

## Review

# Mechanistic studies of palladium-catalysed carbonylation reactions of nitro compounds to isocyanates, carbamates and ureas

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### Abstract

Many different palladium-based catalytic systems have been reported for the carbonylation reactions of organic nitro compounds to isocyanates, carbamates and ureas. Almost all of these can be roughly divided into three groups: (i) those containing a second (or even a third) metal (usually a Lewis acid or a metal oxo compound or both), (ii) those in which phenanthroline or similar chelating nitrogen ligands are used and (iii) those in which monodentate phosphines are employed as ligands. The systems in which chelating phosphines are used as ligands lie in between the last two groups. The reaction mechanisms for the catalytic systems in each group appear to be related. Most of the information available does not derive from strictly mechanistic studies, but rather from synthetic studies and it is here critically analysed and compared with the information obtained from other related fields.

*Keywords:* Carbonylation; Nitro compounds; Isocyanates; Carbamates; Ureas; Palladium; Mechanistic studies

### 1. Introduction

The catalytic carbonylation of nitro compounds is currently a field of high interest, since a number of important industrial products can be obtained in one step by these reactions: isocyanates ( $\text{ArNCO}$ ), carbamates ( $\text{RNHCOOR}'$ ), ureas ( $\text{RNHC(O)NHR}$ ), azoarenes ( $\text{ArN=NAr}$ ) and azoxyarenes ( $\text{ArN(O)=NAr}$ ), amines, amides, oximes and several types of heterocyclic compounds [1]. Ureas and carbamates are important final products and intermediates in the synthesis of fertilisers, pesticides and isocyanates. On the other hand, mono- and di-isocyanates are very impor-

tant intermediates in the synthesis of polyurethanes, pesticides, synthetic leather, adhesives and coatings. Even a superficial description of the different catalytic systems employed for all of these syntheses is out of the scope of this review. A comprehensive review has been published by one of us some years ago [1] and we are currently writing a book on this subject. Among the possible products of deoxygenation reactions of nitro compounds, isocyanates appear to be the ones most interesting from the industrial point of view. On the other hand, isocyanates can be obtained even from carbamates (by thermal cracking [2]) or ureas (either by direct thermal cracking [3] or through the

intermediate conversion to carbamates, see later) and the synthesis of these last compounds can be performed with higher yields and catalytic efficiencies than those of the isocyanates themselves. Thus the synthesis of carbamates and ureas has attracted an increasing attention during the years. The most active catalytic systems for the synthesis of isocyanates, carbamates and ureas by carbonylation of nitro compounds are based on the use of palladium compounds. Most of the available literature on these catalytic systems is found in the form of patents and few mechanistic studies have been conducted. This is also in part due to the fact that almost all of the catalytic processes, and all of those potentially of interest from an industrial point of view, are conducted under high temperature and pressure conditions, so that examination of the catalytic solutions during the reactions is very difficult. However, much information can be gained even from synthetic studies in which the effect of different promoters and experimental conditions has been examined. Moreover, some information can also be gained from studies of other reactions related to the ones described here, such as the oxidative carbonylation of amines.

Almost all of the palladium-based catalytic systems reported for the reactions discussed here can be roughly divided into three groups: (i) those containing a second (or even a third) metal (usually a Lewis acid or a metal oxo compound or both), (ii) those in which phenanthroline or similar chelating nitrogen ligands are used and (iii) those in which monodentate phosphines are employed as ligands. The systems in which chelating phosphines are used as ligands lie in between the last two groups. The reaction mechanisms for the catalytic systems in each group appear to be related. The first group of catalytic systems has been investigated for many years. Its application has been hindered by the corrosive nature of the cocatalysts used, but it still appears to be interesting since these systems are the only one reported to efficiently catalyse the carbonylation of the economically

important dinitroarenes. Catalytic systems using phenanthroline or its substituted analogues as ligands are the most active monometallic catalysts reported up to now for these reactions. The use of the third group of catalysts is less appealing from a practical point of view, but some studies have been conducted on it which shed some light on some aspects of the other catalytic systems. Thus it will also be discussed in some detail.

In the present paper we will not limit ourselves to simply reporting the published information, but we will also try to critically analyse the conclusions drawn and suggest, where the available data allow it, possible alternative explanations. In this respect, several parts of this paper should be considered as an original contribution, rather than as a simple review article. The mechanism of palladium-catalysed carbonylation reactions of nitro compounds has never been specifically reviewed before.

The paper has been divided into sections, devoted to the three classes of catalysts mentioned above. Some general trends do exist and these will be emphasised under a specific sub-heading. Although the focus of this review is on the use of palladium-based catalytic systems, several mechanistic features are common to catalytic systems based on other metals. Although the latter are not discussed here, their behaviour has been considered while writing this paper and parallels will be reported when regarded as useful. An independent section is devoted to the possible involvement of nitrene intermediates in the catalytic cycle.

## 2. General trends

The carbonylation of nitro compounds requires their intermediate reduction and deoxygenation. Although the degree of reduction that is required, before coupling with CO occurs, probably varies with the catalytic system and it is still a matter of debate, in all of the cases in

which the first step of the reduction has been investigated [4–6], it has been shown to involve an electron transfer *from* a metal complex *to* the nitro compound. In at least two cases, involving  $[\text{Rh}(\text{CO})_4]^-$  [5] and  $\text{Ru}(\text{CO})_3(\text{DPPE})$  (DPPE = 1,2-bis(diphenylphosphino)ethane) [6] respectively, this electron transfer has been shown to occur through an outer-sphere mechanism. However, whereas the occurrence of an electron transfer appears to be a general rule, possibly without exception, the generality of the outer-sphere nature of this process is not at all obvious at this stage. Although this electron transfer has never been directly observed in the case of palladium complexes, there appears to be little doubt that it occurs even in these cases. Especially in earlier papers, it has sometimes been suggested (without experimental evidence) that the nitro compound may act as a nucleophile with respect to a metal complex, with an oxygen atom of the nitro group attacking either a coordinated CO or the metal center. However, this proposal can be discounted on the basis of the very low nucleophilicity of the nitro group and on the consideration that all of the complexes known to react with nitro compounds contain a metal in a low oxidation state (–I to I), which is contrary to what would be expected if the nitro compounds were acting as nucleophiles.

Nitroso compounds, either free or coordinated, are usually regarded as intermediates in the reduction of nitro compounds. This also appears to be a general phenomenon, which is supported by the isolation of several complexes containing the nitrosoarene moiety, following reaction of the corresponding nitroarene with a metal complex. However, under catalytic conditions, nitroso compounds are not generally observed. This is due to the fact that nitrosoarenes are more easily reduced than their corresponding nitroarenes [7], so that they react faster than the starting compounds and never accumulate in solution. The reaction of nitrosobenzene with metal complexes in a low oxidation state has also been shown to proceed through an interme-

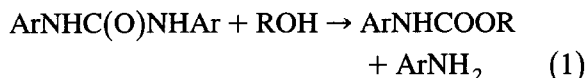
mediate electron transfer in all of the cases in which this possibility has been examined [4].

Azo- and azoxyarenes are often found as by-products in reduction and carbonylation reactions of nitroarenes and they are also often mentioned as alternative starting materials in patents on carbonylation reactions of nitroarenes. It has been shown in several cases that both these products can be further reduced and/or carbonylated by the same catalytic systems that reduce and carbonylate nitroarenes, to afford the same products. However, though the reduction from azoxy- to azoarene may be fast under certain conditions, the subsequent reactions of azoarenes are very slow compared to the global reaction rate when the corresponding nitroarenes are used as substrates, indicating that, unlike nitrosoarenes, azo- and azoxyarenes cannot be intermediates in the main catalytic pathway. In at least three cases involving palladium catalysts [8], the effect of several promoters were shown to be opposite when nitroarenes or the corresponding azo- and azoxyarenes were used as substrates, further supporting the above mentioned conclusion.

As more completely discussed in [1], some of the catalytic systems can produce both isocyanates and carbamates (or ureas) depending on the experimental conditions, whereas others only produce carbamates or ureas, but no isocyanate. When considering the synthesis of carbamates and ureas, one may expect isocyanates to be intermediates in the first type of catalytic system, but not in the second. However, this is not always true and the situation is more complex, as will become apparent in the discussion of the individual systems.

In the case of several catalytic systems for the synthesis of carbamates, the addition of an amine corresponding to the starting nitro compound has been shown to accelerate the reaction. In some cases, it has also been proposed that ureas are formed as intermediates during the reaction, even when no urea is present at the end of the reaction. Arylureas are known to react with alcohols at the high temperatures

commonly employed for the catalytic reactions, to quantitatively afford carbamate and amine (Eq. 1):



So ureas are proposed to be the kinetic products, whereas the carbamates are the thermodynamic ones. This proposal appears to be very likely in many cases, but it is probably not a general rule, as we will discuss in the individual cases.

Anilines are nearly always present as byproducts, however, in some cases, they are also intermediates in the synthesis of carbamates and ureas. This last possibility will be discussed in more detail for the individual catalytic systems. When the aniline is a byproduct, the necessary hydrogen atoms can originate from small amounts of water or H<sub>2</sub> present as impurities in the solvent and/or the CO gas, but can also be produced by alcohol dehydrogenation (when an alcohol is present) or, to a minor extent, by direct hydrogen-atom extraction from the solvent or from the nitro compound itself. Of the primary alcohols, methanol is the least prone to dehydrogenation [9].

In many patents, supported palladium catalysts have been used. However, many reports (see [1], but more have been more recently reported) indicate that heterogeneous catalysts dissolve at least partly in solution under the reaction conditions, and the homogeneous species appear to be the most (if not the only) catalytically active species. Although the existence of a competitive 'heterogeneous cycle' cannot be excluded, it does not appear to play an important role and we will not consider it any more in the following.

