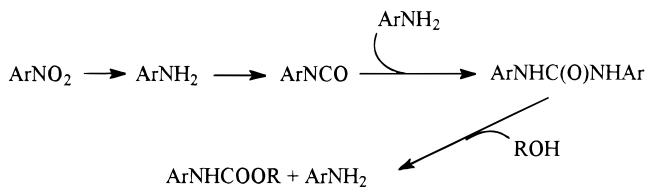
Scheme 3
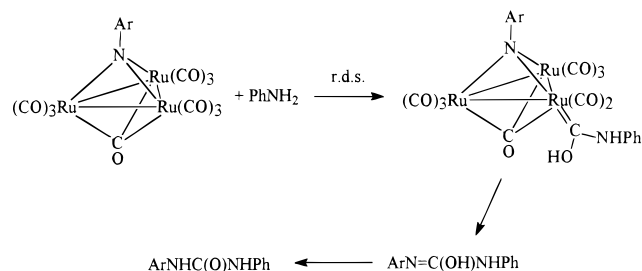
starting nitroarene should be obtained, whereas if it is, both of the carbamates deriving from the nitroarene and the aniline should be obtained. However, more recently Gargulak and Gladfelter have shown that, at least in the case of Ru(CO)$_3$(DPPE) as a catalyst, attack of aniline on a carbomethoxy complex initially generates free isocyanate that then reacts with excess aniline in solution to afford a diarylurea. Only later this last product is alcoholyzed to afford 1 equiv of carbamate and 1 equiv of aniline.[12h] So, at least for this ruthenium catalyst, the reaction sequence (only the organic products are shown) is the one shown in Scheme 2.

With this knowledge in mind, the aforementioned test cannot be considered any longer generally valid. Indeed, if we consider isocyanate as a possible intermediate, this may generate a mixed urea in any case, even if it derives only from the original nitroarene and not from the aniline. A mixed urea would then alcoholyze to yield a mixture of all possible carbamates and anilines.[13] In principle, mixed ureas may even be formed in other ways (e.g., by aniline attack to a coordinated isocyanate or to a metal fragment already containing a nitroarene-derived moiety, see Scheme 3). The only way to distinguish between a mechanism in which the nitro compound is intermediately reduced to the corresponding aniline and one in which it is not is to work in the

(13) (a) The conclusion drawn in previous papers[12e,13b] on the involvement of aniline as an intermediate in related reactions should be considered as well-based even if the test on the formation of mixed carbamates is inconclusive, as other independent evidence as pointed to the same conclusion. (b) Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1994**, *13*, 1178–1189.

absence of alcohols and in the presence of at least a stoichiometric amount of an aniline bearing different substituents on the ring with respect to those of the nitroarene (under these conditions the product is a urea), working under conditions such that scrambling of substituents between the formed urea and free aniline does not occur. Indeed, we can consider a reaction scheme in which an imido cluster is formed from Ru$_3$(CO)$_{12}$ and the nitro compound and this cluster is then attacked in the rds by the added amine, followed by reactions similar to those described by Geoffroy and co-workers. In case an alcohol is present, we must consider that urea alcoholysis under the reaction conditions would afford carbamate and regenerate the amine necessary to bring about the carbonylation reaction (Scheme 3).

This scenario would explain a rate dependence on the added aniline, without requiring that all the nitro compound is intermediately converted to amine. A similar trend would be observed even if the rds followed the attack of aniline on the cluster. A feature of this reaction scheme is that a mixed urea should selectively be formed. On the other hand, if all of the nitro compound was reduced to amine, then a mixture of ureas containing all of the combinations of different aryl groups should be obtained. Note that the present test allows one to asses if aniline is an intermediate or just a "catalyst" for the carbonylation reaction independent of the precise pathway followed by the reaction. The test is valid even if species different from those reported in Scheme 3, even mononuclear ones, were formed.

To render the results more clear-cut, we used unsubstituted aniline as an amine and a nitroarene bearing electron-withdrawing substituents (3,5-Cl$_2$C$_6$H$_3$NO$_2$ or its 3,4 isomer), so that the nucleophilicity of the corresponding aniline would be low, and we also worked with a 4-fold molar excess of unsubstituted aniline. The reaction was run at 120 °C, as this was the highest temperature at which no appreciable (<1%) exchange between the urea-bound ArNH− moieties and free aniline was observed under the reaction conditions.

The results (Table 1) clearly showed that, in the case of 3,5-Cl$_2$C$_6$H$_3$NO$_2$, the obtained urea was essentially pure diphenylurea, containing only 0.8–2.4% of mixed urea and no symmetrical urea deriving from the substituted aryl ring. The only other nitroarene-derived product was 3,5-Cl$_2$C$_6$H$_3$NH$_2$.

