Carbonylation of nitrobenzene catalysed by palladium and heteropolyanions; a mechanistic approach

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Abstract

The previously reported catalytic system $PdCl_2$–Keggin heteropolyanion for the carbonylation of nitrobenzene to methyl phenylcarbamate has been analysed in more detail. $PdCl_2$ has been confirmed to be the best palladium precursor and the addition of pyridine hinders the reaction. The addition of aniline promotes the reaction at high nitrobenzene concentrations, but depresses it at low nitrobenzene concentrations. Performing the reaction in the presence of aniline, but in the absence of methanol, and using deuterated nitrobenzene, data are collected indicating that the reaction, which affords the corresponding urea, follows at least three different pathways, one of which consumes more aniline than nitrobenzene. Aniline is an intermediate in this as well as in one of the other two processes, but not in the third. The fate and possible reactivation of the spent catalyst have been examined. © 1997 Elsevier Science B.V.

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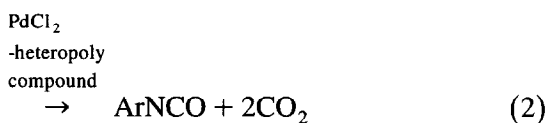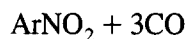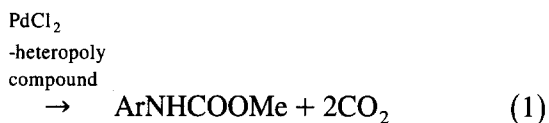
1. Introduction

Heteropolyacids and their salts (heteropoly-molibdates, tungstates, vanadates, and mixed species) have attracted much attention in the last years and are the subject of numerous reviews [1–3]. These compounds are interesting for their strongly acidic (only for the parent acids) and oxidising properties (both the acids and the salts), which make them effective catalysts or cocatalysts in various important reactions. Heteropolyacids have particularly found application as cocatalysts for palladium in Wacker-type reactions, as substitutes for copper salts [4].

The best studied class of heteropolyacids (Keggin-type heteropolyacids) can be represented by the general structure $H_nY_{12}XO_{40}$, where $n = 3$ or 4, X = P or Si, and Y = V, Mo, W, or a combination thereof, such that a total of 12 metal atoms is achieved. The acids can also be deprotonated to a variable extent to yield the corresponding salts or reduced in situ by some chemical reductant. The chemistry of these heteropoly compounds has been studied in several groups in the last few years and they are known to exist in several oxidation states [1–3]. Some reports, several in the form of patents, have also appeared on their use as promoters for the $PdCl_2$-catalysed carbonylation of nitroarenes to

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carbamates [5–8] and isocyanates [5,9,10] (Eqs. (1) and (2)).

$$ArNO_2 + ROH + 3CO$$

$$\xrightarrow[\text{compound}]{\substack{PdCl_2 \\ \text{-heteropoly}}} ArNHCOOMe + 2CO_2 \qquad (1)$$

$$ArNO_2 + 3CO$$

$$\xrightarrow[\text{compound}]{\substack{PdCl_2 \\ \text{-heteropoly}}} ArNCO + 2CO_2 \qquad (2)$$

It should also be noted that heteropoly compounds are probably formed during the catalytic reactions even in several other catalytic systems where they were not added since the beginning [11]. The results were much better when the direct synthesis of methyl phenylcarbamate was investigated, rather than the synthesis of isocyanates (as generally found even for other systems), and we will focus on the first reaction. In previous works, a variety of different heteropoly compounds was tested. The main results can be summarised as follows:

(i) Best results were obtained with P–Mo and P–Mo–V heteropolyacids. Si–Mo compounds gave worst results and heteropolytungstates were almost inactive. Similarly, very low activities were shown by a simple molybdate, $(NH_4)_6(Mo_7O_{24})$, and by H_2MoO_4, indicating that it is not the acidity of the cocatalyst or its polynuclear structure that is responsible for the promoting activity. At the same Pd/cocatalyst molar ratio (0.5), $FeCl_3$, which is one of the most used promoters for palladium-catalysed carbonylation reactions of nitroarenes [11], was completely ineffective.

(ii) In the Mo–W systems, the activity increased monotonically with increasing number of molybdenum atoms in the Keggin unit. For the Mo–V systems, the highest activity (and, as a matter of fact, the best activity among all systems tested) was obtained when a single vanadium atom was substituted for one of the twelve molybdenum atoms.

(iii) The use of a heteropolyacid as such or of its lithium salt gave similar results, but somewhat higher conversions were obtained when the acid was used.

(iv) As a qualitative understanding, the promoting ability of heteropolyacids appears to be related to their redox potential, that is the more easily reducible (more strongly oxidising) heteropolyacids are the most effective.