### 3. Palladium and metal-containing cocatalysts

Catalytic systems in which a palladium compound, usually PdCl<sub>2</sub> or PdCl<sub>2</sub>Py<sub>2</sub> (Py = pyridine), is activated by a Lewis acid such as

FeCl<sub>3</sub> or VOCl<sub>3</sub>, or a metal oxide such as MoO<sub>3</sub>, or even by a combination of the two, were among the first to be discovered, and many papers and patents have been devoted to their study. Depending upon the experimental conditions and the presence of additional alcohols or amines, isocyanates, carbamates and ureas can all be obtained in good yields. The list of papers and patents related to these catalytic systems is too long to be included here. Only the literature relevant to the topics here discussed has been mentioned. We refer to [1] for a more complete list of papers and patents in this area. Despite the interest in bimetallic catalysts of this class, no in-depth mechanistic study has been conducted, and only a few characteristics of these systems are known. One of the problems is the apparent irreproducibility of some of the reported data. Several authors have published contrasting results and/or have failed to reproduce previously reported experiments. One reason for this is probably the highly corrosive nature of many of the cocatalysts used, coupled with the use of steel autoclaves and with the problem of the deposition of palladium metal on their walls [10]. In some of the catalyst systems, part of the function of the Lewis acid may be just to clean the reactor walls from the deposited palladium, taking it into solution. It is our experience, that a solution of molybdic acid (MoO<sub>3</sub> · H<sub>2</sub>O) will etch a stainless steel spatula immediately even at room temperature, with concomitant reduction of Mo<sup>VI</sup> to a 'molybdenum blue'. In a paper in which the promoting effect of FeCl<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> on the PdCl<sub>2</sub>/MoO<sub>3</sub> catalytic system was investigated, a similar activating effect of the steel reactor walls was observed [11]. Moreover, this role of the Lewis acid does not appear to be the only one, as we will see in the following, although it may account for some of the differences reported by various groups.

Despite the aforementioned limitations some general trends emerge from an examination of the literature, which must be accounted for in any mechanistic picture:

(i) All of the active Lewis acids or oxides are redox-active compounds. Non redox-active acids such as  $\text{AlCl}_3$  are ineffective or show at best a limited promoting activity.

(ii) The most active systems appear to include a metal chloride, most often  $\text{FeCl}_3$ , and a metal oxide, with  $\text{MoO}_3$  and several vanadium compounds apparently being the best choice. The two metals may also be introduced as a single compound, such as iron molybdate,  $\text{Fe}_2\text{Mo}_7\text{O}_{24}$ . More recently, heteropolyacids such as  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  [12,13] have been found to be efficient promoters and heterogeneous catalysts prepared from mixed Pd–Mo [10] and Pd–Fe [14] clusters have also been reported. The same general kind of system is used irrespectively of the desired product (isocyanate, carbamate or urea), although the order of efficiency of the promoters may not be the same for the three products.

(iii) All of the reported systems contain chlorine, either as  $\text{PdCl}_2$  or bound to the cocatalyst or both. In one case in which both palladium and the copper cocatalyst were added as the corresponding acetates, hydrochloric acid had to be added to the system in order for the reaction to proceed [15]. To the best of our knowledge, the only exception to this rule is represented by the catalytic systems reported in [10,14], where, however, dichlorobenzene was used as a solvent. Since palladium catalysts have been widely used to carbonylate aromatic halides, the formation of Pd–Cl groups by oxidative addition of the solvent to a palladium center cannot be excluded. The generality of the requirement for the presence of chloride anions does not appear to have been previously appreciated and, to the best of our knowledge, only in one specific case [12] was it reported that chlorine-free catalytic systems of the kind reported in that paper were completely inactive.

(iv) Excess ligand, usually pyridine or isoquinoline, is often reported to increase the stability of the system against precipitation of palladium metal. However, a large excess of base lowers the selectivity in isocyanate, probably

due to its polymerisation, a reaction known to be catalysed by nitrogen bases [16]. A number of heterocyclic nitrogen bases have been reported to be effective, but chelating ligands such as 2,2'-bipyridine deactivate the catalytic system [17]. (However, in one patent [18] bipyridine has been reported to be a promoter for a  $\text{PdCl}_2$ – $\text{FeCl}_3$  catalytic system, but the molar amount of Bipy was much lower than the one of  $\text{FeCl}_3$ . Thus the ligand probably remains almost completely bound to this last metal and does not interact with palladium.) It has been proposed [11,19] that the active species may be a palladium(I) complex, formed by synproportionation of palladium(II) and palladium(0) species present in solution. However, an ESCA study of the metallic compounds after catalytic runs of model reactions showed the presence of only palladium(II) and palladium(0) and no palladium(I) could be detected [20].

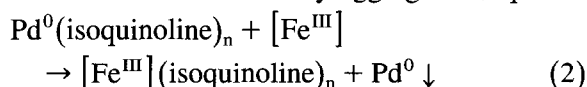
Apart from these general trends, some more specific findings and mechanistic proposals have been reported.

It appears that at least one role of  $\text{FeCl}_3$  is to oxidise Pd(0) to Pd(II), preventing the formation of inactive Pd black [11]. Halide derivatives of transition metals of other groups have also been reported to promote the reactivation of palladium metal formed during the reaction [21]. The so formed  $\text{Fe}^{\text{II}}$  compound reduces nitrobenzene, or accelerates its reduction, in a complex of unknown composition, regenerating  $\text{Fe}^{\text{III}}$  [11,20]. Molybdenum and vanadium compounds probably play a similar role. Heteropolymolybdates and vanadates have been reported to be reduced under the reaction conditions [12], whereas  $\text{VCl}_3$  is known to be oxidised by nitromesitylene to some compound containing a  $\text{V}=\text{O}$  bond [22]. Although the reduced form of one of the heteropolyacids used ( $\text{H}_6\text{PMo}_3^{\text{V}}\text{Mo}_9^{\text{VI}}\text{O}_{40}$ ) was reported not to react with nitrobenzene in the absence of  $\text{PdCl}_2$  [12], similar types of photoreduced heteropolytungstates reduce nitrobenzene to aniline in aqueous media [23]. One should always keep in mind that similar species may be generated in

solution every time some molybdenum or vanadium compound is added to the catalytic system, although we are unaware of any work in which a complete characterisation of the metal-containing species at the end of the catalytic reaction has been reported. More recently, it has been reported that  $\text{VOCl}_3$  quantitatively reacts with  $2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3\text{NCO}$  to yield  $2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3\text{N=VCl}_3$  [24]. Similarly, the synthesis of several polyoxomolybdates and tungstates containing one or more imido groups (e.g.  $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{CH}_3)]$ ) has been reported [25–29]. The synthesis of some of these compounds proceeds by reaction of a polyoxomolybdate or of  $[\text{WO}_4]^{2-}$  with isocyanates [27,28], that is, all the starting products may be present under typical catalytic conditions. In other cases the starting organic material is an amine, which is also surely present under the reaction conditions at least where the synthesis of carbamates and ureas is concerned. The possible role of such species during the catalytic cycle has apparently never been taken into consideration, at least partly because of their very recent discovery. It should be noted that more complex heteropolytungstates bearing a coordinated rhodium or iridium metal atom have also been reported [30]. Although these compounds have not been used as catalysts for the reactions discussed in this paper, similar complexes may be formed even in these last cases under the reaction conditions.

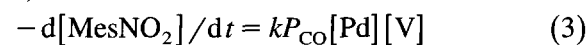
In one paper [31], a completely different explanation for the promoting effect of  $\text{Fe}_2(\text{MoO}_4)_3$  has been given. The authors have examined the rate of reduction of  $\text{Pd}(\text{isoquinoline})_2\text{Cl}_2$  to palladium metal at  $170^\circ\text{C}$  and under one CO atmosphere. The rate was faster when iron molybdate was also added to the solution and it was concluded that its function in the catalytic system is to increase the reactivity of  $\text{Pd}^{\text{II}}$  with CO, promoting the formation of a  $\text{Pd}^0$  complex that then reacts with the nitro compound. However, since  $\text{Fe}^{\text{III}}$  is known to oxidise  $\text{Pd}^0$  to  $\text{Pd}^{\text{II}}$  (and  $\text{MoO}_4^{2-}$  is surely not a reductant) the proposal that it may promote the

opposite reaction appears to be untenable. A different explanation can be given for the observed effect, which also accounts for the fact that the rate of reduction to palladium metal was independent of the excess  $\text{Fe}_2(\text{MoO}_4)_3$ . Palladium (II) compounds are well known to be easily reduced to  $\text{Pd}^0$  under a variety of conditions and, under the conditions employed in that paper, the reduction is probably complete. In the absence of other compounds, the palladium(0) so formed is at least partly stabilised by the isoquinoline ligand, which retards its aggregation. Heteroaromatic compounds such as isoquinoline are sufficiently 'soft' ligands to bind to  $\text{Pd}^0$ , but they are still relatively 'hard', so that they bind more strongly to a higher oxidation-state metal. In the presence of  $\text{Fe}^{\text{III}}$ , the two metals compete for the available ligand and the 'naked'  $\text{Pd}^0$  formed easily aggregates (Eq. 2):



Since the equilibrium in Eq. 2 is probably almost completely shifted to the right (even before precipitation of the metal actually occurs), the independence of the rate of palladium metal formation on the excess of iron molybdate is also explained. Indeed, once enough  $\text{Fe}^{\text{III}}$  is present to sequester all the available isoquinoline, any excess of it has no effect. This explanation, which also holds in the case that some of the  $\text{Fe}^{\text{III}}$  present is reduced to  $\text{Fe}^{\text{II}}$  under the reaction conditions (vide infra), is also consistent with the previously mentioned fact that excess ligand is known to stabilise the catalytic system against precipitation of palladium metal.

