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Promotion of the [PPN][Rh(CO)$_4$]-catalysed carbonylation of nitrobenzene by 2-hydroxypyridine and related molecules: an apparent bifunctional activation

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Dedicated to Professor Fausto Calderazzo in recognition of his important contribution to organometallic chemistry.

Abstract

2-Hydroxypyridine and related molecules have a large activating effect on the previously reported [PPN][Rh(CO)$_4$]-based catalytic system for the reductive carbonylation of nitrobenzene to methyl phenylcarbamate ($PPN^+ = (PPh_3)_2N^+$). The effect is not due to the known 2-hydroxypyridine–2-pyridone tautomeric equilibrium, since 4-hydroxypyridine, for which the same tautomeric equilibrium exists, completely inhibits the reaction. A promoting effect of 2-hydroxypyridine is also observed in the reactions of a previously isolated metallacyclic complex, [PPN][Rh(CO)$_2$ON(Ar)C(O)O], believed to be an intermediate in the catalytic reactions. However, the dependence of the rate of the catalytic reactions on the aniline concentration indicates that the effect found for the stoichiometric reaction cannot be the one that is relevant for the acceleration of the catalytic reactions. Thus, two different effects are present, both of which appear to be due to the proximal positions of a basic and an acidic site in the promoter molecules.

Keywords: Homogeneous catalysis; Nitrobenzene; Carbonylation reactions; Rhodium; 2-Hydroxypyridine

1. Introduction

Bifunctional activation of reacting molecules is usually the rule in enzymatic catalysis, but it is an, as yet, little explored field in traditional homogeneous catalysis [1–3]. Several years ago, we reported on the use of [PPN][Rh(CO)$_4$] ($PPN^+ = (PPh_3)_2N^+$) as a catalyst for the carbonylation reaction of nitrobenzene to methyl phenylcarbamate [4].

$$PhNO_2 + MeOH + 3CO \xrightarrow[\substack{P_{CO}=40-80\ bar\\ 170-200°C}]{\text{[PPN][Rh(CO)}_4\text{]}} PhNHCOOMe + 2CO_2 \quad (1)$$

Since carbamates can be thermolysed to yield the corresponding arylisocyanates, this type of process represents a viable alternative for the synthesis of this last type of product, which avoids the use of the toxic phosgene employed in the industrial process [5]. It should be noted that the activity of the catalytic system reported here is higher than that of all other rhodium- or ruthenium-based catalytic systems for this reaction. Only a few palladium-based catalytic systems showing an even higher activity have been reported [5].

Previously reported data [4,6] that are relevant to the present paper are the following:

1. Nitrogen organic bases such as 2,2′-bipyridine (Bipy) or pyridine (Py) have a promoting effect on the catalytic reaction.
2. It was shown that during the catalytic reactions nitrobenzene is intermediately reduced to aniline and only at a later stage of the reaction is this last product carbonylated to the carbamate.
3. A probable intermediate in the catalytic reaction, [PPN][Rh(CO)$_2$ON(Ar)C(O)O] (Ar = 3,4-$Cl_2C_6H_3$ **1a,** Ph **1b**) was isolated and found to react with methanol under an atmosphere of CO to yield

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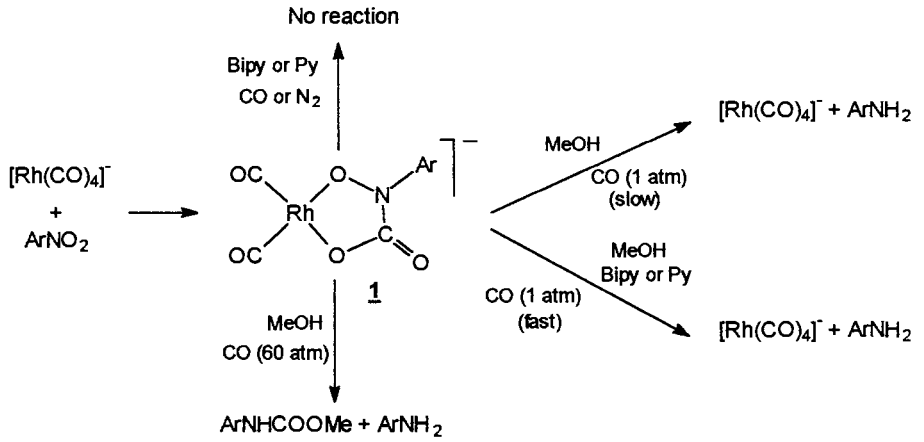


Scheme 1.