With 3,4-Cl$_2$C$_6$H$_3$NO$_2$, the percentage of mixed urea was somewhat higher (2.8–8.4% depending on the conditions, see later) in accord with the lower global electron-withdrawing effect of a chlorine substituent in *para* rather than in *meta* position. To check if any variation in mechanism was occurring when the total ruthenium concentration was varied, we performed the same experiment several times, by varying the initial Ru$_3$(CO)$_{12}$ amount. A change in this parameter should alter the product distribution in the case in which competing catalytic cycles based on mononuclear and cluster species were operating, as better discussed in the next section. As the initial Ru$_3$(CO)$_{12}$ amount was increased, at a constant reaction time, the percentage of mixed urea in the product increased, but this must be attributed to an effect of the higher concentration of free 3,4-Cl$_2$C$_6$H$_3$NH$_2$ in solution, resulting from the

higher conversion of nitroarene associated with the higher amount of catalyst. A higher amount of dichloroaniline more efficiently competes with unsubstituted aniline for the reactive form of the catalyst and results in a higher amount of mixed urea. That this is the only effect is clearly shown by the fact that if a reaction is performed with a low amount of catalyst but for a longer time, so that the conversion is the same as for an experiment at normal time and higher amount of catalyst, the selectivity is virtually the same as for the experiment with the higher amount of catalyst (compare runs 4 and 7). A mathematical treatment of the available data for all of the reactions in Table 1 supports the same conclusion (see Supporting Information).

The comparison of the data for related reactions using either 3,4- or 3,5-$Cl_2C_6H_3NO_2$ also shows that the conversion is independent of the substrate used (compare run 1 with run 3 and run 2 with run 6). This indicates that even under these conditions the interaction of the nitro compound with the catalyst is not rate determining, otherwise a different conversion (specifically a higher conversion for the 3,5-isomer, see later) should have been observed.

These results unequivocally show that aniline is an intermediate during the reaction and its formation is not a function of the $Ru_3(CO)_{12}$ concentration. Thus any mechanistic picture not implying the intermediate reduction of the nitro compound to aniline, including all of the previously suggested reactions, cannot be of any relevance to the actual catalytic cycle.

Cluster or Mononuclear Nature of the Active Catalyst. Cluster species have been held responsible for the reaction in all of the previous literature concerning the mechanism of the present catalytic system. However, $Ru_3(CO)_{12}$ is known to be in equilibrium with $Ru(CO)_5$ under high CO pressure, and the equilibrium has been studied even from a quantitative point of view, albeit only in isooctane (eq 2):[14]

$$Ru_3(CO)_{12} + 3CO \rightleftharpoons 3Ru(CO)_5 \qquad (2)$$
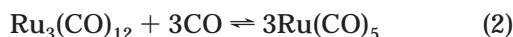
By use of a high-pressure IR cell and spectral subtraction techniques we have evidenced that, under our conditions, the reaction is almost completely shifted toward $Ru(CO)_5$ (Figure 1), only about 5% of the starting $Ru_3(CO)_{12}$ remaining at equilibrium. A typical test to identify the real cluster nature of the active catalyst in systems of this kind is to examine the turnover frequency as a function of the total metal concentration.[15] As it is clear from general considerations and from the data reported,[14] the equilibrium cluster–monomer is more shifted to the right at lower ruthenium concentrations. It follows that a decrease in turnover frequency as the metal concentration increases indicates that the lower nuclearity species is the active one, whereas an increase in conversion in the same series indicates that a cluster compound is active as catalyst. As we are in a region where almost all of the ruthenium is present as $Ru(CO)_5$, a very small variation should be observed if the mononuclear compound is active (the concentration of $Ru(CO)_5$ will vary very little in percentage), whereas
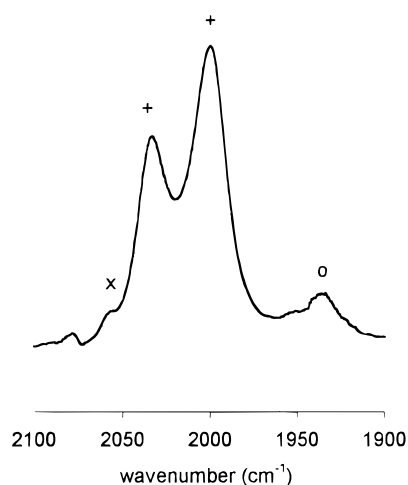

Figure 1. High-pressure IR spectrum of a solution of $Ru_3(CO)_{12}$ (0.035 mmol) and $[Et_4N][Cl]$ (1.08 mmol) in toluene (23 mL) and methanol (2 mL). $T = 170$ °C, $P_{CO} = 60$ bar. $\times = Ru_3(CO)_{12}$, $+ = Ru(CO)_5$, $\bigcirc$ = toluene.

a marked increase in activity upon an increase in the metal concentration should be observed if the cluster is active.

The turnover frequencies for the synthesis of methyl phenylcarbamate in the presence of excess $C_6H_5NH_2$ as a function of the initial amount of $Ru_3(CO)_{12}$ are reported in Table 2.

The TOF is constant within experimental error up to 70 mg of $Ru_3(CO)_{12}$ and then even decreases if the ruthenium concentration is further increased. Thus it is clear that $Ru(CO)_5$ is the real catalyst and the cluster is inactive or, at best, has a much lower activity. Since the cluster is also present in low relative amount under the catalytic conditions, its contribution to the overall reaction is surely negligible. The existence of one only catalytically active complex upon variation of the total ruthenium concentration is in good agreement with the conclusion drawn from the experiments on the synthesis of mixed ureas that aniline is formed as an intermediate through the entire range of ruthenium concentrations examined.