For the cases in which the isocyanate is the product, a little more is known. It has been reported that, in the carbonylation of nitromesitylene catalysed by various palladium halide compounds such as  $[\text{Bu}_4\text{N}][\text{PdCl}_3(\text{CO})]$  and  $\text{VCl}_3 \cdot 3\text{THF}$  or  $\text{VOCl}_2 \cdot 2\text{THF}$ , the rate is first order in palladium, vanadium and CO pressure, but zeroth order in nitro compound [22,32] (Eq. 3):



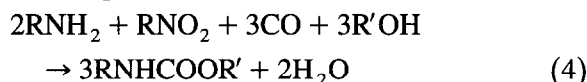
where [Pd] and [V] are the total concentrations of the palladium and vanadium species, respectively. In the case in which the cocatalyst was  $\text{VOCl}_2 \cdot 2\text{THF}$ ,  $\Delta H^\ddagger = 34 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -233 \text{ J mol}^{-1} \text{ K}^{-1}$  [22]. For a series of different nitro compounds, the rate of the reaction does not correlate with the Hammett  $\sigma$  constant of the substituents on the phenyl ring of the nitro compound, but higher rates were found when a substituent was present in the *ortho* position with respect to the nitro group [33]. A linear correlation was found with the sum of the Van der Waals radii of the *ortho* substituents. This situation is similar to that encountered with some rhodium catalysts [34] for which the rate acceleration following the steric effect was proposed to derive from a tilting of the nitro group plane out of the phenyl ring plane. However, how this tilting influences the rate is not clear. Since nitroaromatic compounds bearing some substituents in the *ortho* position are more difficult to reduce [35,36], the initial reduction cannot be the step responsible for acceleration. Comparison with a different catalytic system for the hydrogenation of nitroarenes by  $\text{H}_2$ , employing  $\text{RuCl}_2(\text{PPh}_3)_3$  as catalyst precursor [36] throws more light on this. With this last system, the sterically hindered  $2,6\text{-Me}_2\text{-C}_6\text{H}_4\text{NO}_2$  was reduced at a faster rate than its isomer  $3,4\text{-Me}_2\text{-C}_6\text{H}_4\text{NO}_2$  in separate experiments. However, when the two compounds were reacted together in a competitive reaction, the latter reacted at a much higher rate than the first. These data can be explained if we consider that the interaction of the nitro with the metal center is easier for the sterically unencumbered nitro compound, which can thus trap the active metal species as soon as it is reformed at the end of a catalytic cycle, but the slower step is not this initial interaction and is accelerated by the presence of the *ortho* substituents. It may be advanced that steric encumbrance destabilises some complex formed (e.g. a metallacyclic one) as intermediate, increasing its reactivity, although this explanation is admittedly highly conjectural at the moment.

The kinetic law when  $\text{PdCl}_2\text{L}_2$  (L = pyridine, isoquinoline) is used as a catalyst *in the absence* of any metal promoter has also been reported [37] and is similar to the one previously mentioned. Again the rate is first order in palladium and CO pressure, but zeroth order in nitrobenzene. A complex has been isolated after the reaction with *m*-chloronitrobenzene as substrate [38] and proposed to be an intermediate in the catalytic cycle. However, the proposed structure,  $\text{Pd}(\text{CO})(\text{Py})(\text{ArNO})\text{Cl}_2$ , is inconsistent with the spectroscopic data reported, since a  $\nu_{\text{CO}} = 1920 \text{ cm}^{-1}$  value is too low to be due to a terminal CO group coordinated to a  $\text{Pd}^{\text{II}}$  complex. Moreover there is no evidence that the isolated complex, whatever it is, is an intermediate in the reaction pathway.

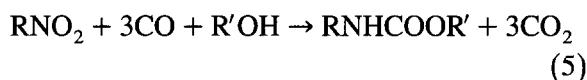
The above reported data will be discussed after the systems affording carbamates and ureas have been also discussed.

When an alcohol or an amine are added to the catalytic systems discussed in this paragraph, carbamates and ureas are formed, respectively, under conditions similar, though usually milder, to the ones under which isocyanates are obtained. A mechanistically significant discovery, first reported in a patent, concerning the synthesis of carbamates is that the addition of an amine to the reaction mixture accelerates the formation of the carbamate. The added amine is also partly carbonylated during the reaction and, if an amine is employed that corresponds to the nitro compound, the final yield of the carbamate exceeds 100% when calculated with respect to the starting nitro compound [39]. The addition of water, which very likely causes the formation of some amine during the reaction, also accelerates the rate of carbamate formation. The same kind of accelerating effect of added amine is observed whether an iron chloride [39] or  $\text{VOCl}_3$  [40] is used as cocatalyst (In this last case the amine was produced *in situ* by addition of a small amount of  $\text{H}_2$ ). The reason for this acceleration was not discussed in these patents, but a discussion of this effect, together with a summary of the results reported in other patents,

was later published in two other patents [41,42]. Two reaction stoichiometries are possible, corresponding to two different reaction pathways, and the prevailing of one of the two over the other depends on the relative ratio of the amine and nitro reagents. When a large amount of amine is present, the reaction can be described as in Eq. 4:

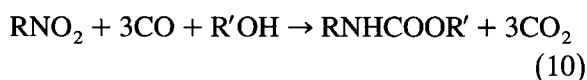
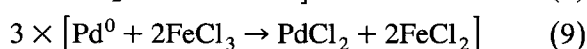
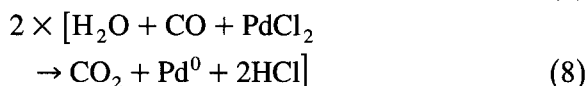
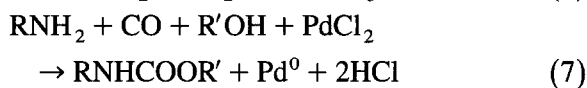
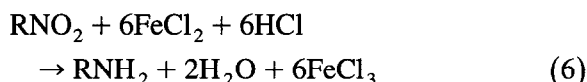


When the amine concentration is low, the following stoichiometry prevails (Eq. 5):



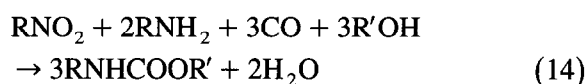
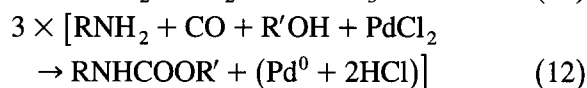
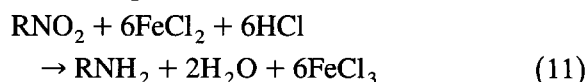
It was also proposed [41] that, even under the conditions in which the stoichiometry in Eq. 5 holds, the nitro compound is intermediately reduced to the corresponding amine, before it is carbonylated. Although the experimental evidence on which this proposal is based is not clearly discussed in the patents, it appears that this conclusion follows from kinetic experiments. Since the intermediate formation of aniline is a common feature in several catalytic systems even based on rhodium and ruthenium complexes [5,6] and is also consistent with what reported in [11] and [20], it appears to be well based.

The reaction in Eq. 5 can be divided into four (formal) steps [41] (Eqs. 6–10):



When a large amount of amine is present,

reaction of  $\text{PdCl}_2$  with water (Eq. 8) is not competitive with the reaction of  $\text{PdCl}_2$  with the amine (Eq. 7), so that the stoichiometry becomes (Eqs. 11–14):



Note that Eqs. 10 and 14 are the same as Eqs. 5 and 4, respectively. Although these equations account for some of the characteristics of this catalytic system, they should not be considered to perfectly describe the precise reaction pathway. For example, it is clear that free HCl will not be formed in the presence of a large excess of a basic amine and the possible formation of binuclear complexes (*vide infra*) is also not considered.

The change in stoichiometry depending on the experimental conditions is not limited to this catalytic system. An identical problem is found in another system, still based on palladium, but without any other metal-containing cocatalyst. In this last case, the same type of competing stoichiometries has been found and confirmed by the use of deuterated nitrobenzene (see Section 5).

The little sensitivity the above mentioned catalytic systems show toward even relatively high levels of water is noteworthy. To the best of our knowledge, when catalytic systems are used that are based on any other metal than palladium, any trace of water will be consumed to produce an amine in a high yield and at a higher rate than that of the carbonylation reaction. However, it has been reported that even in the presence of a 2:1 molar ratio  $\text{H}_2\text{O}/\text{PhNO}_2$  and under experimental conditions chosen so as to favour the formation of aniline, the selectivity in this last product was only 38%, compared



to a 45% yield in diphenylurea, when  $\text{PdCl}_2(\text{PPh}_3)_2$  was used as catalyst [43].

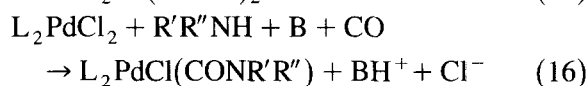
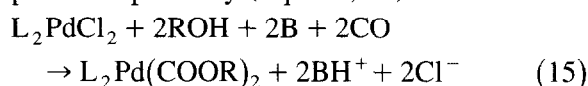
Since it appears that, with the catalytic systems discussed in this paragraph, nitro compounds are first reduced to the corresponding anilines, which are then carbonylated, it is necessary to examine this second step in more detail.

It is known [44] that  $\text{PdCl}_2$  reacts with amines and CO to yield the corresponding isocyanate and palladium metal. Later it was shown that the reaction can be made catalytic by the addition of a suitable oxidant that regenerates  $\text{Pd}^{\text{II}}$  from  $\text{Pd}^0$ , although the isocyanate is present at the end of the reaction combined with the excess aniline, to yield a diarylurea, or with an eventually added alcohol, to yield a carbamate. This reaction sequence is the basis for a class of reactions which is generally referred to as 'oxidative carbonylation of amines' (for some examples see [45]). Apparently the best catalytic systems for this reaction are based on some palladium compound, in the presence of oxygen as an oxidant and a copper compound as a cocatalyst. The similarity with the catalytic systems described here is remarkable and it becomes even greater when we learn that, among the possible oxidants other than oxygen, nitro compounds can also be used [46]. From a chemical point of view, there is no difference between the 'oxidative carbonylation' of an amine, in which the corresponding nitro compound is used as an oxidant, and the 'reductive carbonylation' of a nitro compound, in which the corresponding amine is an intermediate, once we consider that, in the first case, the nitro compound will be either reduced to amine or will directly yield the carbonylated product. (The similarity holds if either of the stoichiometries in Eqs. 4 or 5 is considered.) The fact that most of the catalytic systems for the oxidative carbonylation of amines, with oxygen as an oxidant, employ copper compounds as cocatalysts, whereas iron compounds are preferred when the carbonylation of nitro compounds is performed, may be explained by considering that  $\text{Cu}^{\text{I}}$  reacts

rapidly with oxygen, but its reaction with nitro compounds is sluggish [47]. On the other hand, iron is known to be a good reductant for nitro compounds [48].