$ArNH_2$. Under a higher CO pressure, the corresponding methyl carbamate was also obtained.

4. The reaction of **1** with methanol was accelerated by the addition of Bipy or Py, but these bases did not react with the complex in the absence of methanol (Scheme 1).
5. Methylation experiments showed that in the reaction of **1** with methanol, the site of interaction between the hydroxylic proton of methanol and **1** is neither of the two 'CO_2' oxygen atoms, but it could not be ascertained if the nitrogen or oxygen atoms of the Ar–NO moiety was involved in this reaction.

A simplified reaction sequence is reported in Scheme 2. Note that the precise identity of the carbalkoxy complex is not known and the Scheme was drawn by analogy with a ruthenium complex identified in related mechanistic studies [7]. Note also that the formation of the methyl carbamate from the carbalkoxy complex and aniline is probably not straightforward. In the case of the $Ru(CO)_3$(DPPE) (DPPE = 1,2-bis(-diphenylphosphino)ethane) catalytic system, this step was shown to involve the nucleophilic attack of aniline on a coordinated CO (*not* on the –COOMe group), the formation of isocyanate (PhNCO) and its trapping by excess aniline to afford diphenylurea (PhNHC(O)NHPh), and finally the alcoholysis of the urea to afford the carbamate and to regenerate an equivalent of aniline.

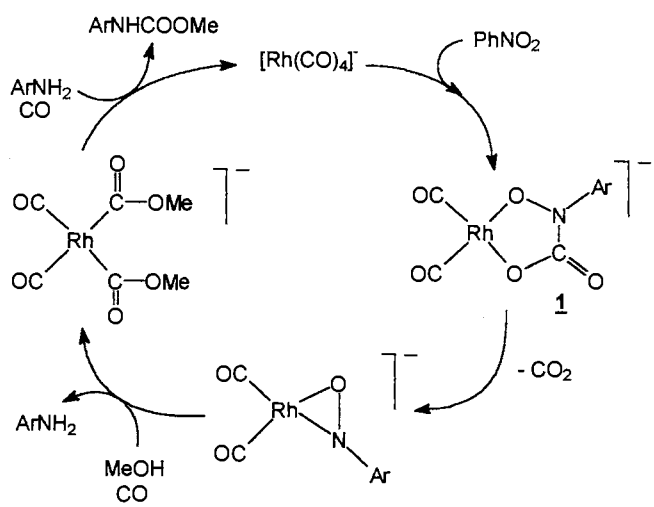
Point (4) suggested to us that the simultaneous presence of a nitrogen base and an alcohol close to the metal centre is a preferred situation for the reaction to proceed. We investigated the effect of the addition of molecules bearing both a basic nitrogen atom and an –OH group on both the catalytic reactions and the stoichiometric decomposition of **1**. At least, under certain conditions, a promotional effect was found for both reactions, although some inhibiting effects were also present that rendered the situation more complex.

2. Results

2.1. Stoichiometric reactions

We have already reported [6] that complex **1a** is obtained in good yield by reaction of [PPN][$Rh(CO)_4$] with 3,4-$Cl_2C_6H_3NO_2$ in THF under CO at room temperature. However, the work-up of the reaction mixture was very delicate, because a dark polymeric impurity was also formed. During this work, we found that the reaction could be rendered more selective by working at − 78°C. In this way, no dark products were formed and the isolated yield could be increased to 86%.