Effect of Chloride Anion. Chloride has already been reported to accelerate the reaction of nitrosoarenes with $Ru_3(CO)_{12}$ and also to promote the formation of phenylisocyanate from a trinuclear imido-halide cluster.[5] However, both of these effects cannot be relevant to the effect observed in catalysis. In fact, apart from the problem of the cluster nature of the compounds involved, nitrosoarenes are always much more reactive than their nitro counterparts,[16] and the reaction of a free nitroso intermediate should be very fast with respect to other steps in the catalytic cycle. The promotion effect on the isocyanate-producing step, on the other hand, cannot be relevant to the catalytic cycle because in the absence of methanol only a trace amount of isocyanate is obtained.[2,17]

During our studies, we found that chloride anion much increases the rate of interconversion of $Ru_3(CO)_{12}$ and $Ru(CO)_5$, which would be otherwise slow (several hours) even at high temperature.[14] Thus the presence of chloride in the reaction mixture allows for a quicker

(14) (a) Bor, G. *Pure Appl. Chem.* **1986**, *58*, 543–552. (b) Koelliker, R.; Bor, G. *J. Organomet. Chem.* **1991**, *417*, 439–451.
    (15) Laine, R. M. L. *J. Mol. Catal.* **1982**, *14*, 137–169.

(16) For an example involving $Ru_3(CO)_{12}$ see: Smieja, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1986**, *25*, 2667–2670.

formation of the active $Ru(CO)_5$ under the reaction conditions (Figure S2, Supporting Information). Under the same conditions, even a larger amount of aniline is ineffective in accelerating the same equilibration. On the other hand, when we examined the equilibration reaction with a Hastelloy C high-pressure IR cell, instead of recording the spectrum of the solution after reactions conducted in a glass liner placed inside an autoclave, the equilibration reaction was almost as fast in the absence of chloride than in its presence and considerably faster than the reaction in the glass liner. Notably, Koelliker and Bor reported very long equilibration times when they studied the same reaction in a stainless steel high-pressure IR cell.[14] Thus it appears that Hastelloy C is also able to catalyze the equilibration between $Ru_3(CO)_{12}$ and $Ru(CO)_5$ (while stainless steel is not), an observation that may have great importance even to other reactions catalyzed by ruthenium carbonyls.

The importance of a slow conversion of $Ru_3(CO)_{12}$ into $Ru(CO)_5$ and its acceleration by chloride goes well beyond the present mechanistic study, as it may be relevant to many of the catalytic carbonylation reactions in which the trinuclear cluster is used as a precatalyst with halides as cocatalysts,[23] especially when short reaction times are employed.

Moreover, chloride much increases the reactivity of both $Ru_3(CO)_{12}$ and $Ru(CO)_5$ toward nitroarenes. Han and others could not evidence any accelerating effect of chloride in the reaction between $Ru_3(CO)_{12}$ and nitrobenzene,[5] but this is likely to be ascribed to the decomposition of the initially formed $[Ru_3(CO)_{11}(Cl)]^-$

Scheme 4

to the less reactive $[Ru_4(CO)_{13}(\mu\text{-}Cl)]^-$,[24] under the reaction conditions. To prevent this decomposition, we worked under a CO atmosphere and employed a nitroarene bearing electron-withdrawing substituent on the ring, which was expected to react at lower temperature. Indeed, it is known that the initial activation of nitroarenes by transition metal complexes always proceeds through an intermediate electron transfer from the complex to the nitro compound.[12i,13b,25−30] Indeed by working with 3,4-dichloronitrobenzene under a CO atmosphere, no reaction is observed at 50 °C with $Ru_3(CO)_{12}$ if no chloride is added. However, in the presence of chloride, $Ru_3(CO)_{12}$ is rapidly converted into the known $[Ru_3(CO)_{11}(Cl)]^-$, and this cluster in turn rapidly reacts with the nitro compound, to generate a mixture of at least two different clusters.[31] The same result is obtained if the chloride-containing cluster is first generated and the nitro compound is only subsequently added. Thus, contrary to what was previously believed, chloride does activate $Ru_3(CO)_{12}$ toward nitro compounds (Scheme 4).

The promoting effect of chloride on the activation of nitroarenes is even more pronounced in the case of $Ru(CO)_5$. To better discriminate the reactions involved, we used a nitroarene having only one electron-withdrawing substituent on the ring. If $Ru(CO)_5$ is treated with chloride in THF at room temperature, conversion to $[Ru_3(CO)_{11}(Cl)]^-$ is observed in a few minutes. However this last cluster does not react to any detectable extent with $p\text{-}FC_6H_4NO_2$ at room temperature even after a prolonged time. $Ru(CO)_5$ alone also does not react with $p\text{-}FC_6H_4NO_2$ at room temperature, but, if chloride is also added, a fast reaction is observed that consumes the nitroarene and produces CO_2. Thus an unobservable intermediate, probably either $[Ru(CO)_4(COCl)]^-$ or $[Ru(CO)_4(Cl)]^-$, must be formed, which very rapidly reacts with the nitro compound before aggregating to form the inactive cluster. Several attempt to observe this intermediate compound, even by working at low