(v) The best molar ratio cocatalyst/Pd was found to be 1. A ratio of 1.5 gave similar results, but ratios lower than 1 gave increasingly worst conversions. This was interpreted as an evidence for a 1:1 complex between palladium and the heteropoly compound as the active catalyst.

(vi) Only chlorine-containing palladium compounds were active (with $PdCl_2$ being the best).

(vii) Medium polarity solvents such as acetone and other ketones gave best results. More polar solvents such as DMSO and DMF were unsuitable, which was taken as an indication that they prevent the interaction between palladium and the cocatalyst.

(viii) During the reaction, the heteropolyacids were reduced, but maintained their structure intact [5]. By using heteropolyacids in different states of reduction as starting modifiers, it was determined that the catalytic activity of palladium increased with the extent of the reduction of the heteropolyanion until each anion was reduced with three electrons. This observation indicates that the active form of the heteropolymolybdate was $[Mo_n^V Mo_{12-n}^{VI} PO_{40}]^{(3+n)-}$ ($n \geq$ 3), in line with the higher activity shown by more easily reduced heteropolyanions, which can more easily reach and maintain this oxidation state.

(ix) It was also tested that the reduced form of the heteropolymolybdate is not able to reduce nitrobenzene in the absence of palladium (however, photoreduced heteropolytungstates can effect this reaction [12]).

(x) The complexity of the reaction mechanism is also indicated by the fact that the reaction was first order in CO pressure and catalyst

concentration, but showed 0.43-order dependence on the concentration of nitrobenzene.

The turnover frequencies obtained with this catalytic system are still limited (a 100% conversion at a molar ratio $PhNO_2/Pd = 100$ required 3 h at 170°C and 41 atm CO) but the system was active even at 11 atm CO, that is at a pressure much lower than those reported for almost all of the systems reported to effect the same reaction. We thus decided to further investigate this catalytic system, to see if there was any room for improvement.

2. Results and discussion

2.1. Catalytic experiments

First of all we reproduced some of the results reported by Izumi et al. [5]. We can confirm that the Keggin heteropolyacid $H_4Mo_{11}VPO_{40}$ does indeed affords better results than the omometallic Mo_{12} and V_{12} analogues, although the selectivity in carbamate was lower in our work than that reported. We typically obtained selectivities in the range 75–90% depending on the experimental conditions instead of the 90–99% reported (Table 1, a 2:1 Pd/heteropolyanion molar ratio was used in most of the experiments in this paper, despite a 1:1 ratio should afford better results, since a larger amount of compari-

Table 1
Effect of heteropolyanions as promoters in the $PdCl_2$-catalysed carbonylation of nitrobenzene to methyl phenylcarbamate [a]

Heteropoly compound	t (h)	Nitrobenzene conv. (%) [b]	Carbamate select. (%) [c]
$H_3Mo_{12}PO_{40}$	2	28	78
$(Bu_4N)_3Mo_{12}PO_{40}$	2	27	80
$Li_3Mo_{12}PO_{40}$	2	27	81
$H_4Mo_{11}VPO_{40}$	2	86	87
$H_7V_{12}PO_{36}$	0.5	~0	—

[a] Experimental conditions: $PhNO_2 = 8.75$ mmol, $PdCl_2 = 0.1$ mmol, heteropolyanion = 0.05 mmol, MeOH = 1.6 ml, DME = 2 ml, $P_{CO} = 41$ bar, $T = 170$°C.
[b] Calculated with respect to the starting $PhNO_2$.
[c] Calculated with respect to the reacted $PhNO_2$.

Table 2
Effect of pyridine and acetonitrile [a]

Catalyst and organic additive	Nitrobenzene conv. (%) [b]	Carbamate select. (%) [c]
$PdCl_2$	86	87
$PdCl_2 + 2$ mmol Py	26	39
$PdCl_2Py_2$	29	35
$PdCl_2(CH_3CN)_2$	70	78

[a] Experimental conditions: $PhNO_2 = 8.75$ mmol, palladium catalyst = 0.1 mmol, $H_4Mo_{11}VPO_{40} = 0.05$ mmol, MeOH = 1.6 ml, DME = 2 ml, $P_{CO} = 41$ bar, $T = 170$°C, for 2 h.
[b] Calculated with respect to the starting $PhNO_2$.
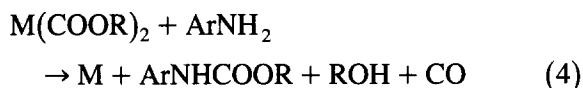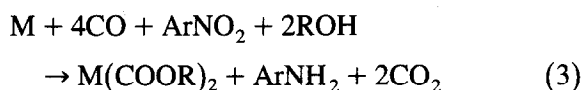[c] Calculated with respect to the reacted $PhNO_2$.

son data was available in the previous literature for this ratio). Only a trace amount of aniline was detected as by-product in the gas-chromatogram (however see also later). We also confirmed the reaction to have a complex order in nitrobenzene concentration, although it should be considered that the amount of nitrobenzene added represents a significant part of the solvent mixture and this affects both the concentrations and the solvent polarity. Increasing the amount of solvent (1,2-dimethoxyethane, DME) to render this effect negligible led to an almost inactive catalytic system. Use of $[Mo_{12}PO_{40}]^{3-}$ as its Bu_4N^+ salt instead of the acid or the lithium salt gave essentially the same results.