Reinvestigation of the reaction between **1a** and methanol showed that, quite unexpectedly, no reaction at all occurs, at least at room temperature or slightly above it, when it is performed under a dinitrogen atmosphere, even under concentration conditions where the reaction is very fast under CO. Interestingly, the addition of pyridine to the reaction mixture under dinitrogen allows the reaction to proceed, although, as



Scheme 2.

also previously reported [6], no reaction is observable between **1a** and pyridine in the absence of methanol. In any case, the reaction is slower than the corresponding reaction in the presence of CO. 3,4-Dichloroaniline was formed as the organic product, analogously to what was found for the reaction in the presence of CO (Scheme 1), but $[Rh(CO)_4]^-$ could not be reformed and a mixture of complexes (apparently rhodium clusters), which could not be identified, was obtained instead.

Although **1a** was stable in the presence of either methanol or pyridine alone and under a dinitrogen atmosphere, 2-hydroxypyridine reacted with the metallacycle even in the absence of both methanol and CO. 3,4-$C_6H_3NH_2$ was formed, but no rhodium complexes could be isolated.

As mentioned in Section 1, the hydroxylic proton of methanol (and probably even that of hydroxypyridine) appears to interact with either the oxygen or nitrogen atom of the Ar–NO moiety of **1**, but which of the two atoms is responsible for the initial interaction has not been determined. In this work, we have examined the reactivity of other electrophiles to gain a deeper insight into this problem.

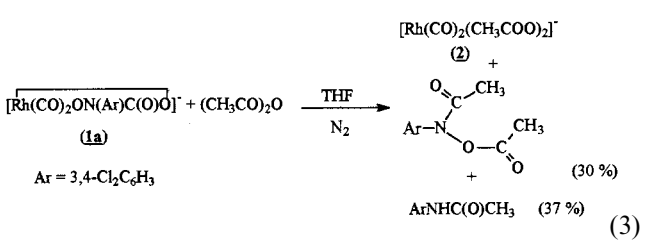
Reaction of **1a** with *p*-toluolyl chloride afforded $[Rh(CO)_2Cl_2]^-$ and 4-$MeC_6H_4C(O)NH$(3,4-$Cl_2C_6H_3$). No intermediate could be isolated from this reaction (Eq. (2)):

$$[\underset{\textbf{(1a)}}{Rh(CO)_2ON(Ar)C(O)O}]^- + 4\text{-}CH_3C_6H_4C(O)Cl \xrightarrow[N_2]{THF} [Rh(CO)_2Cl_2]^- + CO_2 + ArNHC(O)C_6H_4CH_3 \quad (2)$$

where Ar = 3,4-$Cl_2C_6H_3$.

Some non-carbonyl-containing rhodium complexes must also be formed, but they could not be observed by IR spectroscopy, since the reduction of the metal-bound nitrosoarene requires the consumption of an equivalent amount of CO, which can only derive from a decomposition of **1a** that does not afford a carbonyl complex.

When a similar reaction was performed with acetic anhydride, both the arylacetamide 3,4-$Cl_2C_6H_3NHC$-(O)Me and the *bis*-acetylated product $Cl_2C_6H_3N$-(C(O)Me)OC(O)CH_3 were obtained in 37 and 30% isolated yield, respectively (Eq. (3)). No product could be detected in which only the oxygen atom of the nitrosoarene moiety had been acylated. From the same reaction, a complex could be isolated showing absorptions in the IR spectrum (THF) at 2054, 1972 and 1621 cm^{-1}. This complex was characterised by single-crystal X-ray diffractometry and shown to be [PPN][$Rh(CO)_2(OAc)_2$] (**2**) [8]. The same complex has been previously characterised by X-ray spectroscopy, with Bu_4N^+ as a countercation [9].



(3)

Even the use of a bulkier anhydride, di-*tert*-butyl anhydride, did not allow for the isolation of an intermediate in which the nitrogen atom was still part of a ligand moiety; a complex showing absorptions in the IR spectrum identical to those of **2** was observed, which is thus proposed to be $[Rh(CO)_2(Bu^tCOO)_2]^-$.