(17) It has been reported that isocyanates can be obtained by treating $PhNO_2$ or 2,4-dinitrotoluene with CO under pressure using $Ru_3(CO)_{12}$ or $[HRu_3(CO)_{11}]^-$ as catalyst.[18] Phenylisocyanate was claimed to be obtained in up to 70% selectivity in acetonitrile as solvent. The same group has also reported the use of THF as solvent for the same reaction.[19−21] The selectivity is apparently much lower (15%), and aniline (10%) and diphenylurea (25%) are also formed. Better results have been reported in a paper from the same authors,[22] and a reaction mechanism has been proposed, based on the intermediate formation of trinuclear mono- and diimido clusters $Ru_3(CO)_{10}(NPh)$ and $Ru_3(CO)_9$-$(NPh)_2$. We have reexamined the catalytic reactions reported in ref 22, performing them in a glass liner and with carefully dried solvents. Under all the conditions reported, we observed no reaction at all, and we thus regard the previously mentioned data as erroneous. A possible explanation for the formation of *small* amounts of isocyanate is that the solvents and/or CO gas may have contained some moisture or dihydrogen. These last reagents may have generated some aniline, which in turn promoted the carbonylation of nitrobenzene, affording diphenylurea. Partial thermolysis of this last product may afford the isocyanate, regenerating at the same time aniline. This explanation is consistent with the results reported for the reactions run in THF,[19−21] where aniline and diphenylurea are indeed the main products despite that no water was intentionally added among the reagents.

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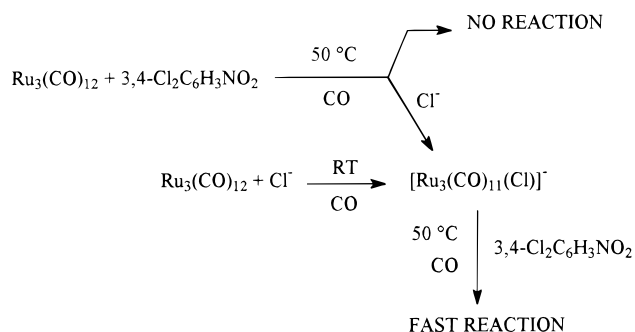
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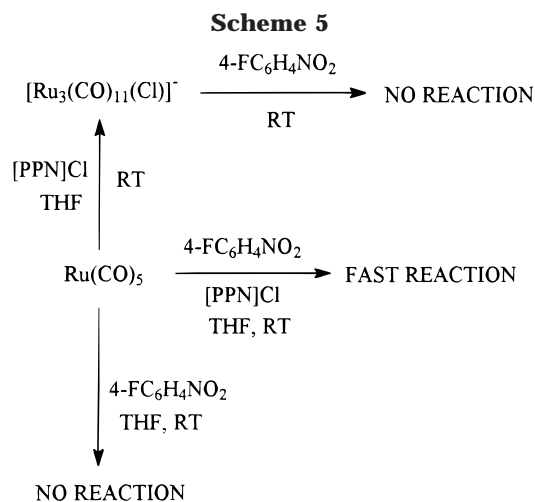(26) Liu, P.-H.; Liao, H.-Y.; Cheng, C.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 2441−2442.

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(31) Despite intense effort and use of different countercations, the products of the reaction, which are only stable under a CO atmosphere, could not be separated and univocally identified, but their IR spectra show they are not any known cluster.

Scheme 5

$[Ru_3(CO)_{11}(Cl)]^-$ $\xrightarrow[\text{RT}]{4\text{-}FC_6H_4NO_2}$ NO REACTION

$\Big\uparrow$ [PPN]Cl RT
     THF

$Ru(CO)_5$ $\xrightarrow[\substack{[\text{PPN}]\text{Cl} \\ \text{THF, RT}}]{4\text{-}FC_6H_4NO_2}$ FAST REACTION

$\Big\downarrow$ $\substack{4\text{-}FC_6H_4NO_2 \\ \text{THF, RT}}$

NO REACTION

temperature, did not meet with success, but stronger nucleophiles such as MeO^- and OH^- are known to attack the coordinated CO of $Ru(CO)_5$ and, in the case of methoxide, the adduct $[Ru(CO)_4(COOMe)]^-$ can be isolated.[32] Moreover, the formation of the adduct of chloride with $Fe(CO)_5$ has been observed in the gas phase, and the interaction energy was found to be low, thus justifying the fact that the same adduct is unobservable in solution.[33] Unfortunately, no mononuclear product could be isolated from this reaction. The IR spectrum of the solution after the reaction showed the presence of some $[Ru_3(CO)_{11}(Cl)]^-$, deriving from some intermediate that had not been trapped by the nitro compound, and several bands, some of which fall close to some of the absorptions observed after the reaction of $[Ru_3(CO)_{11}(Cl)]^-$ with 3,4-dichloronitrobenzene. In any case, even if the obtained compound (or compounds) is analogous to one obtained in the reaction of $[Ru_3(CO)_{11}(Cl)]^-$, it must arise from a subsequent aggregation reaction of an initially formed mononuclear product and not from a reaction of the cluster itself since, as already said, no reaction is observed between the preformed $[Ru_3(CO)_{11}(Cl)]^-$ and $p\text{-}FC_6H_4NO_2$ at room temperature (Scheme 5).