In the previous literature, palladium chloride has been used as catalyst for the carbonylation reactions of nitroarenes together with a large variety of redox-active cocatalysts [11]. In most cases, it was found that the addition of pyridine to the reaction was beneficial from both the point of view of the activity and the stability of the catalytic system. We thus attempted to add pyridine (2 mmol, 0.16 ml) to the heteropoly-molybdic acid-promoted system, but a sharp decrease in activity was observed (Table 2). Even the simple use of preformed $PdCl_2Py_2$ (Py = pyridine) led to a somewhat lower activity with respect to the use of $PdCl_2$, as also did the use of $PdCl_2(CH_3CN)_2$, despite the fact that these two complexes are relatively soluble, whereas $PdCl_2$ is a polymeric species which is completely insoluble in the solvent employed at

room temperature and surely takes some time to dissolve even under the reaction conditions. This finding supports the opinion of Izumi and coworkers that the heteropolyanions act as ligands towards palladium. Apparently, the formed complexes are very labile and even traditionally weak ligands as pyridine or acetonitrile can perturb their formation.

2.2. Role of aniline as an intermediate and stoichiometry of the reaction

The activity of several PdCl$_2$-based catalytic systems for the reactions here discussed is also known to be promoted by the addition of an aniline corresponding to the nitroarene employed [11]. The reason appears to rely in the fact that the aniline is an intermediate in the reaction and its carbonylation is often slower than its formation from the nitroarene [13,14]. In a schematic way (for a monometallic catalyst), the reaction can be divided in two formal steps. In the first the nitroarene is reduced to aniline by a reduced metal complex and the alcohol, to afford aniline and an alcoxycarbonyl complex that then reacts in the second step with the aniline itself to afford the carbamate (Eqs. (3) and (4)):

$$M + 4CO + ArNO_2 + 2ROH$$

$$\rightarrow M(COOR)_2 + ArNH_2 + 2CO_2 \qquad (3)$$

$$M(COOR)_2 + ArNH_2$$

$$\rightarrow M + ArNHCOOR + ROH + CO \qquad (4)$$

These two steps should not be considered to reproduce exactly the mechanism of the reaction. Both of the two are the sum of several independent steps. Aniline may also not attack the alcoxycarbonyl group, but a CO group possibly coordinated to the metal, as has been shown to occur in the case of a ruthenium complex [15]. In any case, this does not affect the general observation that if reaction (3) is rate-determining, the reaction should be first order in nitroarene and zero order in aniline, whereas if the slowest step is reaction (4), the

Table 3
Effect of the addition of aniline [a]

PhNO$_2$ (mmol)	PhNH$_2$ (mmol)	t (h)	Nitrobenzene conv. (%) [b]	Carbamate select. (%) [c]
8.75	—	0.5	63	48
8.75	2.5	0.5	41	62
20	—	2	61	65
20	2.5	2	72	62
20	5	2	71	75

[a] Experimental conditions: PhNO$_2$ = 8.75 mmol, PdCl$_2$ = 0.1 mmol, H$_4$Mo$_{11}$VPO$_{40}$ = 0.05 mmol, MeOH = 1.6 ml, DME = 2 ml, P_{CO} = 41 bar, T = 170°C.
[b] Calculated with respect to the starting PhNO$_2$.
[c] Calculated with respect to the reacted PhNO$_2$.

reaction should be zero order in nitroarene and first order in aniline. In the case of a bimetallic catalyst, like the present one, the detailed mechanism may be more complex [13], but the reaction sequence in reactions (3) and (4) can still be applied to rationalise the observed kinetics.