The reaction of **1a** with aniline did not proceed at all at room temperature under a dinitrogen atmosphere, but, analogously to what was observed for methanol, the reaction started immediately when the dinitrogen atmosphere was replaced by CO. The complex $[Rh(CO)_4]^-$ was again obtained as the only organometallic product, while diphenylurea and the mixed urea $PhNHC(O)NHC_6H_3Cl_2$ were isolated in a 41/9 molar ratio (Eq. (4)). A reaction was also observed in the absence of CO if pyridine was also added, but in this case a mixture of cluster complexes was formed and no urea, but only 3,4-dichloroaniline, was detected as the organic product.

$$[\underset{\textbf{(1a)}}{Rh(CO)_2ON(Ar)C(O)O}]^- + PhNH_2 \xrightarrow[CO]{THF} [Rh(CO)_4]^- + PhNHC(O)NHPh + ArNHC(O)NHPh \quad (4)$$

where Ar = 3,4-$Cl_2C_6H_3$.

The fact that diphenylurea is strongly predominant over the mixed urea supports the view that the arylamine is an intermediate in the carbonylation reaction. Indeed, once 3,4-$Cl_2C_6H_3NH_2$ is formed it must compete with the more nucleophilic $PhNH_2$ and the product derived from this last amine prevails. We have previously observed the same outcome for catalytic reactions between 3,4-$Cl_2C_6H_3NO_2$ and $PhNH_2$ in the presence of either palladium or ruthenium complexes [10,11].

2.2. Catalytic reactions

We first compared the effect of the addition of 2,2′-bipyridine and 2-hydroxypyridine under the originally employed conditions [4] and the results are reported in Table 1[1].

In agreement with the original results [4], the addition of 2,2′-bipyridine to the reaction carried out at

[1] The results reported here for entries 1 and 2 of Table 1 are slightly different from those reported in Ref. [4]. However, this is due to the fact that the experiments have been repeated after several years, using freshly distilled THF, instead of THF dried but then stored for several weeks before use. Anyway, the trends are the same as previously reported.

Table 1
Effect of 2,2′-bipyridine and 2-hydroxypyridine on the [PPN][$Rh(CO)_4$]-catalysed carbonylation of nitrobenzene to methyl phenylcarbamate in THF [a]

Run	Promoter	Prom./Rh mol ratio	$PhNO_2$ conv. (%) [b]	Carbamate select. (%) [c]	Aniline select. (%) [c]	Azobenzene select. (%) [c]	Azoxybenzene select. (%) [c]
1	–	–	37.5	75.5	8.3	–	–
2	2,2′-Bipyridine	6	56.4	56.4	12.4	0.8	16.4
3	2-Hydroxypyridine	12	59.8	74.5	9.4	1.2	–

[a] Experimental conditions: [PPN][$Rh(CO)_4$] = 0.125 mmol, mol ratio $PhNO_2$/Rh = 300, T = 170°C, P_{CO} = 60 bar, in THF (8 ml) + MeOH (3 ml), for 1.5 h.
[b] Calculated with respect to the starting nitrobenzene.
[c] Calculated with respect to converted nitrobenzene. The selectivity in azo- and azoxybenzene was lower than 1% in all cases where no value is reported. Some diphenylurea was always present as a by-product, which could be detected by gas chromatography but not quantified in a precise manner.

Table 2
Effect of several promoters on the [PPN][$Rh(CO)_4$]-catalysed carbonylation of nitrobenzene to methyl phenylcarbamate in toluene [a]

Run	Promoter	$PhNO_2$ conv. (%) [b]	Carbamate select. (%) [c]	Aniline select. (%) [c]	Azobenzene select. (%) [c]	Azoxybenzene select. (%) [c]
1	Et_3N	66.1	73.1	8.5		
2	Pyrazole	~0		traces		
3	*N*-Methylimidazole	62.2	79.7	10.3		
4	Pyridine	63.5	76.3	9.6		
5	2,2′-Bipyridine [d]	65.0	74.5	10.5	0.8	1.6
6	2-Hydroxypyridine	80.3	87.2	9.3	1.9	
7	2-Hydroxymethyl-pyridine	65.9	69.8	12.1		
8	2(2-Hydroxyethyl)-pyridine	59.5	81.0	12.4		
9	4-Hydroxypyridine	~0	traces	traces		
10	4-Hydroxyquinazoline	~0				
11	2-Hydroxypyrimidine hydrochloride	~0				
12	2-Hydroxypyrimidine hydrochloride + proton sponge	~0				
13	2-Pyridinethiol	15.6	37.7	45.7		4.1
14	Picolinic acid	5.7	traces	traces		
15	2-Hydroxyquinoline	85.4	88.0	9	0.9	
16	8-Hydroxyquinoline	6.4	10.0	48.0		
17	2-Hydroxypyridine [e]	63.3	71.9	11.2	2.9	
18	2,2′-Bipyridine [e]	68.3	77.1	7.3	1.2	1.6