The precise mechanism by which oxidative carbonylation of amines occurs is far from being completely understood. However, some remarkable advances have been recently reported by Giannoccaro et al. [49–51] and Vasapollo et al. [52,53], which are also relevant to the catalytic systems here described:

(i)  $\text{PdCl}_2\text{L}_2$  ( $\text{L}_2 = 2 \text{PPh}_3$  or several N–N or P–N chelating ligands) reacts with alcohols or amines in the presence of CO and a base to yield bis-alkoxycarbonyl or carbamoyl complexes respectively (Eqs. 15, 16):



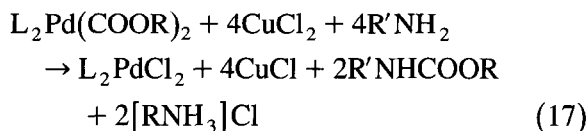
(R = alkyl; R' = H, R'' = alkyl, aryl; R' = alkyl, R'' = alkyl)

(ii) When mixtures of amine and alcohol are used, the carbamoyl complex is usually formed [52]. However, with very basic amines, the alkoxycarbonyl complex is also formed and is apparently the predominant product.

(iii) The examined alkoxycarbonyl complexes are stable in methanol at room temperature even in the presence of aromatic or aliphatic amines, whereas they decompose above 50°C, to give palladium metal, CO and other unidentified products. However, the complexes smoothly yield urea when treated with an amine and its chloride salt  $[\text{RNH}_3]\text{Cl}$ , even in methanol solution. The reaction takes place at room temperature for aliphatic amines and above 50°C for aromatic ones. No carbamate was formed. The reaction is proposed to proceed by the pathway depicted in Scheme 1.

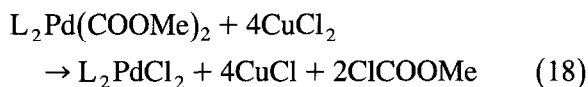
(iv) When  $\text{CuCl}_2$ , instead of the amine hydrochloride, is added to the complex–amine solution, carbamate and not urea is formed. At least in the case of the less basic aromatic amines, the reaction occurs under milder condi-

tions (room temperature) than the ones promoted by the amine hydrochlorides. The reaction obeys the following stoichiometry (Eq. 17):



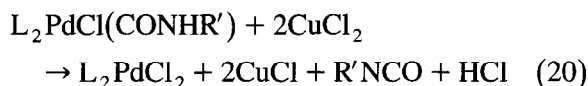
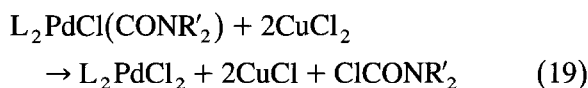
The complex  $PdL_2Cl(COOR)$  can also be used as a starting material and is supposed to be an intermediate in the reaction in Eq. 17. If an alcohol is used in place of the amine (together with a non-nucleophilic base), dialkyl carbonates are obtained.

(v) When the reaction between  $PdL_2(COOME)_2$  and  $CuCl_2$  is performed in the absence of both an amine or an alcohol, methyl chloroformate (ClCOOMe) is formed (Eq. 18):



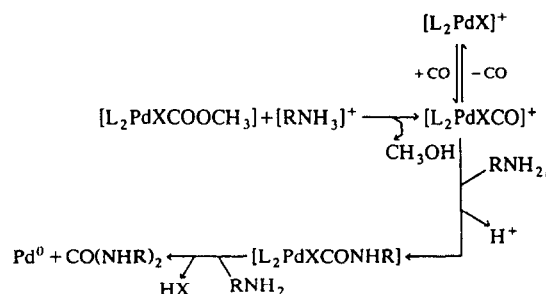
This last product quickly reacts with added amines or alcohol, to afford carbamates and carbonates, respectively, and is supposed to be an intermediate, formed even when the amine or the alcohol are added to the mixture at the beginning to the reaction.

(vi) When carbamoyl complexes of the type  $PdL_2Cl(CONRX)$  ( $X = H, \text{alkyl}$ ) are reacted with  $CuCl_2$ , the corresponding carbamoyl chloride is obtained. If the carbamoyl chloride derives from a primary amine, it immediately decomposes in solution to afford the isocyanate (Eqs. 19, 20):



(vii) In a later paper, Vasapollo et al. have reported that, in addition to  $CuCl_2$ , even  $FeCl_3$  promotes the same type of reactivity in related platinum alkoxy-carbonyl complexes [53].

(viii) Some more information concerning the relative importance of carbamoyl versus alkoxy-carbonyl complexes comes from a synthetic



Scheme 1. From Ref. [50], reproduced with permission of Elsevier.

study [54]. Oxidative carbonylation of aniline catalysed by  $PdCl_2/CuCl_2$ , in methanol and with  $(t-BuO)_2$  as an oxidant, gave a mixture of diphenylurea and methyl phenylcarbamate. The products distribution strongly depended on the reaction temperature. The carbamate predominated at room temperature, but the formation of diphenylurea largely prevailed at  $72^\circ C$ . At this last temperature, the proportion of carbamate increased with the time, that is as the aniline concentration decreased. When most, if not all, of the aniline was consumed, dimethyl carbonate was also formed. Addition of  $LiCl$  to the reaction mixture increased the selectivity in urea, indicating that a delicate balance exists between the various species present in solution (The chloride anion concentration may affect reactions 15 and 16, particularly with respect to the ratio between mono- and bis-alkoxy-carbonyl complexes present in solution. The more basic *n*-butyl amine, which, as mentioned before [52], predominantly yielded the alkoxy-carbonyl complex when reacted with  $PdCl_2L_2$ , still gave methyl *n*-butylcarbamate as the main product even at  $92^\circ C$ . Oxamates were also formed in this reaction under certain conditions. We will not discuss the formation of these products here, however see Section 5.

The similarity between the reactions just described and the ones involved in the catalytic processes discussed in this review is quite close and it becomes even closer when we consider that carbonate esters have also been observed in up to 11% yield during reductive carbonylation reactions of nitro compounds catalysed by  $PdCl_2$

and an iron cocatalyst [55]. Since carbonate esters are volatile compounds, their presence may easily escape attention and their formation is probably much more widespread than it is generally believed.

The last problem we must consider is the way by which the carbamoyl chloride or the alkyl chloroformate are formed. Several alternatives exist, including exchange of the chloride and alkoxy carbonyl (or carbamoyl) groups between palladium and copper, oxidative addition of the Cu–Cl bond to the palladium complex, electron transfer between the two metals and formation of chloride-bridged complexes. Since there is no experimental evidence in favour of any of these, we will not discuss this problem in detail. Precedents exist for more than one possibility [56]. However, we draw attention to two recent reports that, though apparently not related to the topic of this review, contain some information relevant to the reactions considered here. The oxidation of alkenes by PdCl<sub>2</sub>/CuCl<sub>2</sub>/O<sub>2</sub> in non-protic solvents has been shown to involve palladium–copper heterometallic complexes having chloride bridges as the catalytically active species [57]. The palladium-catalysed carbonylation of iodobenzene has been shown to be promoted by CuI and Fe(CO)<sub>5</sub>, both of which independently afforded heterometallic complexes with palladium under the reaction conditions [58]. The formation of heterometallic complexes during the reactions considered here does not appear to have been taken in with the consideration it deserves. To the best of our knowledge, in only one case [12], involving heteropolyanions as cocatalysts, have chloride-bridged Pd-heteropolyanion species been proposed to be the active catalysts (however, a Rh–Mo chloride-bridged complex has also been proposed as an intermediate in a RhCl<sub>3</sub>–MoCl<sub>5</sub>-catalyzed reaction [34]). The results reported in [57] and [58] suggest that heteronuclear complexes may be the active catalysts even in most of the reactions discussed in this Section. However, since the most active systems (in terms of total turnovers/mol Pd)

employ a very large molar excess of metallic cocatalyst with respect to palladium, the formation of a stable heterometallic complex cannot be the only function of the cocatalyst.

By putting together the data discussed up to now we can draw some conclusions that, though not unequivocally proven, appear to be consistent with all the available information:

(i) During the reductive carbonylation of nitroarenes to carbamates catalysed by PdCl<sub>2</sub>-Lewis acids, the nitroarene is first reduced to the corresponding aniline which is then carbonylated. Depending on the conditions, more amine may be consumed than nitro compound.

(ii) The Lewis acid has several roles. It effects, or help to effect, the initial reduction of the nitro compound, possibly as part of a heteronuclear complex, and it also reactivates metallic palladium eventually formed during the reaction. When mixtures of a Lewis acid (e.g. FeCl<sub>3</sub>) and a vanadium or molybdenum oxo compound are used, the formation of heteropolyoxo species is likely. The different metal cocatalysts appear to play a similar role during the catalytic cycle. The differences between the systems appear more likely to be due to a fine tuning of the redox properties of the cocatalyst, rather than to real differences in the reaction pathway.

(iii) Ureas are almost surely intermediates in the synthesis of carbamates, but some carbamate is probably formed directly. The proportion of carbamate which is formed directly likely depends, apart from the identity of the cocatalyst, on the reaction temperature and on the basicity and concentration of the amine.