To asses which of the two effects of chloride identified, the acceleration of the equilibration rate between $Ru_3(CO)_{12}$ and $Ru(CO)_5$ and the increase in the reactivity of the latter toward nitroarenes, is the one responsible for the acceleration of the catalytic reaction, we run the following experiments. Two reactions were performed by initially charging in the autoclave only $Ru_3(CO)_{12}$, the solvents (toluene and methanol), CO (60 bar), and, in one case, $[Et_4N][Cl]$. The autoclave was heated at 160 °C by plunging it into a preheated oil bath, and after 5 min, time deemed sufficient for the solution to reach the required temperature, nitrobenzene and aniline were added by means of a high-pressure reservoir (Table 3, runs 1, 2). The experiment in the absence of the alkylammonium salt was then repeated letting the initial solution equilibrate for 4 h before the addition of nitrobenzene and aniline (run 3). This time is sufficient to allow complete equilibration of $Ru_3(CO)_{12}$ into $Ru(CO)_5$ even in the absence of

Table 3. Effect of Chloride and Equilibration Time on Nitrobenzene Conversion[a]

run	additive	equilibration time	$PhNO_2$ conv. %[b]
1	$[Et_4N][Cl]$	5 min	25.8
2	none	5 min	8.44
3	none	4 h	27.4

[a] Experimental conditions: $Ru_3(CO)_{12}$ = 0.11 mmol, $PhNO_2$ = 32.80 mmol, $PhNH_2$ = 8.35 mmol, $[Et_4N][Cl]$ (only run 1) = 1.1 mmol, in toluene (23 mL) + MeOH (4 mL), P_{CO} = 60 bar, T = 160 °C, t = 1.5 h. [b] Calculated with respect to the starting $PhNO_2$.

chloride. The results clearly show that if $Ru_3(CO)_{12}$ is not allowed to transform into $Ru(CO)_5$ (no chloride and very short equilibration time), the conversion is markedly lower. However, if a long enough equilibration time is allowed, the conversion is within experimental error indistinguishable from the one in the presence of chloride.

This fact clearly shows that the only relevant effect of chloride is to accelerate the equilibration of $Ru_3(CO)_{12}$ to $Ru(CO)_5$, and the acceleration of the reaction between $Ru(CO)_5$ and nitrobenzene by chloride is not kinetically relevant to the global reaction. However, this does not mean that it does not occur, but only that the initial reduction of the nitroarene is not the slow step of the reaction (in accord with the zero-order kinetics in this reagent) and its possible further acceleration is not influential. It should be noted that, although this conclusion holds for most of the reaction course, a different behavior may occur close to the end of the reaction, as discussed in more detail later.

The reason for the higher efficiency of chloride with respect to bromide and iodide cannot be now ascribed to its different tendency to assume a bridging position in a cluster or to any labilization effect.[34] The most reasonable explanation is that chloride is simply more nucleophilic than the other two halides in the reaction medium. It is well-known that the nucleophilicity order of halides depends on the solvent. In protic solvents iodide is more nucleophilic than bromide and chloride, as the last two form increasingly stronger hydrogen bonds. However, the exact reverse occurs in aprotic solvents, with chloride being the stronger nucleophile in the series.[35] The kinetics of the reaction between chloride and $Ru_3(CO)_{12}$ has been studied in several solvents, and protic solvents have indeed been found to slow or even suppress the reaction (at least at moderate temperatures).[36] Evidently, a solution containing 10−20% methanol in toluene is "aprotic enough" to render chloride the stronger nucleophile in the series. It should be noted that hydrogen bonds should be formed less easily at the high temperatures employed in the catalytic reactions, a factor that may also play a relevant role.
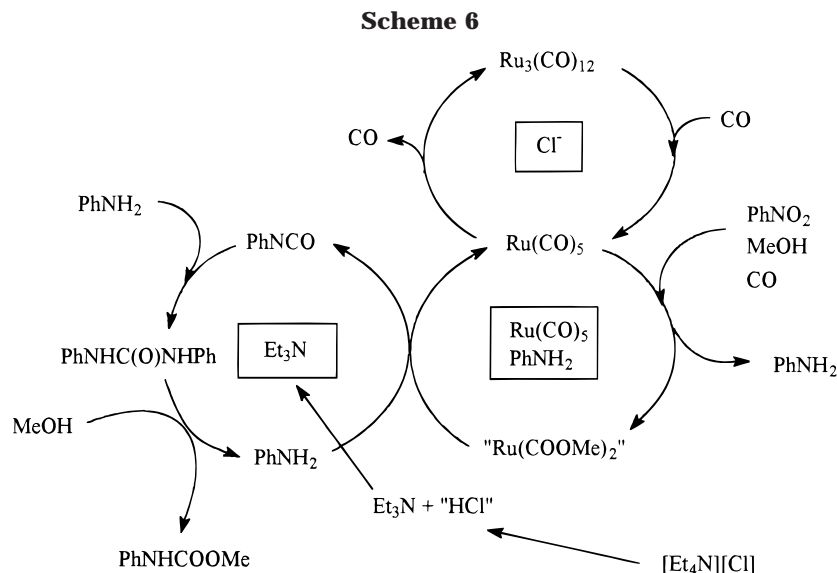
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Scheme 6

The catalytic cycle diagram shows the following species and transformations:

$Ru_3(CO)_{12}$ ⇌ (with Cl^-) $Ru(CO)_5$, releasing CO and taking up CO.