[a] Experimental conditions: [PPN][$Rh(CO)_4$] = 0.125 mmol, mol ratio $PhNO_2$/Rh/promoter = 300:1:6, T = 200°C, P_{CO} = 60 bar, in toluene (8 ml) + MeOH (3 ml), for 1.5 h.
[b] Calculated with respect to the starting nitrobenzene.
[c] Calculated with respect to converted nitrobenzene. The selectivity in azo- and azoxybenzene was lower than 1% in all cases where no value is reported. Some diphenylurea was always present as a by-product, which could be detected by gas chromatography but not quantified in a precise manner.
[d] Mol ratio bipy/Rh = 3.
[e] MeOH = 1.7 ml.

170°C increases the conversion, but causes the formation of a large amount of azoxybenzene (run 2). On the other hand, the addition of 2-hydroxypyridine allows for an increase in reactivity without any loss in selectivity, although the promoting effect on the conversion is only slightly higher than that of 2,2′-bipyridine under these conditions (see below).

Since we had in the mean time discovered that the use of toluene as solvent and a higher temperature (200°C) were beneficial to the reaction [4], a more extensive comparison of several potential promoters was performed under these last conditions; the results are reported in Table 2. The structures of all but the simplest promoters used are shown in Fig. 1.

Table 3
Effect of the amount of aniline on the [PPN][Rh(CO)$_4$]-catalysed carbonylation of nitrobenzene to methyl phenylcarbamate [a]

Run	Promoter	Prom./Rh mol ratio	$PhNH_2$/Rh mol ratio	$PhNO_2$ conv. (%) [b]	Carbamate select. (%) [c]	Aniline select. (%) [c]	Azobenz. select. (%) [c]	Azoxybenz. select. (%) [c]
1	2,2′-Bipyridine	6		21.4	69.0	12.9		28.3
2	2,2′-Bipyridine	6	60	27.1	68.6	7.9		7.0
3	2-Hydroxy pyridine	12		22.3	69.0	12.9		
4	2-Hydroxy pyridine	12	30	36.8	85.7	6.7	1.3	
5	2-Hydroxy pyridine	12	60	50.7	90.4	1.8	1.1	
6	2-Hydroxy pyridine	12	90	52.8	89.8	0.5		
7	2-Hydroxy pyridine	12	120	47.2	87.8	[d]		
8	2-Hydroxy pyridine	6	30	48.2	86.2	6.0		

[a] Experimental conditions: [PPN][Rh(CO)$_4$] = 0.062 mmol, mol ratio $PhNO_2$/Rh = 600, $T = 200$°C, $P_{CO} = 60$ bar, in toluene (8 ml) + MeOH (3 ml), for 1.5 h.
[b] Calculated with respect to the starting nitrobenzene.
[c] Calculated with respect to converted nitrobenzene. The selectivity in aniline refers to the aniline in excess with respect to the amount added, i.e., the value has been calculated from the equation: selectivity = (mol aniline detected − mol aniline added)/mol nitrobenzene converted. The selectivity in azo- and azoxybenzene was lower than 1% in all of the cases where no value is reported. Some diphenylurea was always present as a by-product, which could be detected by gas chromatography but not quantified in a precise manner.
[d] The amount of aniline present at the end was lower than that initially added due to the formation of substantial amounts of diphenylurea.