(iv) The formation of ureas likely proceeds via the formation of a carbamoyl chloride, which eventually intermediately decomposes to isocyanate or is immediately trapped by the excess amine, whereas the direct formation of the carbamate probably requires the formation of an alkyl chloroformate. Some of the carbamate appears to be formed by alcoholysis of the intermediately formed urea. The direct formation of ureas and carbamates by direct reductive

elimination from a carbamoyl-amido (for ureas) or a carbamoyl-alkoxo or alkoxycarbonyl-amido (for carbamates) complexes may also occur, at least as a competitive pathway, which is probably not accelerated by  $\text{CuCl}_2$  or  $\text{FeCl}_3$ . We recall that oxamates are sometimes formed as byproducts, which are not likely to derive from carbamoyl chlorides. Thus reductive elimination of non-chlorinated molecules must also be considered. By analogy, we recall that palladium complexes, possibly in the presence of  $\text{CuCl}_2$  or  $\text{FeCl}_3$ , also catalyse the carbonylation of alcohols to carbonates and oxalates. Irrespectively of the presence of a second metal, the addition of excess chloride anion has been reported to increase the amount of carbonate and decrease that of oxalate [59,60]. The formation of an alkylchloroformate has been considered as a possible pathway to the alkylcarbonate [59]. Water may react with the intermediately formed carbamoyl chloride (or isocyanate) or with the alkyl chloroformate, reforming amine or alcohol (carbamic acid and monoesters of carbonic acid are not stable under forcing conditions and decompose with liberation of  $\text{CO}_2$ ). However this simply corresponds to a shift from the stoichiometry in Eq. 4 to that in Eq. 5 and the competition between water and amine is in line with that previously pointed out concerning the stoichiometry of the reactions.

The relevance of these conclusions to the systems in which the catalytic reactions are performed in the absence of added alcohols or amines, to directly yield the isocyanate is not obvious. However it should be considered that amines are typical byproducts of carbonylation reactions of nitroarenes and they may be formed by hydrogen atom abstraction from the solvent, even in non-protic media. Although the amine, should it be formed, may be considered to be trapped by the formed isocyanate, the product ureas are known to be in equilibrium with the free amine and isocyanate at high temperatures [61]. Thus, some amine is surely always present during the forcing reaction conditions required to effect the synthesis of the isocyanates and it

may account for the proceeding of the reaction. The possibility of the presence of significant amounts of amine even in the presence of an excess of isocyanate is also indicated by the fact that oxidative carbonylation of amines can be driven to yield the isocyanate [44],[45](e). This view is further supported by the observation that the addition of water, dihydrogen, or diphenylurea (all of which can generate some aniline under the reaction conditions) to a  $\text{PdCl}_2\text{Py}_2$ -based catalytic system has been reported to increase the nitroarene conversion and even the selectivity in isocyanate [62](a,b). By comparison, it is also noteworthy that the addition of phenol to a  $\text{PdCl}_2\text{Py}_2/\text{VOCl}_3$ -based catalytic system also increased the nitroarene conversion and isocyanate selectivity [62](c,d). When the same reaction was performed at a slightly lower temperature (190–200°C instead of 210–220°C) the corresponding phenyl arylcarbamates were obtained instead of the isocyanates [62](e–g). Thus it is clear that in this case the phenyl carbamate is formed as an intermediate even under the more forcing conditions, but is immediately thermally cracked to the isocyanate and is not observed among the products.

Unfortunately, the available information on the systems which directly yield the isocyanate is scant. Although the reported kinetic equations [22,32,37] are consistent with the reaction scheme proposed, they may arise from other pathways so that the real mechanism in these cases is still questionable. In numerous papers it has been proposed that the synthesis of the isocyanates proceeds by the carbonylation of an intermediate nitrene complex, with the metal cocatalyst accelerating this step. This possibility will be discussed in Section 6 devoted to the role of nitrene intermediates.

#### 4. Palladium complexes with phenanthroline ligands

Catalytic systems in which palladium complexes of the general type  $\text{PdX}_2\text{L}_2$  ( $\text{L}_2 = 1,10$ -

phenanthroline (Phen) or substituted phenanthrolines,  $X = \text{AcO}^-$  or  $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{COO}^-$ ) or  $[\text{Pd}(\text{L}_2)_2][\text{Y}]_2$  ( $\text{Y} = \text{BF}_4^-$  or  $\text{PF}_6^-$ ), possibly in the presence of a non-coordinating (and non-esterifiable) acid (e.g. 2,4,6-trimethylbenzoic acid (HTMB) or *p*-toluensulfonic acid), have been developed in recent years by several groups including ours [63–67]. These catalytic systems are very versatile, able to afford isocyanates, carbamates, ureas and even heterocyclic compounds, depending on the coreactants, in good yields.

The information available on this catalytic system is limited, but the system appears to be simple enough so that its main features can be quite confidently identified. The data relevant to any mechanistic interpretation is the following:

(i) When the reaction was performed with the neutral complexes in an aromatic solvent, isocyanates were formed with high selectivity. No aniline or urea were detected among the products. An acid promoter had to be added, the anion of which coordinates only weakly to the metal. The acid was necessary even if a palladium salt of the same acid was used as catalyst [56].

(ii) A careful examination of the examples reported in [64] shows that, when the carbonylation of nitrobenzene was performed in methanol as solvents and under ideal conditions (according to the patent: use of phenanthroline as ligand and *p*-toluensulphonic acid as promoter), the addition of aniline to the reaction mixture did not accelerate the reaction, but even slowed it down. The reduced nitrobenzene was present at the end of the reaction in part as methyl phenylcarbamate and in part as diphenylurea, but the total selectivity in carbonylated products (86%) was lower than that in carbamate when no aniline was added (96%). The molar amount of urea produced was very close to that of consumed aniline, indicating that aniline only acts as a trapping agent for some intermediately formed isocyanate, but is not directly carbonylated. However, under non-ideal conditions (use of chelating phosphines as ligands and/or acetic

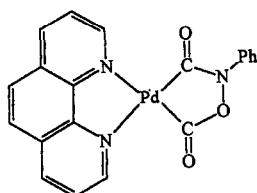
acid as promoter), the addition of aniline to the reaction mixture *did* accelerate the reaction and an appreciable amount of aniline was carbonylated. We will not discuss the mechanism under the non-ideal conditions now. It is related to the topic of next Section.

(iii) In methanol solvent, no acid had to be added when  $[\text{Pd}(\text{Phen})_2][\text{PF}_6]_2$  [58],  $[\text{Pd}(\text{Phen})_2][\text{tosylate}]_2$  [66], or  $[\text{Pd}(4,4'\text{-R}_2\text{-}2,2'\text{-Bipy})_2][\text{tosylate}]_2$  ( $\text{R} = \text{CF}_3, \text{Cl}, \text{H}, \text{Me}, \text{MeO}$ ) [67] were used as catalysts. On the other hand, when  $\text{Pd}(\text{Phen})(\text{OAc})_2$  or  $\text{Pd}(\text{R}_2\text{-Bipy})(\text{OAc})_2$  were used as catalysts, the addition of an excess of non-coordinating acid was still required [64,67]. Apparently the function of the acid in this last case is to remove the coordinated acetate ions from the palladium center, whereas the acidity of methanol itself is sufficient to promote the reactions that follow. In view of the need for an acid promoter when palladium acetate is used as the catalyst, the inhibiting effect of added aniline can be easily rationalised by considering that the amine will deactivate the acid by forming the corresponding anilinium salt.

(iv) The use of  $\text{Pd}(\text{Phen})\text{Cl}_2$  instead of one of the aforementioned palladium salts, caused a sharp loss of activity. However, the presence of small amounts of chloride anion (addition of a 20 wt.% amount of  $\text{Pd}(\text{Phen})\text{Cl}_2$  to pure  $[\text{Pd}(\text{Phen})_2][\text{PF}_6]_2$ ) remarkably increased the conversion (from 74.5 to 99.5%) [65]. An analogous promoting effect of halides was noted in the related carbonylation of nitroarenes to ureas, catalysed by nickel phosphine complexes [68]. When the catalytic activity of some  $\text{Pd}(\text{R}_2\text{-Bipy})\text{Cl}(\text{tosylate})$  complexes was compared with that of the corresponding  $[\text{Pd}(\text{R}_2\text{-Bipy})_2][\text{tosylate}]_2$ , the former gave lower yields, although the difference was not large and a remarkable activity was still observed [67]. Apparently, a one-to-one molar ratio  $\text{Cl}/\text{Pd}$  is already large enough to bring about deactivation. These effects will be discussed later in this paragraph.

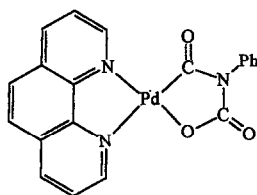
The understanding of the palladium–phenanthroline catalytic system has been greatly

advanced by the isolation of a plausible reaction intermediate [69]. Based on analytical and spectroscopic data, the following structure was proposed for the isolated complex:



(A)

Although the general characteristics of this structure seems to be indisputable, we show a structure in which the orientation of the 'CO<sub>2</sub>' fragment of the metallacycle is reversed:



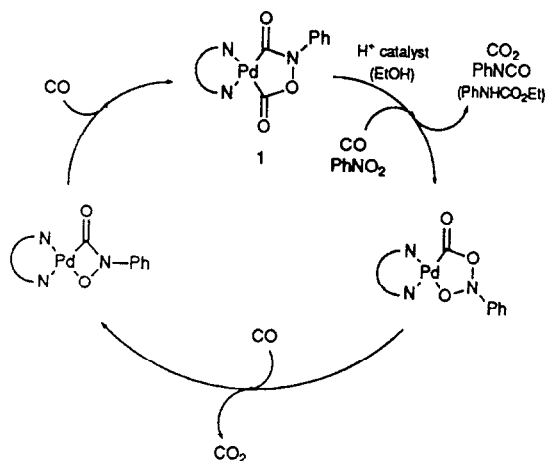
(B)

which is also consistent with the reported spectroscopic data. We consider structure (B) as more plausible based on the fact that all the structurally characterised complexes containing a metallacycle including the  $-N(R)-(CO_2)-$  fragment have the CO<sub>2</sub> carbon atom bound to nitrogen, whereas the oxygen atom binds to the metal [5,70–73]. A ruthenium complex containing a metallacycle including the 'PhNCO' and 'CO<sub>2</sub>' fragments has also been more recently characterised by X-ray crystallography and shown to have a structure corresponding to (B) [74].