$Ru(CO)_5$ + $PhNO_2$, MeOH, CO → via $Ru(CO)_5$·$PhNH_2$ → $PhNH_2$ → "$Ru(COOMe)_2$"

$Ru(CO)_5$ → PhNCO; PhNCO + $PhNH_2$ → $PhNHC(O)NHPh$ (with Et_3N)

$PhNHC(O)NHPh$ + MeOH → $PhNH_2$ + PhNHCOOMe

Et_3N + "HCl" ← [Et_4N][Cl]

High-Pressure IR Studies. To obtain more information on the species intermediately formed during the reaction, we have run some IR spectra in a high-pressure infrared cell that can also be stirred and heated to the required temperature, so that a full catalytic reaction can be performed in the cell. During a catalytic reaction and at temperatures up to 70 °C (under 60 bar CO) only $Ru_3(CO)_{12}$ is observed. At 100 °C this is transformed into a species showing IR absorptions at 2115 (m) and 2036 (vs) cm^{-1}. Some CO_2 is evolved at this stage and some aniline is formed, but no carbamate. Over 120 °C this species transforms into another one displaying two absorptions at 2090 (m) and 2030 (s) cm^{-1} in the IR spectrum, and CO_2 and carbamate start forming at a high rate. The identity of these two species is not known, and attempts are in progress to independently synthesize them. The results will be reported elsewhere. We only remark here that the observed pattern of bands is not consistent with a species of the type $Ru(CO)_4(COOMe)_2$, which would correspond to the $Ru(CO)_2(DPPE)(COOMe)_2$ observed by Gladfelter during the analogous reaction catalyzed by $Ru(CO)_3(DPPE)$. On the other hand, the frequency of the bands suggests the presence of a species of the type $Ru(CO)_3(L)X_2$ (where L is a neutral ligand and X an anionic one).[37] The absence of $Ru(CO)_5$ at this stage is consistent with the zero order in nitroarene of the kinetics of the reaction. However, toward the end of the reaction, $Ru(CO)_5$ starts to accumulate again, and it is the only observable product at the end of the reaction. Importantly, $Ru(CO)_5$ becomes the largely dominant species before the nitroarene is completely consumed and indicates that the reaction kinetics must change toward the end of the reaction, the activation of nitrobenzene becoming rate determining at this stage. Under these conditions (very low nitrobenzene concentration) an active role of chloride even in promoting the nitrobenzene activation (as in Scheme 5) may occur.

Recently, a high-pressure IR study has been conducted for the analogous reaction of nitrobenzene and aniline to afford diphenylurea, but in the absence of methanol and chloride.[9] A much larger amount of aniline with respect to nitrobenzene (30:1) was also employed. Under these conditions, the authors identified by spectral subtraction techniques the formation and subsequent disappearance of $Ru_3(CO)_9(NPh)_2$, which was thus held responsible for the catalytic reaction. Another unidentified species was also observed, for which an active role could not be excluded. As in the absence of chloride the conversion of $Ru_3(CO)_{12}$ to $Ru(CO)_5$ is very slow, it is possible that, under the conditions of this last study, the reaction is partly proceeding through a cluster pathway. However, clusters are surely not involved under our conditions, and the IR absorptions of the unidentified species in ref 9 indicate it may be mononuclear.

Conclusions

In this paper we have investigated the mechanism of the $Ru_3(CO)_{12}$/tetraalkylammonium halide catalyzed carbonylation of nitroarenes to carbamates. We have shown that, contrary to what was earlier believed, the carbonylation reaction of nitroarenes catalyzed by $Ru_3(CO)_{12}$ proceeds through the intermediate formation of aniline. Second, the active species is mononuclear and not a cluster. The effect of chloride is to accelerate the formation of $Ru(CO)_5$. The role of the countercation of chloride will be the topic of a future paper. However, we anticipate here that tetraethylammonium, the best countercation found in our original study, partly decomposes during the catalytic reaction to yield triethylamine, and this in turn accelerates the alcoholysis of the intermediately formed diarylurea. Some of these conclusions are summarized in Scheme 6.

The actual catalytic cycle is composed of at least three independent catalytic cycles (the decomposition of the tetraalkylammonium salt 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. Thus chloride *catalyzes* the transformation of the precatalyst $Ru_3(CO)_{12}$ into the active catalyst $Ru(CO)_5$. This in turns catalyzes the transformation of the nitroarene into the corresponding isocyanate (formation of free isocyanate appears to be likely, by analogy with the work on $Ru(CO)_3(DPPE)$,[12] although formation of a ruthenium-bound isocyanate that directly reacts with

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external aniline would also explain the available data). Aniline is intermediately formed in this cycle, but it is later consumed, and it accelerates the rds. Thus it has all the features to be considered a *catalyst* for this cycle. The formed isocyanate then reacts with aniline to first yield the urea that is then alcoholyzed by methanol to the carbamate and aniline, a reaction that is *catalyzed* by Et_3N. This in turn is formed by the decomposition of the tetraethylammonium cation, a reaction that may be *catalyzed* by some ruthenium complex formed during the reaction.