As can be seen from the data reported, the use of 2,2′-bipyridine or of a double molar amount of pyridine, methylimidazole or triethylamine afforded very similar results, whereas pyrazole was ineffective (Table 2, runs 1–5). The use of 2-hydroxypyridine, on the other hand, gave a significantly higher conversion and selectivity (run 6), but its isomer 4-hydroxypyridine completely inhibited the reaction (run 9).

Moving the hydroxy group further away from the nitrogen atom had a detrimental effect. The promoting efficiency of 2-hydroxymethylpyridine (run 7) was comparable to that of unsubstituted pyridine, whereas that of 2-(2-hydroxyethyl)pyridine (run 8) was even lower, probably because of the unfavourable position of the two functional groups of this promoter.

Other promoters were tested, having the same, or similar, geometrical features as 2-hydroxypyridine. Of these, the more acidic 4-hydroxyquinazoline (run 10) and 2-hydroxypyrimidine hydrochloride (run 11) completely suppressed the reaction. Addition of an equivalent amount of proton sponge (1,8-*bis*(dimethylamino)naphthalene) to the second promoter, in order to neutralise the hydrochloric acid bound to the free base, did not improve the conversion (run 12).

A very poor conversion was also observed when 2-pyridinethiol was employed as promoter (run 13) and picolinic acid completely inhibited the reaction (run 14).

Of the tested promoters, only the use of 2-hydroxyquinoline (run 15) gave a somewhat higher conversion than 2-hydroxypyridine, but its much higher price did not justify its use. The isomeric 8-hydroxyquinoline was not effective either (run 16).

As the hydroxy group in 2-hydroxypyridine was supposed to enter the reaction at some stage in place of methanol, we reasoned that the difference in promoting activity between 2-hydroxypyridine and 2,2′-bipyridine should have increased upon a decrease in the methanol concentration in the reaction mixture. However, a comparison of the two reactions, performed with these two promoters under the conditions of Table 2, but with the addition of only 1.7 ml of methanol instead of 3 ml (1.54 ml is the amount of methanol required by the stoichiometry of the reaction to convert all of the starting nitrobenzene into methyl phenylcarbamate) shows that the nitrobenzene conversion is only slightly altered in the case of 2,2′-bipyridine (it even increases a little, run 18), but markedly decreases in the case of 2-hydroxypyridine (run 17). The effect is such that, under these particular conditions, the use of 2,2′-bipyridine affords better results than that of 2-hydroxypyridine. Clearly, this observation cannot be rationalised by any bifunctional effect and suggests that, analogously to what is found for 4-hydroxypyridine, even for its 2-isomer some inhibiting effects on the reaction must exist and changes in the experimental conditions may cause these negative effects to prevail over the positive ones.

As mentioned in Section 1, aniline is known to be formed as an intermediate during reaction (1). Thus, the effect of the addition of variable amounts of aniline to the reaction mixture, with both 2,2′-bipyridine and 2-hydroxypyridine as promoters, was examined and the results are reported in Table 3.

In order to avoid reaching complete conversion, the amount of rhodium was halved, but all of the other concentrations were left unchanged. The data reported clearly show that the addition of up to 60 equivalents of aniline per equivalent of rhodium leads to a sharp increase in reaction rate with both 2,2′-bipyridine and with 2-hydroxypyridine as promoters, although this effect levels off for higher amounts of aniline. Even the selectivity in carbamate follows a similar trend, with a small decrease at higher aniline concentrations being due to the formation of larger amounts of diphenylurea, a product that is anyway known to alcoholyse to the carbamate under suitable conditions and can thus be partly recycled into the desired product. Under these conditions, the negative effect of a higher 2,2′-bipyridine/Rh ratio is clearly evident and a large amount of azoxybenzene is formed (run 1, Table 3) even at this high temperature (compare with run 5, Table 2). Even in this case, however, the addition of aniline markedly increases the selectivity in carbamate. Although we have not attempted to fully optimise all the experimental conditions, halving the amount of 2-hydroxypiridine, so as to re-establish the 2-hydroxypyridine/Rh ratio used in Table 2, leads to a higher conversion (compare runs 8 and 4 in Table 3), but the selectivity is only slightly altered.