As it was not completely clear if the heteropolyanion-promoted system could be included in the wide class of the PdCl$_2$-based catalytic systems with redox-active cocatalysts, it was important to test its behaviour with respect to this important parameter. The addition of aniline (2.5 mmol) was found to decrease the conversion (from 63 to 41%, for a 30 min reaction, Table 3) when added to a reaction mixture containing a relatively low amount (8.75 mmol) of nitrobenzene, however the addition of the same amount of aniline to a more concentrated solution of nitrobenzene (20 mmol) increased the conversion (from 61 to 72%). If a higher amount of aniline (5 mmol) was added under these last conditions, an essentially equal conversion was obtained, but the selectivity increased. This data is indicative of a change of rate-determining step (the situation is even a bit more complex, see later). At a low nitrobenzene concentration, its activation is apparently the rate-determining step. Under these conditions the rate should be independent of the aniline concentration, but a negative effect may arise from the fact that the heteropolyacid is neutralised by the aniline to afford an anilinium salt

that has been shown by us to be markedly less soluble in the reaction mixture. When the nitrobenzene concentration is higher, its activation is no longer rate-determining (in the absence of significant amounts of aniline) and the slowest step becomes the equivalent of reaction (4). Now the positive effect of a higher aniline concentration overwhelms the negative effect previously discussed. The rates of the two reactions are probably very close under both concentration conditions and the fact that the addition of a higher amount of aniline does not further increase the conversion indicates that the addition of 2.5 mmol of aniline was already sufficient (or very close) to accelerate reaction (4) enough that reaction (3) becomes again rate-determining despite the high nitrobenzene concentration. The above observations are sufficient to explain the strange kinetic order in nitrobenzene (0.43) reported by Izumi and co-workers [5]. Indeed a change in rate-determining step occurs smoothly as the initial nitrobenzene concentration is increased and (at least in some cases) even during any single run, as the nitrobenzene concentration decreases during the reaction and the 'kinetic inversion point' is surely passed in several cases during the reaction.

The above reported data is sufficient to confirm that the PdCl$_2$-heteropolyacid catalytic system is indeed a member of the general family of the PdCl$_2$-redox active cocatalyst systems for the carbonylation of nitroarenes, but we wanted to seek further support for this conclusion and for the role of aniline as an intermediate. For some years, a typical test to evidence 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 starting nitroarene should be obtained, whereas if it is, both of the carbamates deriving from the nitroarene and the aniline should be
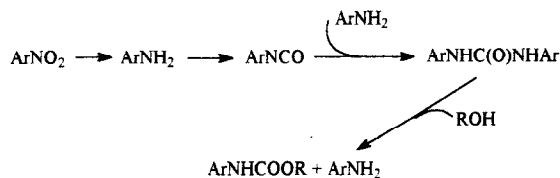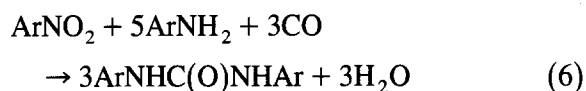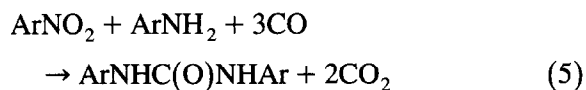

Scheme 1. 1

obtained. However, more recently Gargulak and Gladfelter have shown that, at least in the case of Ru(CO)$_3$(DPPE) as a catalyst (DPPE = 1,2-bis(diphenylphosphinoethane)), 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 alcoholysed to afford one equivalent of carbamate and one of aniline [16]. So, at least for the ruthenium catalyst, the reaction sequence (only the organic products are shown) is (Scheme 1):

At this point, the aforementioned test cannot be considered any longer generally valid. Indeed, if we consider free 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 alcoholyse to yield a mixture of all possible carbamates and anilines [1]. We reasoned that the only way to evidence the intermediate formation of aniline was to work in the 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 (the temperature must not exceed 120°C). As previously shown by us in another work [19], the experiment can be rendered even

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[1] The conclusion drawn in previous papers 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 also pointed to the same conclusion [17,18].

more clear cut by using a nitroarene bearing electronwithdrawing substituents (we used 3,4-$Cl_2C_6H_3NO_2$ in the present work) and unsubstituted aniline as starting material. If the substituted aniline is not an intermediate, only the mixed urea, 3,4-$Cl_2C_6H_3NHC(O)NHPh$, should be obtained as product. On the other hand, if the aniline is an intermediate, the formed 3,4-$Cl_2C_6H_3NH_2$ will be in competition with the much more nucleophilic $PhNH_2$ and symmetric diphenylurea should be obtained as the largely predominant product, at least at low conversion.

Before describing the results of our experiments, we must recall that two different stoichiometries, associated with two different reaction paths, have been observed for urea formation from nitroarenes and anilines. They can be described by the following two equations:

$$ArNO_2 + ArNH_2 + 3CO$$
$$\rightarrow ArNHC(O)NHAr + 2CO_2 \qquad (5)$$
$$ArNO_2 + 5ArNH_2 + 3CO$$
$$\rightarrow 3ArNHC(O)NHAr + 3H_2O \qquad (6)$$

A more thorough discussion of these processes has been given elsewhere [13,14]. Here it suffices to say that both the processes can simultaneously operate in a single reaction and the second is clearly favoured when a large excess of aniline with respect to the nitroarene is employed. When the synthesis of carbamates is concerned, the second process is likely to play a minor role, as the concentration of aniline (even in the cases in which it was added in small amounts to the reaction mixture) is always much inferior to the one of nitrobenzene (possibly except close to complete conversion of the nitroarene).