In this new mechanistic picture, essentially nothing has remained of the previously proposed pathway. This shows the importance of coupling mechanistic studies based on the reactions of isolated compounds with other more direct evidence gained under catalytic conditions in order to support the real relevance of the reactions investigated to the actual catalytic cycle.

Experimental Section

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. $Ru_3(CO)_{12}$[38] was synthesized by the method reported in the literature. All other compounds, except for those mentioned below, 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. Ri values (Ri = 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. HPLC analyses were performed on a Hewlett-Packard 1050 chromatograph equipped with a Purosphere RP-18 e column (CH_3CN/water as eluant). NMR spectra were recorded on a Bruker AC 200 FT (200 MHz) or on a Bruker AC 300 FT (300 MHz) at room temperature. High-pressure IR spectra were recorded by means of a custom-made high-pressure Hastelloy C reactor equipped with IRTRAN 1 (MgF_2) windows and heating and stirring facilities, placed inside a FTS-7 Bio Rad FT-IR spectrometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Catalytic Reactions. In a typical reaction, the nitroarene, the aniline, $Ru_3(CO)_{12}$, and the cocatalyst (see Tables for amounts) were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at − 78 °C with dry ice, evacuated, and filled with dinitrogen, after which the solvent was added. After the solvent was also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth, which allows for gaseous reagent exchange, and rapidly transferred to a 200 mL stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure, and the autoclave was immersed in an oil bath preheated at the required temperature. Other experimental conditions are reported in the footnotes to the tables. At the end of the reaction the autoclave was cooled with an

ice bath and vented, and the products were analyzed by gas chromatography (for nitroarenes, anilines, and methyl phenylcarbamate; naphthalene as an internal standard) and HPLC (for the ureas; naphthalene as an internal standard). In the cases where the mixture of ureas was the main product, the ureas were mainly present as a precipitate at the end of the reaction. In this case the solid was separated by filtration over a Buchner and washed with toluene, and the solution plus toluene washings and the solid were subjected to separate HPLC analysis to determine the relative amounts of diphenylurea and of mixed urea. In every case, the relative contents of the two ureas in the solid and in solution were indistinguishable within experimental error, as the mixed urea tends to cocrystallize with the symmetric one. In the cases in which diphenylurea was only a byproduct, it was soluble in the final reaction mixture and the solution was analyzed without any separation.

Synthesis of $3,4\text{-}Cl_2C_6H_3NHC(O)NHPh$. An authentic sample of this mixed urea was prepared by adding freshly distilled PhNCO (1.64 g, 1,5 mL, 13.8 mmol) to a Schlenk flask also containing $3,4\text{-}Cl_2C_6H_3NH_2$ (2.35 g, 14.5 mmol) and toluene (15 mL). The solution was stirred at 60 °C for 4 h, after which the precipitate was collected by filtration over a Buchner in the air. The crude product was recrystallyzed two times from THF to eliminate any impurity of diphenylurea (81.3% yield). ^1H NMR ($CDCl_3$): 3.6 (s, 2H, NH), 7−8.4 (m, 8H, Ar−H) ppm. IR (Nujol, cm^{-1}): ν(NH) 3335, ν(C=O) 1653. Mp 219−220 °C. MS: $M^+ = 280$ (calcd 280). Anal. Calcd for $C_{13}H_{10}N_2OCl_2$: C, 55.54; H, 3.59; N, 9.96. Found: C, 55.50; H, 3.43, N, 9.91. The same procedure was used for the 3,5 isomer. $M^+ = 280$ (calcd 280). Anal. Calcd for $C_{13}H_{10}N_2OCl_2$: C, 55.54; H, 3.59; N, 9.96. Found: C, 55.20; H, 3.45, N, 9.81.