Irrespective of its precise structure, the isolated complex displays a reactivity consistent with its role as an intermediate. In particular, it reacts at 170°C in dichlorobenzene as solvent, under CO (20 bar), and in the presence of 1.6

equiv. of 2,4,6-trimethylbenzoic acid, to yield PhNCO (0.6 equiv), (PhNH)<sub>2</sub>CO (0.1 equiv.) and CO<sub>2</sub> (1 equiv.) [69]. The rate of the reaction and the selectivity in isocyanate were lower if the acid was absent. Under these last conditions, some triphenylbiuret, (PhNHCO)<sub>2</sub>NPh (0.1 equiv.), was also formed. If the above experiments were carried out in ethanol as solvent, a much lower temperature (90°C) was required to allow the reaction to proceed. Even in the absence of any added acid, PhNHCOOEt (0.8 equiv.), (PhNH)<sub>2</sub>CO (0.1 equiv), and CO<sub>2</sub> (1 equiv.) were formed. On addition of the acid, an increase in rate but little change in selectivity was observed. The accelerating effect of added acid even in an alcoholic solvent is in slight contrast to what was previously mentioned about the insensitivity of the catalytic reactions to added acid when [Pd(Phen)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> [65] or [Pd(Phen)<sub>2</sub>][tosylate]<sub>2</sub> [66] were used as catalysts in methanol solvent. However, the difference may be simply due to the use of the less acidic ethanol and, perhaps, to the lower temperature with respect to the ones used in catalysis. Ethanol was suggested to act as a nucleophile on the carbonyl group attached to the nitrogen atom of the metallacycle, thus accelerating the opening of the metallacycle and directly affording the carbamate. The role of the acid should be to protonate the amide nitrogen, further accelerating the reaction. Finally, when the isolated metallacyclic complex was used as catalyst for the carbonylation of nitrobenzene, good conversion and selectivity were observed, further supporting the role of this complex during the catalytic cycle.

The simplified catalytic cycle proposed as a working hypothesis [69] is depicted in Scheme 2. The intermediate on the left in the scheme appears to have been inspired by a similar ruthenium complex [75] and is also consistent with previous studies by our group, showing that insertion of electrophiles occurs into the metal–nitrogen rather than into the metal–oxygen bond of Pt(PPh<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-PhNO) [73]. The complex on the right in the scheme is a com-



Scheme 2. From Ref. [69], reproduced with permission of the Royal Chemical Society.

monly supposed intermediate for the first deoxygenation reaction of nitrobenzene. However, no such complex has ever been isolated or observed, and it may also be better considered as a transition state rather than a true intermediate.

In a subsequent paper [76], some of the same authors reported the synthesis and reactivity of some other metallacyclic complexes related to the one previously analysed. However, these complexes do not appear to be involved in the main catalytic cycle and we will not further discuss them here.

A characteristic of the catalytic cycle in Scheme 2 is that it does not require the formation of a nitrene complex. This aspect will be analysed in more detail in Section 6.

One last problem, which is not addressed by the mechanism in Scheme 2 is the promoting–deactivating effect of variable amounts of chloride anion. The deactivating effect of a 2:1 molar amount  $\text{Cl}^-/\text{Pd}$ , which parallels the deactivating effect of chelating nitrogen ligands on the  $\text{PdCl}_2$ -catalysed reactions discussed in the previous paragraph, can be easily explained by the formation of  $\text{Pd}(\text{Phen})\text{Cl}_2$  upon simple mixing of the reagents. In our experience, this is a very stable and remarkably insoluble compound. It dissolves only slightly in coordinating

solvents such as DMSO and pyridine. In the latter solvent, some reactivity data show that the phenanthroline ligand is at least in part displaced by the pyridine solvent [77]. In an alcoholic solvent, like the ones usually employed in the catalytic reactions with this system, the compound is virtually insoluble at moderate temperatures and it probably remains very little soluble even under more forcing conditions.

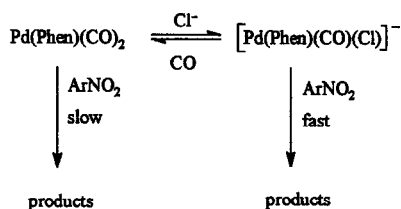
The origin of the promoting effect of small amounts of halide anions is, on the other hand, not obvious. It has been proposed [65] that a small amount of chloride anion causes the formation of  $[\text{Pd}(\text{Phen})(\text{Cl})(\text{CO})]^+$ , which is considered to be the most catalytically active species in solution, inhibiting, at the same time, the formation of the inactive  $[\text{Pd}(\text{Phen})_2]^{2+}$ . No explanation was proposed for the promoting effect of halides on the nickel system [68]. The assumption that a  $\text{Pd}^{\text{II}}$  complex is the active catalyst for the carbonylation of nitrobenzene is in contrast to the information gained by the isolation of the metallacyclic intermediate. The formation of such a neutral complex may only follow from a  $\text{Pd}^0$  complex, which is also consistent with the notion that a low oxidation state complex is required to reduce a nitrocompound and no other metal is present in solution in this catalytic system (in contrast, formation of a palladium(0) complex is not strictly required in the catalytic system discussed in the previous Section, where a second metal probably brings about the initial reduction of the nitro compound). Thus the formation of a  $\text{Pd}^{\text{II}}\text{–Cl}$  complex is not an acceptable explanation for the promoting effect of chloride anion. Some help as to the correct explanation comes from studies in a different field. In a series of papers [78], Amatore, Jutand et al. have analysed the products of the electrochemically induced reduction of  $\text{PdX}_2(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ), possibly in the presence of added  $n\text{-Bu}_4\text{NX}$ , and shown them to be an equilibrium mixture of  $[\text{Pd}(\text{PPh}_3)_2\text{X}]^-$ ,  $[\text{Pd}(\text{PPh}_3)_2(\mu\text{-X})]_2^{2-}$ , and  $[\text{Pd}(\text{PPh}_3)_2\text{X}_2]^{2-}$  with the first largely predominating in the absence of added halide and the last becoming

increasingly important as the concentration of  $X^-$  increases. As to the reactions discussed here, it is particularly important that the polarographic oxidation wave potential of a solution of  $\text{Pd}^0(\text{PPh}_3)_4$  decreased by as much as 0.3 V when  $n\text{-Bu}_4\text{NCl}$  was also added [79]. Since the first step of the reduction of the nitro compound is almost surely an electron transfer from a  $\text{Pd}^0$  (or  $\text{Ni}^0$ ) complex to the nitro compound (see Section 2), a similar shift of the oxidation potential of the complex will markedly accelerate it. The addition of halides increased the rate of oxidative addition of  $\text{ArI}$  [79] and  $\text{ArOTf}$  [80] to  $\text{Pd}(\text{PPh}_3)_4$ . An analogous promoting effect of iodide anion on the oxidative addition of  $\text{MeI}$  to  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  has been noted and the formation of  $[\text{Rh}(\text{CO})_2\text{I}_3]^{2-}$  proposed [81]. Based on this general reactivity, we propose that the effect of halide even in the Pd–phenanthroline and Ni–phosphine catalytic systems for the carbonylation of nitrobenzene discussed in this paragraph can be described by the reaction scheme depicted in Scheme 3.

It should be noted that iodide anion also promoted the palladium–phosphine-catalysed oxidative carbonylation of amines [82]. Since (in the absence of added copper compounds), the slow step of this reaction is probably the oxidation by  $\text{O}_2$  of the palladium(0) complex formed after the carbonylation step, the formation of a more electron-rich  $\text{Pd}^0\text{-I}$  anionic complex is supposed to render this step easier too. (The coordination of  $\text{I}^-$  to an heterogeneous palladium catalyst for the oxidative carbonylation of amines has been proposed to favour the oxidative addition of the N–H bond of the amine [45](g,h). However, we view this expla-

nation as unlikely for the reasons detailed in the next Section.). The formation of negatively charged complexes may even increase the activity of the catalytic systems by disfavoured the aggregation of palladium(0) complexes, to yield inactive palladium metal. Although this explanation may play a role in the Pd–Phen system, due to the known lability of nitrogen ligands, it is unlikely to be significant in the cases in which the more tightly-binding phosphines or nickel complexes are used and is very unlikely to represent the only explanation for the halide effect even in the first case. The order of promoting activity of several halides, with  $\text{I}^-$  being better than  $\text{Cl}^-$  in some cases, is easily explained by considering the order of the relative nucleophilicities in various solvents, with iodide being a more powerful nucleophile than chloride in protic solvents and the reverse being true in aprotic ones [83]. The beneficial role of chloride in palladium-based catalytic systems for the carbonylation of nitroarenes is not limited to Phen as a ligand. An even more evident promoting effect of chloride is observed when monodentate phosphines are used as ligands (see next Section). Although this reaction is out of the scope of this review, we recall that halides also promote the catalytic activity of  $\text{Ru}_3(\text{CO})_{12}$  in the carbonylation of nitroarenes [84] and a similar explanation for their role can be given.