When we performed the carbonylation reaction of 3,4-$Cl_2C_6H_3NO_2$ (8.75 mmol) in the presence of aniline (8.75 mmol) under usual conditions ($PdCl_2 = 0.1$ mmol, $H_4Mo_{11}VPO_{40}$ = 0.1 mmol, $P_{CO} = 41$ bar, DME = 2 ml, for 1 h), but at 120°C and in the absence of methanol, a 15.3% conversion of the nitroarene was observed in 1 h and a precipitate of ureas was

obtained. HPLC analysis of the precipitate evidenced that it was composed of 98.4 mol% diphenylurea and only 1.6 mol% mixed urea. No symmetrical urea having both aryl groups chlorinated was observed. It is important to note that, despite arylureas are little soluble in the reaction mixture, part of them remained dissolved in solution. However, we have previously shown [19] that diphenylurea and the mixed urea coprecipitate and their relative ratio in the precipitate is the same as in the fraction remained dissolved. Although this data already supports the notion that aniline is an intermediate in the reaction, a closer examination of the data deriving from the gas-chromatographic analysis of the solution after the reaction shows something more. Although only 1.34 mmol of the nitroarene reacted, 6.73 mmol of aniline was consumed! If we take into account the amount of 3,4-$Cl_2C_6H_3NH_2$ formed during the reaction (0.85 mmol) and the fact that about 4 mmol of aniline for each mmol of starting heteropolyanion is unobservable by GC due to protonation from the acid (see also later), we obtain a molar ratio reacted arylamines/reacted nitroarene = 4.10, which is much closer to the 5:1 ratio expected for the process in Eq. (6) than the 1:1 ratio expected for the one in Eq. (5).

To test if the prevalence of the stoichiometry corresponding to Eq. (6) was induced by the different nitroarene employed or by the higher amount of aniline with respect to the usual reactions for the synthesis of carbamates we repeated the same reaction employing perdeuterated nitrobenzene and undeuterated aniline, analogously to what was reported by Lee et al. [20]. The results were partly a surprise. By running the carbonylation reaction with equimolar (8.9 mmol) amounts of aniline and perdeuterated nitrobenzene for 2 h ($PdCl_2$ = 0.1 mmol, $H_4Mo_{11}VPO_{40}$ = 0.1 mmol, T = 120°C, P_{CO} = 41 bar, DME = 2 ml) a 49.8% conversion of aniline against a 15.7% conversion of nitrobenzene was observed. Taking again into consideration that about 4 mmol of aniline for each mmol of starting heteropolyanion are
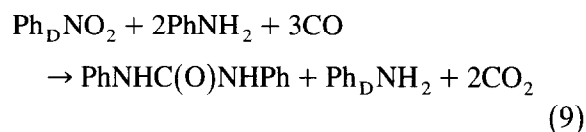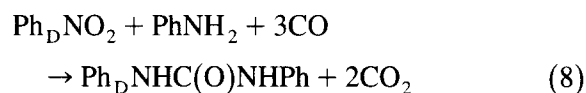
unobservable by GC, a molar ratio consumed aniline/consumed nitrobenzene = 2.9 is obtained. The mass spectrum of the product urea showed it to contain 92.3% undeuterated diphenylurea, 7.7% pentadeuterated diphenylurea, and no decadeuterated product. However the aniline in solution contained (by GC-MS) only 2.9% deuterated product.

Although the undeuterated urea is clearly the dominant product, the fact that the deuterium amount in the urea is higher than the double of the one in the free aniline in solution implies that a process must be present which selectively includes the nitroarene-derived fragment without passing through the free aniline (note that a 50% of pentadeuterated urea corresponds to a 25% inclusion of deuterated rings in the product. Thus, if the percentage of deuterated aniline in solution were 2.9% since the beginning, the maximum possible deuteration level in the urea for a reaction passing through the aniline should be 5.8%. However, the deuterated aniline is initially absent and is produced during the reaction. Thus 2.9% is the maximum deuteration level for the free aniline during the reaction and its medium value is surely lower during the reaction. This further lowers the maximum amount of pentadeuterated urea that may be obtained by a 'free aniline-based' process). The obtained 2.9 molar ratio between reacted aniline and nitrobenzene indicates that the stoichiometries in Eqs. (5) and (6) account for about 50% each in this experiment. In a previous work [20], Lee and co-workers examined the carbonylation of perdeutero nitrobenzene in the presence of a large excess of undeuterated aniline, catalysed by palladium phosphine complexes. Under their conditions, the process associated with the stoichiometry in Eq. (6) was strongly predominant. The product essentially contained undeuterated urea and perdeutero aniline was found in solution. This implies that the nitroarene in this process is not directly included in the product urea and it is intermediately completely transformed into aniline. Working at low conversion, as in our experiments, the aniline derived from