Reaction of $Ru_3(CO)_{12}$ with [PPN][Cl] and $3,4\text{-}Cl_2C_6H_3NO_2$. To a 50 mL Schlenk flask under a CO atmosphere was added $Ru_3(CO)_{12}$ (155 mg, 0.243 mmol), [PPN][Cl] (155 mg, 0.270 mmol), and THF (20 mL). The flask was warmed at 40 °C while stirring until all $Ru_3(CO)_{12}$ was consumed (disappearance of the absorption at 2060 cm^{-1} in the IR spectrum), and $[PPN][Ru_3(CO)_{11}(Cl)]$[24] was formed as the only observable product (by IR). At this point $3,4\text{-}Cl_2C_6H_3NO_2$ (467 mg, 2.43 mmol) was added and the solution heated to 50 °C. The reaction was continued until all $[Ru_3(CO)_{11}(Cl)]^-$ was consumed (disappearance of the IR absorption at 1830 cm^{-1}). The IR spectrum of the red solution showed bands at 2095 (vw), 2070 (w), 2057 (sh), 2044 (m), 2035 (m), 2016 (s), 1989 (s), 1967 (m), 1944 (sh), 1928 (sh), 1811 (sh), and 1801 (w) cm^{-1}. The bands do not rise all at the same time, indicating that they are due to a mixture of at least two different compounds. The same outcome was obtained if the nitroarene was added from the beginning. In this case, the intermediate formation of $[Ru_3(CO)_{11}(Cl)]^-$ was also observed, but the following reaction started before $Ru_3(CO)_{12}$ was completely consumed. The reaction was also repeated by using $3,5\text{-}Cl_2C_6H_3NO_2$ instead of its 3,4 isomer or 1,4-dinitrobenzene with similar results (the reaction was slower in the last case). In place of [PPN][Cl], also the corresponding Bu_4N^+, Et_4N^+, PPh_4^+, Cs^+, and $[Na\text{-}(15\text{-Crown-5})]^+$ chlorides were employed. In the case of the cesium salt, the solvent mixture also contained DMSO (10 mL) in order to dissolve CsCl. Switching the atmosphere from CO to N_2 or evaporating the solvent in vacuo caused the decomposition of the products to a brown compound showing in the IR spectrum two broad bands at 2030 (s) and 1960 (vs) cm^{-1}. Attempts to purify and completely characterize the products of the reaction failed.

Preparation of a Solution of $Ru(CO)_5$. $Ru_3(CO)_{12}$ (230 mg, 0.360 mmol) and THF (40 mL) were added to a glass liner, and the liner was placed in an autoclave with a procedure analogous to the one described for the catalytic reactions. The autoclave was charged with 80 bar CO and heated at 150 °C for 5 h, after which it was cooled at dry ice temperature (to decrease volatility of $Ru(CO)_5$) and vented. The solution,

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containing $Ru(CO)_5$ together with a small amount of $Ru_3(CO)_{12}$, was vacuum transferred to a Schlenk flask. The residual $Ru_3(CO)_{12}$ weighed 63 mg, which implies the yield of the reaction to be 73%.

Reaction of $Ru(CO)_5$ with [PPN][Cl]. A 5 mL sample of the $Ru(CO)_5$ solution prepared as previously described (containing 24 mg, 0.098 mmol of $Ru(CO)_5$) was placed in a Schlenk flask under a CO atmosphere, and [PPN][Cl] (64 mg, 0.11 mmol) was added. After 10 min, time required for [PPN][Cl] to dissolve, $Ru(CO)_5$ had completely disappeared and the only observable product in solution (by IR) was $[PPN][Ru_3(CO)_{11}(Cl)]$.[24]

Reaction of $Ru(CO)_5$ with [PPN][Cl] and p-$FC_6H_4NO_2$. A 5 mL sample of the $Ru(CO)_5$ solution prepared as previously described (containing 24 mg, 0.098 mmol of $Ru(CO)_5$) was placed in a Schlenk flask under a CO atmosphere, and p-$FC_6H_4NO_2$ (279 mg, 1.98 mmol) was added. No reaction occurred at room temperature during 1 h. At this point [PPN][Cl] (64 mg, 0.11 mmol) was added. After 5 min, an absorption at 2336 cm^{-1} in the IR spectrum, due to CO_2, was clearly observable. At the end of the reaction (about 10 min) the IR spectrum of the solution showed absorptions at 2075, 2045, 1989, 1959, 1932, and 1800 cm^{-1}, in addition to absorptions attributable to $[PPN][Ru_3(CO)_{11}(Cl)]$.

Exchange of Amido Moieties of Urea with External Anilines. To a glass liner was added PhNHC(O)NHPh (403 mg, 1.90 mmol), 3,4-$Cl_2C_6H_3NH_2$ (758 mg, 4.68 mmol), 3,4-$Cl_2C_6H_3NO_2$ (752 mg, 3.92 mmol), and toluene (8 mL). The liner was placed in an autoclave with a procedure analogous to the one described for the catalytic reactions. The autoclave was charged with 10 bar CO and heated at the desired temperature for 3 h. At the end of the reaction the autoclave was vented, toluene (10 mL) was added to the solution, and the urea residue was decanted. The solution was then analyzed by GC (naphthalene as an internal standard), to detect the possible formation of $PhNH_2$, and the solid was analyzed by HPLC. $PhNH_2$ formation was observed at 140 and 160 °C, but not at 120 °C. The presence of a nitroarene appears to increase the rate of the exchange reaction of the urea, as, in its absence, no exchange was observed up to 180 °C, even when the reaction was repeated in the presence of $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and $[Bu_4N][Cl]$ (59 mg, 0.21 mmol). One effect of the nitroarene is surely to increase the solubility of the urea, which is otherwise very little soluble in toluene.

Supporting Information Available: Correlation between the percentage of mixed urea in the products and the nitroarene conversion for the experiments reported in Table 1. IR spectra showing the effect of $[Et_4N][Cl]$ on the equilibration reaction between $Ru_3(CO)_{12}$ and $Ru(CO)_5$. This material is available free of charge via the Internet at http://pubs.acs.org.