The Pd–Phen (or Pd–Bipy) catalysed synthesis of carbamates from nitroarenes is usually very selective, with diphenylurea being the dominant byproduct when nitrobenzene is used as a starting material [67]. However some minor byproducts have been identified in the reaction of  $\text{PhNO}_2$  catalysed by several Pd–Bipy systems [67]. They all contain a methoxy group (derived from the methanol solvent) bound to the aryl ring of aniline, diphenylurea, and carbamate products. The methoxy groups are always in the 2 or 4 positions with respect to nitrogen, but never in the 3 position. No substituted nitrobenzene was observed. Arguments were given against the involvement of nucleophilic aro-



Scheme 3.

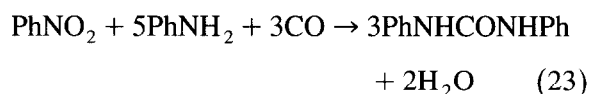
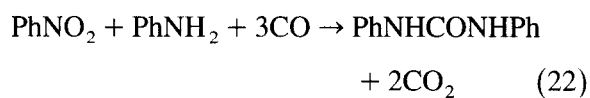


matic substitutions in the formation of these products and it was proposed that palladium-catalysed C–H activation of the aromatic ring may play a role. We also recall that coupling of rhodium phenylimido complexes with dichloromethane to yield a *para*-CH<sub>2</sub>Cl substituted phenylimido complex has been reported [85]. This and related reactions were proposed to occur through an intermediate one-electron oxidation of the imido complexes, whose oxidation potential was found to be very low. Although several differences are surely present between these last reactions and the ones possibly involved in the system discussed here, the similarities are worthy of consideration.

## 5. Palladium–phosphine complexes for the synthesis of ureas.

Palladium–phosphine based catalytic systems for the synthesis of ureas from nitroaromatic compounds and amines have been first described by Heck et al. [86]. The same catalytic system has been later modified and some characteristics of the reaction mechanism have been described by Lee et al. in a series of papers [87–92]. Use of mixtures of perdeuterated nitrobenzene and undeuterated aniline have allowed the authors to draw the following conclusions:

(i) The reaction may obey two different and competing stoichiometries described by Eqs. 22 and 23.



Note that Eqs. 22 and 23 are perfectly equivalent to Eqs. 5 and 4, respectively, once accounted for the fact that alcoholysis of urea in the former cases affords one mole of carbamate and regenerates one mole of aniline *per* mole

of urea. The relative importance of the two stoichiometries depends on the relative amount PhNH<sub>2</sub>/PhNO<sub>2</sub> and on the ligand used. With a 6:1 molar ratio PhNH<sub>2</sub>/PhNO<sub>2</sub> and triphenylphosphine as ligand, the stoichiometry in Eq. 23 largely predominates, but, when chelating phosphines or phenanthroline ligands are used in place of PPh<sub>3</sub>, the stoichiometry in Eq. 22 becomes more and more important as the number of carbon atoms in the chain connecting the two phosphorus atoms decreases. The consumed aniline/nitrobenzene ratio is minimum (3.24) in the case of Phen.

(ii) The addition of [Et<sub>4</sub>N]Cl is essential to promote the activity when PPh<sub>3</sub> is used as ligand, but it inhibits the reaction when chelating ligands are used. Since the amount of added chloride is always relatively large with respect to palladium, it is impossible to say if there is any promoting effect of low amounts of chloride analogous to that discussed in the previous paragraph. At least in the case of phenanthroline ligands, this should be the case.

(iii) A very small amount (about 1% with respect to urea) of *N,N'*-diphenylloxamide (PhNHC(O)C(O)NHPh, DPOA) was formed. Doubly carbonylated products are sometimes also found in oxidative carbonylation reactions of amines and, under suitable experimental conditions, they may represent the main products [54,93].

(iv) At the end of the reaction, part of the remaining aniline is deuterated, indicating that some of the reacted nitrobenzene has been reduced to aniline.

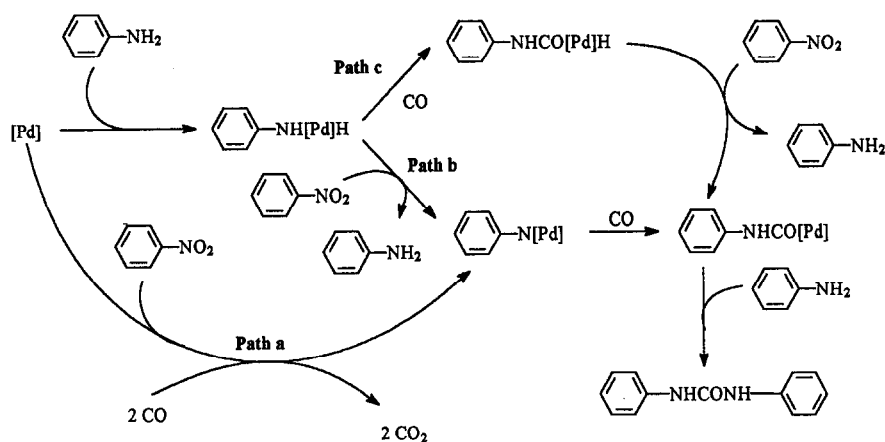
(v) The ratio undeuterated/deuterated phenyl groups (*vide supra*) in the produced DPOA is much higher than in the diphenylurea, indicating that it derives completely from a reaction of aniline, whereas diphenylurea is formed at least in part through a pathway that does not involve the intermediate reduction to the amine. The ratio of undeuterated/deuterated phenyl groups in the diphenylurea obtained is 6.94 which is even higher than the ratio calculated from Eq. 23, with the assumption that the nitrobenzene

acting as an oxidant is completely included in the products.

On the basis of the data mentioned above, the reaction scheme (Scheme 4) was proposed. The process responsible for the reaction associated with the stoichiometry in Eq. 22, path a in Scheme 4, was proposed to proceed through an intermediate nitrene complex, although, in the latest papers of the series, it was recognised that a mechanism involving a metallacyclic complex analogous to that discussed in the previous paragraph is also a viable alternative. We consider that this last possibility is much more likely the correct one.

The alternative process, corresponding to the stoichiometry in Eq. 23, is proposed to proceed mainly through oxidative addition of aniline to a palladium(0) complex, followed by CO insertion to afford a carbamoyl complex (path c). However, whereas the formation of some carbamoyl complex is also supported by the formation of DPOA and appears to be a firm point, the way in which it is proposed to be formed is highly questionable. The intermolecular oxidative addition of an aniline N–H bond to a mononuclear metal complex is a difficult process, for which very few examples have been reported [94–98]. Moreover, in at least some of the known examples of this reaction, the mechanism appears to be more complex [97,98] and

possibly involves a heterolytic step favoured by one of the ligands in the complex. To the best of our knowledge, none of the reported examples involves a  $\text{Pd}^0$  complex. Moreover, oxidative addition of aniline to  $\text{Pd}^0(\text{PR}_3)_2$  complexes have been suggested to be thermodynamically unfavourable even in the case of basic phosphines ( $\text{R} = i\text{-Pr}, \text{Cy}$ ) [99]. Even the CO insertion into a metal–nitrogen bond does not seem to be a general reaction. Two examples have been reported of a CO insertion reaction into a metal–anilido bond [100], but the complex involved lacked a hydrido ligand. On the other hand, in all of the cases in which the reaction between an hydrido-anilido complex and CO was studied [97,101,102], including the case of the complex  $\text{Pt}(\text{H})(\text{NHPh})(\text{PEt}_3)_2$  [101], related to the one supposed to be formed, a clean reductive elimination of aniline was observed, with no trace of the insertion product being detectable. Based on general reactivity, reductive elimination from a corresponding palladium complex should be even easier. The reaction between  $\text{HPd}(\text{NHPh})(\text{PR}_3)_2$  ( $\text{R} = i\text{-Pr}, \text{Cy}$ ) and CO, which would be even more related to the case discussed here, has not been reported in the literature, but the reaction between the same complexes and an olefin affords aniline, strongly suggesting that the same would occur in the case of the reaction with CO (The insertion of



Scheme 4.

an olefin into the M–N bond appears to be easier than that of a CO group, since the previously mentioned Pt(H)(NHPh)(PEt<sub>3</sub>)<sub>2</sub> does insert acrylonitrile into the Pt–N bond, but affords aniline upon reaction with CO [101].) Another fact that argues against the formation of an amido complex is that it would be expected to be very sensitive to moisture [99,101], in contrast with the presence in solution of appreciable amounts of water (carbamoyl complexes, on the other hand, have been reported to be remarkably insensitive to moisture [103]). As an alternative, carbamoyl complexes are known to be easily formed by attack on a CO group coordinated to a palladium (II) center (for some examples see [49–53,56], many more have been reported). It should also be recalled that paths b and c correspond to an oxidative carbonylation reaction of aniline and abundant evidence suggests that Pd<sup>II</sup> complexes are responsible for this reaction (the relevant literature has been discussed only in part in this review; comparisons are also interesting with the related catalytic systems for the carbonylation of alcohols to carbonates and oxalates).

The shift from path a to paths b or c when chelating ligands with an increasing chain length between the two binding atoms are used (with paths b or c being most important in the limit case of monodentate ligands), has been attributed to the ability of chelating ligands with a wider bite angle (and of monodentate ligands) to stabilise both square planar and trigonal bipyramidal coordination environments. The latter are considered to be important in paths b and c. However, the global reaction rate is up to 15 times faster when chelating ligands are used in place of PPh<sub>3</sub> (the best non-chelating ligand used), indicating that, on going from the first type of system to the second, the change in stoichiometry is due to a slowing down of the process associated with Eq. 22, rather than to an acceleration of that associated with Eq. 23.