the nitroarene has only a small chance of reentering the catalytic cycle and to be transformed into urea. Thus the process in Eq. (6) may be better described by Eq. (7):

$$Ph_D NO_2 + 6PhNH_2 + 3CO$$
$$\rightarrow 3PhNHC(O)NHPh + Ph_D NH_2 + 3H_2O \tag{7}$$
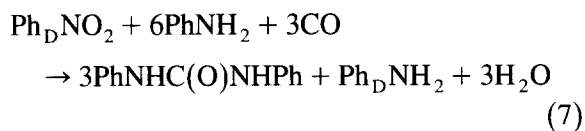
If we assume (as it is very likely) that even with our catalyst the process in Eq. (6) can be better described as Eq. (7), then all (or almost all) of the pentadeuterated urea must derive from the process in Eq. (5). If this process were selective in including all of the nitroarene-derived fragments in the urea, then a 12.5% deuterium incorporation would be expected (even without taking into account the amount of deuterated aniline that is produced, but than partly consumed in process (6)). The lower amount of deuteration with respect to this value indicates that the stoichiometry in Eq. (5) is followed by at least two different reaction pathways (taking the total to at least three), one of which selectively retains all of the nitroarene-derived fragment in the product, whereas the other intermediately produces aniline (Eqs. (8) and (9)).

$$Ph_D NO_2 + PhNH_2 + 3CO$$
$$\rightarrow Ph_D NHC(O)NHPh + 2CO_2 \tag{8}$$
$$Ph_D NO_2 + 2PhNH_2 + 3CO$$
$$\rightarrow PhNHC(O)NHPh + Ph_D NH_2 + 2CO_2 \tag{9}$$

Unfortunately, although in theory it should be possible to calculate the relative weight of these two processes from the available data, this number is extremely sensitive to the nitroarene conversion, which is affected by a relatively large error as, at low conversion, even a small error in the amount of the remained nitrobenzene measured by GC affects more severely (in percent) the amount of nitrobenzene reacted.

In conclusion, the carbonylation of nitrobenzene with the PdCl$_2$-heteropolycompounds appears to proceed through at least three different

pathways. One is the oxidative carbonylation of aniline with the nitroarene acting as an oxidant (i.e., Eq. (6) or Eq. (7)). This process appears to be the dominant one in the presence of excess aniline, but probably plays only a minor role if only the nitroarene is added since the beginning. Two other processes appear to follow the stoichiometry in Eq. (5). One of the two (Eq. (9)) intermediately produces aniline (in a sequence similar to the one in Eqs. (3) and (4), whereas the other (Eq. (8)) does not. The rate-determining step of at least one of the processes in Eqs. (8) and (9) appears to depend on the aniline and nitrobenzene concentrations, thus explaining the strange kinetic order observed.

2.3. Attempts to identify intermediate complexes

We also attempted to identify the residue after the reactions run with $Mo_{12}PO_{40}^{3-}$. However, the ^{31}P NMR spectrum of the solutions at the end of the reactions (dried in vacuo and redissolved in acetonitrile) showed signals in different positions (between -10 and -12 ppm) depending upon the conditions and the reaction time. The insoluble part of the catalyst after the reaction was also too little soluble even in other solvents to allow for a ^{31}P NMR spectrum to be recorded, but its elemental analysis gave values consistent with the presence of the 'NPh' fragments. We recalled that several groups have reported the synthesis of several polyoxomolybdates and tungstates containing one or more imido groups (e.g., $[Bu_4N]_2[Mo_6O_{18}(NC_6H_4–CH_3)])$ [21–27]. The synthesis of some of these compounds proceeds by reaction of a polyoxomolybdate with isocyanates or amines. The last in particular are surely present under our reaction conditions. Heteropolymolybdates have been used as substrates in only one case [28], in a reaction with p-tolylisocyanate, and the only characterised product did not contain the phosphorus atom any more, but it contained as much as 12 imido groups for 10 molybdenum atoms. To assess if imido-containing products were formed even in