The fact that part of the starting perdeuterioaniline is found at the end of the reaction as perdeuteroaniline, coupled with the other selec-

tivity data, indicates that the nitrobenzene acting as an oxidant is, at least to a large extent, transformed into aniline (which may eventually reenter the catalytic cycle only at a later stage) and is not directly converted to carbonylated products. (Some of the perdeuteroaniline may derive from a direct reduction of nitrobenzene by CO and the water formed in Eq. 23 [43], a reaction which has not been considered in Scheme 4, but the other selectivity data cannot be explained if this were the only source of perdeuteroaniline.) This conclusion is also supported by the observation that, by using PPh<sub>3</sub> as ligand, the ratio between the molar amounts of consumed aniline and nitrobenzene is 6.94. This indicates that nitrobenzene is converted to aniline and not directly to urea, otherwise the maximum possible value for this ratio (the one corresponding to the process in Eq. 23) should be 5. This is an important point, since it is also relevant to the catalytic systems described in the previous paragraphs, for which the fate of the nitro compound used to perform the oxidative carbonylation of the amine could not be assessed.

The proposal that nitrobenzene oxidises an intermediate Pd<sup>II</sup> carbamoyl complex, rather than a Pd<sup>0</sup> complex formed after elimination of urea, is stimulating. However, there is no experimental evidence supporting this proposal, which must be considered as speculative at the moment.

The possible role of chloride anion has already been discussed in the previous Section and will not be further discussed here. Similar arguments hold in this case too. Note that, when triphenylphosphine is used as a ligand, the possible Pd<sup>0</sup>–Cl complexes are exactly the same as those obtained by Amatore et al. Their formation is thus even less speculative in this case.

## 6. The role of nitrene intermediates

The possible role of nitrene intermediates in the carbonylations and reductions of nitro and

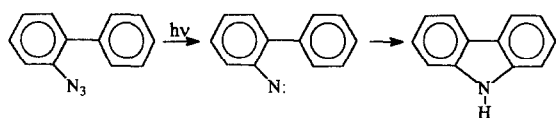
nitroso compounds has been a matter of speculation since the very beginning. However, most, if not all, of the experimental data on this topic is not univocal in giving an answer to this problem and the common belief has evolved during the years mainly because of a general feeling, rather than on the basis of new clear-cut data. Since this problem is common to the catalytic systems based on other transition metals, we will discuss it in a more general way and not limit our attention only to palladium-based systems.

The first chemists working in the area of the carbonylation of nitro compounds immediately noted many similarities between the products obtained from these reactions and the ones obtained from the reactions of organic azides ( $R-N_3$ ), which were known to be sources of free nitrenes when activated either photochemically or thermally (for some examples see [104,105]). Similarities were found especially in the formation of coupled products such as azoarenes and in the formation of products derived from hydrogen-abstraction from the solvent or the nitro compound itself [104], a reaction typical for nitrenes in the triplet state [106]. It was also noted that high pressures were required to drive the reactions of both azides and nitro compounds with CO towards the synthesis of isocyanates rather than towards hydrogen abstraction-derived products and this was attributed to the formation of a same nitrene intermediate which can competitively react with CO or the solvent [104]. Thus papers published in the late '60s or the very early '70s often contain proposals for the formation of free nitrenes as intermediates.

However, an increasing number of bridging-imido compounds from reactions of several nitrogen compounds, including nitro compounds, and metal carbonyl complexes, especially trinuclear clusters (*vide infra*), were novel products in the same period. These immediately attracted the attention of those working in the field and, in papers published in the early and mid '70s, the suggestion that a 'nitrene compound, either

free or coordinated to the metal' may be an intermediate in the reaction, is found frequently. With the accumulation of new imido compounds, the idea that a free nitrene, generally considered to be an high-energy compound, may be an intermediate gradually disappeared and is almost never found in papers published after the mid '70s, whereas the idea that imido compounds, especially cluster compounds, were involved became generally accepted. It should be noted that this change in the general opinion was not due to any specific experiment which had shown that free nitrenes cannot be or that coordinated nitrenes are indeed intermediates. It appears that the fascination and the stimulating power of the new compounds, supported by their crystal structures, played the mayor role. Indeed, more than a decade had to pass before it was shown that free isocyanates and carbamates can in fact be obtained from a triply-bridging imido group coordinated to an iron or ruthenium cluster [107] and the CO insertion into the M–N bond of mononuclear [72] or dinuclear [108] complexes has been observed only even more recently. In most of the cases in which a second metal (which can be generally be considered to be a Lewis acid, e.g.  $FeCl_3$ ,  $VOCl_3$  or  $MoO_3$ ) was also present in the catalytic system, it was supposed to act by increasing the rate of CO insertion into the M=N bond by binding to the coordinated CO, in analogy with the well known effect in the corresponding migration of coordinated alkyl groups. However, despite the wide acceptance of this role for the second metal, we are aware of no example in which CO insertion into a M=N bond has been observed to be favoured by a Lewis acid of any kind and a more likely explanation for the role of these metal-containing cocatalysts has been given in Section 3.

Apart from the isolation of discrete imido complexes from the reaction mixtures, the bulk of the evidence for the formation of nitrene species as intermediates has been represented by the formation of carbazole when *o*-nitro-biphenyl is used as a substrate. It has been



Scheme 5. Adapted from Ref. [91].

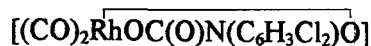
known for a long time [109] that *o*-azido-biphenyl yields carbazole when photochemically activated. The reaction is believed to occur *via* an intermediate nitrene (Scheme 5). It has been considered that a coordinated nitrene may give the same reaction and work in our group has shown that this is indeed possible in at least one case [110]. However, other pathways may be responsible for the formation of carbazole. Nitrosoarenes were considered as possible intermediates in similar types of cyclisation reactions [111]. It should also be noted that we now know that most reactions of nitro and nitroso compounds with a metal complex occur through an intermediate electron transfer to the organic compound (*vide supra*). Thus the formation of the radical anion of *o*-nitro- and/or *o*-nitroso-biphenyl should be considered as probable during the reaction. The reactivity of such radicals is virtually unknown and it cannot be excluded that these species, and not a nitrene intermediate, are responsible for the carbazole formation. The validity of carbazole formation as an indication for nitrene intermediates has been questioned very early [112]. It was shown that other reactions (including oxidation of 2-amino-biphenyl) can afford carbazole. Thus the results of this test should be taken with caution.

Following the aforementioned studies showing that carbonylated products can be obtained from imido complexes, the general believing that such complexes are involved in the carbonylation and reduction reactions of nitroarenes reinforced to the point that it has been, and often still is, given for granted for a long period of time. However, in recent years this believing has been challenged by the discovery that two important catalysts,  $\text{Ru}(\text{CO})_3(\text{DPPE})$  [113] and  $\text{Pd}(\text{Phen})(\text{OAc})_2$  [69], work through mechanisms which apparently do not require the

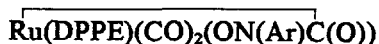
formation of an intermediate imido complex (*vide supra*). Moreover, we have also shown that, contrary to what was earlier believed,  $[\text{HFe}_3(\text{CO})_9(\mu_3\text{-NPh})]^-$  is not an intermediate in the phase transfer-catalysed reduction of nitrobenzene to aniline by  $\text{Fe}_3(\text{CO})_{12}$  [114] and that, for the  $\text{Ru}_3(\text{CO})_{12}$ /halide catalytic system, no mechanism supposing the carbonylation of an imido intermediate directly to the isocyanate or carbamate can have any kinetic relevance to the catalytic cycle [115].

Thus it now appears that the two classical pathways for the synthesis of isocyanates and carbamates, insertion of CO into a metal–imido bond or direct reductive elimination of an imido and an alkoxy-carbonyl groups, are much less widespread than previously believed and may even bear no relevance to any known catalytic system.

Despite these observations, the question of the intermediate formation of nitrene species cannot be considered concluded. Some of the palladium-based catalytic system previously discussed, the  $[\text{Rh}(\text{CO})_4]^-$ -based and all the ruthenium-based catalytic systems for the carbonylation of nitroarenes require the intermediate formation of an aniline [5,113,115]. We can now wonder which pathway is responsible for the formation of this product. The last complex of the cycle giving rise to the aniline is very likely an amido complex, but the nature of the complex affording this amido complex is controversial. Several types of complexes may play this role, including carbamoyl (by CO de-insertion), metallacyclic (by decomposition through protonation at the nitrogen atom) or imido (by protonation) ones. Although the first possibility seems unlikely, the last two appear a priori equally probable. In our mechanistic study on the  $[\text{Rh}(\text{CO})_4]^-$  system, we have studied the reactions of a metallacyclic intermediate,



, and shown that trapping of an intermediately formed (but unobservable) complex by nitrosobenzene yielded mixed azoxybenzenes [5]. This experiment was considered to be an evidence (although not a conclusive one) in favour of the imido intermediate. In the same paper, we have also applied the same type of reaction to a ruthenium complex of type



analogous to the ones reported by Gladfelter et al., and to a palladium metallacycle of type (A) (or (B)). In both cases the nitroarene-derived fragment originally present in the complex was again almost quantitatively recovered as the mixed azo or azoxy compound. In the case of ruthenium, we consider this reaction as an evidence in favour of an imido complex as an intermediate in the reaction pathway. In the case of the palladium complex, the situation may be more complex. The metallacyclic complex used already contains an arylisocyanate moiety and the evidence previously reported indicates that, in the presence of an acid and at high temperatures, this moiety is expelled from the complex [69]. However, when no acid was added, products were also obtained which may derive from the decomposition of an imido complex. The observed data can be easily explained if one considers that an intermediately formed isocyanate complex may reversibly decarbonylate, a reaction which has many precedents [116,117], and that the nitrene moiety in the imido complex can be trapped by external nitroarene. However, other pathways may also be involved in this case.

Finally it should be noted that many heterocyclic compounds have been synthesised by deoxygenation reactions of nitro compounds by CO [118] and, although no definitive evidence exists for this assumption, the formation of intermediate imido complexes appears to be the best explanation accounting for the observed products and their selectivities.

In conclusion, after having been a firm point for about twenty years, the intermediate formation of nitrene species is now a matter of debate. As mentioned in the introduction to this paragraph, the debate has been based more on indirect evidence and general feelings rather than on any unquestionable evidence. Such evidence is still required before a definitive answer can be given to this problem.

## Acknowledgements

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