our conditions, we attempted several model reactions between $H_3Mo_{12}PO_{40}$ or its salts and amines. The reactions (either under a dinitrogen or CO atmosphere) led in any case to reduced products (as judged from the blue colour and the position of the ^{31}P NMR signals) whose elemental analysis indicates the presence of 5 to 6 (closer to 6) equivalents of aniline per mole of heteropolyanion when the acid was used as substrate and 2 to 3 (closer to 3) when the lithium or tetrabuthylammonium salts were employed. While the difference between these precipitates may be attributed to the neutralisation of the acid by aniline, with formation of anilinium salts, which is not possible in the cases of the other two salts, the data indicate anyway the presence of some excess 'aniline fragments' in the residue. However, after repeated attempts at growing crystals of these materials, we succeeded in growing crystals suitable for X-rays of a sample with Et_4N^+ as countercation, which was shown to be a reduced heteropolyanion with no imido fragment bound to the metal framework. The exact charge could not be determined due to partial disorder of the countercations, but appears to be between 5 and 6 and the aniline moiety is present only in the form of anilinium cations, which compensate the extra charge originated in the reduction process. Thus aniline does not appear to bind to the heteropolyanion to a large extent under our conditions, although the formation of imido adducts as minor product cannot be excluded.

2.4. Reactivation of the spent catalyst

We also examined the reusability of the catalyst after the reaction. After a typical reaction the heteropolyanion is present part as a precipitate and part in solution. When the suspension after a reaction run using $H_3Mo_{12}PO_{40}$ as cocatalyst was dried, washed with toluene to remove all organic products, and reused as catalyst, no activity was found. Even upon adding fresh $PdCl_2$, to test if only the palladium was deactivated, only a 4.3% conversion was ob-

served, much lower than the 48.9% conversion observed in the first run. In an attempt to regenerate the cocatalyst, we treated another portion of the same spent catalyst with water at 170°C for 3 h, in the aim of displacing any nitrogen-containing group possibly bound to the heteropolyanion in any form. The solid after this treatment was used as catalyst, after addition of fresh $PdCl_2$. The conversion was 7.2% that is higher than the one obtained with the non-treated spent cocatalyst, but still far from the original one, indicating that the treatment with water is only partially successful in regenerating the heteropolyanion. It should be noted that reduction of the heteropolyanion by itself is not sufficient to account for deactivation, as reduced heteropolyanions had earlier been found to be more active as cocatalysts than the non-reduced heteropolyanion [5].

3. Experimental

3.1. General procedure

Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring, but the products of the catalytic reactions had to be handled in the air for at least some time. Solvents were dried and distilled by standard procedures and stored under dinitrogen. Water was degassed by three freeze–pump–thaw cycles. 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. $(Bu_4N)_3Mo_{12}PO_{40}$ [29], $H_3VMo_{11}PO_{40}$ [30], and $H_7V_{12}PO_{36}$ [31,32] were synthesised by methods reported in the literature. $H_3Mo_{12}PO_{40}$ (Aldrich) was found to contain a small amount of a water-insoluble white impurity, likely MoO_3, and was dissolved in water, filtered, and dried in vacuo before use. $Li_3Mo_{12}PO_{40}$ was obtained by reaction of the corresponding acid with the stoichiometric amount of Li_2CO_3. All other compounds were commercial products and were used as received. Gas chromatographic analyses were performed on a Perkin Elmer 8420 capillary gas chromatograph equipped with a PSS 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. 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 HPLC Chem Station. NMR spectra were recorded on a Bruker AC 200 FT (200 MHz) at RT. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

3.2. Catalytic reactions

In a typical reaction, the reagents (see Tables 1–3) were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth under nitrogen. The liner 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 rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring, and the autoclave was evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure. Other experimental conditions are reported in Tables 1–3. At the end of the reaction the autoclave was cooled with an ice bath, vented and the products were analysed by gas chromatography (naphthalene as an internal standard). In the cases in which ureas were formed, 10 ml of toluene was added to the reaction mixture and the liner was frozen at −78°C with a dry-ice/acetone bath in order to favour urea precipitation. The precipitate was then filtered, washed with toluene and analysed by HPLC or mass spectrometry as required.

3.3. Reactions of heteropolyanions with aniline

The experimental procedure was similar to the one described for catalytic reactions. The solvent was 1,2-dimethoxyethane in most cases, but CH_3CN was also used in some cases. At the end of the reaction, most of the heteropolyanion was present as a precipitate, which was filtered, washed with 1,2-dimethoxyethane and toluene and dried in vacuo. ^1H and ^{31}P NMR spectra of the residue in CD_3CN or DMSO-d_6 always showed the presence of mixtures of products (see also text). Typical elemental analyses for the residue after a reaction starting from $H_3Mo_{12}PO_{40}$ or $Li_3Mo_{12}PO_{40}$ are as follows: C, 18.4; H, 2.3; N, 3.6. Calculated for $(PhNH_3)_3Mo_{12}PO_{37}(NPh)_3$: C, 18.6; H, 1.7; N, 3.6, and C, 10.4; H, 1.5; N, 1.63. Calculated for $Li_3Mo_{12}PO_{37}(NPh)_3$: C, 10.5; H, 0.7; N, 2.0.

Acknowledgements

References

[1] M.T. Pope, A. Muller, Angew. Chem. Int. Ed. Engl. 30 (1991) 34.
[2] G.M. Marksimov, Usp. Khim. 64 (1995) 480. Engl. Transl. in Russ. Chem. Rev. 64 (1995) 445.
[3] I.V. Kozhevnikov, K.I. Matveev, Appl. Catal. 5 (1983) 135.
[4] A. Heumann, K.-J. Jens, M. Reglier, Prog. Inorg. Chem. 42 (1994) 483, and references therein.
[5] Y. Izumi, Y. Satoh, H. Kondoh, K. Urabe, J. Mol. Catal. 72 (1992) 37.
[6] Y. Izumi, Y. Satoh, K. Urabe, Chem. Lett. (1990) 795.
[7] Y. Izumi, Jpn. Kokai Tokkyo Koho JP 03 93,765 [91, 93,765] (1991). Chem. Abstr.: 115:182846d.
[8] J.S. Lee, J.W. Woo, C.W. Lee, K.S. Hong, J.K. Yeo, Korean J. Chem. Eng. 7 (1990) 145. Chem. Abstr.: 114:84243q.
[9] Mitsui Toatsu Chemicals, Jpn. Kokai Tokkyo Koho JP 81,138,159 (1981). Chem. Abstr.: 96:52875r.
[10] Y. Izumi, Jpn. Kokai Tokkyo Koho JP 04 89,465 [92 89,465] (1992). Chem. Abstr.: 117:69596a.
[11] S. Cenini, F. Ragaini, Catalytic reductive carbonylation of organic nitro compounds, Kluwer Academic Publishers, Dordrecht, 1997, ch. 2 and 3.
[12] R. Amadelli, G. Varani, A. Maldotti, V. Carassiti, J. Mol. Catal. 59 (1990) L9.
[13] S. Cenini, F. Ragaini, Catalytic reductive carbonylation of organic nitro compounds, Kluwer Academic Publishers, Dordrecht, 1997, ch. 6.
[14] F. Ragaini, S. Cenini, J. Mol. Catal. A 109 (1996) 1.
[15] J.D. Gargulak, W.L. Gladfelter, Organometallics 13 (1994) 698.
[16] J.D. Gargulak, W.L. Gladfelter, J. Am. Chem. Soc. 116 (1994) 3792.
[17] J.D. Gargulak, A.J. Berry, M.D. Noirot, W.L. Gladfelter, J. Am. Chem. Soc. 114 (1992) 8933.
[18] F. Ragaini, S. Cenini, F. Demartin, Organometallics 13 (1994) 1178.
[19] F. Ragaini, A. Ghitti, S. Cenini, 11th FECHEM Conf. on Organometallic Chemistry, Parma, Italy, 1995, p. 45; F. Ragaini, A. Ghitti, S. Cenini, manuscript in preparation.
[20] C.W. Lee, J.S. Lee, S.M. Lee, K.D. Kim, N.S. Cho, J.S. Oh, J. Mol. Catal. 81 (1993) 17, and references therein.
[21] Y. Du, A.L. Rheingold, E.A. Maatta, J. Am. Chem. Soc. 114 (1992) 345.
[22] A. Proust, R. Thouvenot, M. Chassade, F. Robert, P. Gouzerth, Inorg. Chim. Acta 224 (1994) 81.
[23] J.B. Strong, R. Ostrander, A.L. Rheingold, E.A. Maatta, J. Am. Chem. Soc. 116 (1994) 3601.
[24] T.R. Mohs, G.P.A. Yap, A.L. Rheingold, E.A. Maatta, Inorg. Chem. 34 (1995) 9.
[25] W. Clegg, R.J. Errigton, K.A. Fraser, S.A. Holmes, A. Schäfer, J. Chem. Soc. Chem. Commun. (1995) 455.
[26] J.L. Stark, V.G. Young Jr., E.A. Maatta, Angew. Chem. Int. Ed. Engl. 34 (1995) 2547.
[27] A. Proust, R. Thouvenot, M. Chaussade, F. Robert, P. Gouzerth, Inorg. Chim. Acta 224 (1994) 81.
[28] A. Proust, S. Taunier, V. Artero, F. Robert, R. Thouvenot, P. Gouzerth, Chem. Commun. (1996) 2195.
[29] C. Sanchez, J. Livage, J.P. Launay, M. Fournier, Y. Jeanninm, J. Am. Chem. Soc. 104 (1982) 3194.
[30] G.A. Tsigdinos, C.J. Hallada, Inorg. Chem. 3 (1968) 437.
[31] R. Von Hagenbruch, H. Hahn, Z. Anorg. Allg. Chem. 438 (1978) 273.
[32] R. Von Hagenbruch, H. Hahn, Z. Anorg. Allg. Chem. 467 (1980) 126.