3. Discussion

The investigation of the reaction between **1a** and methanol under a dinitrogen atmosphere led to the unexpected observation that no reaction occurs if neither CO nor pyridine is present. Interaction of CO with any part of **1a** except for the metal is impossible. Thus the only possible explanation for the observed effect is that the tetracoordinated **1a** is unreactive towards methanol, but is in equilibrium with a very small and unobservable amount of a pentacoordinated complex that instead displays a high reactivity. Tetracoordinated cationic rhodium(I) dicarbonyl complexes are known to be in equilibrium with their pentacoordinated tricarbonyl analogues under CO and the equilibrium can even be almost completely shifted towards the tricarbonyl complex [12]. However, to the best of our knowledge, this is the first time that the onset of an analogous equilibrium has been reported for an anionic complex. The fact that the equilibrium is clearly almost completely shifted to the dicarbonyl complex side is probably responsible for the lack of earlier reports on similar

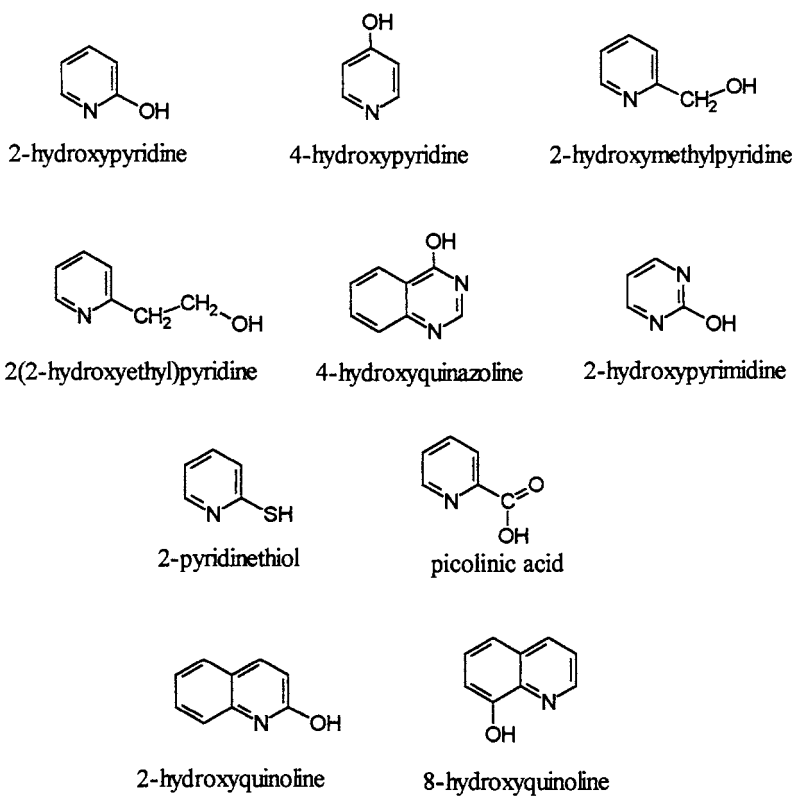
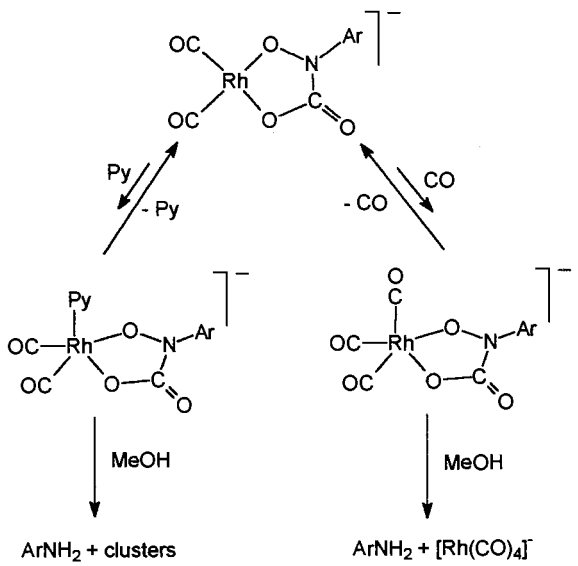
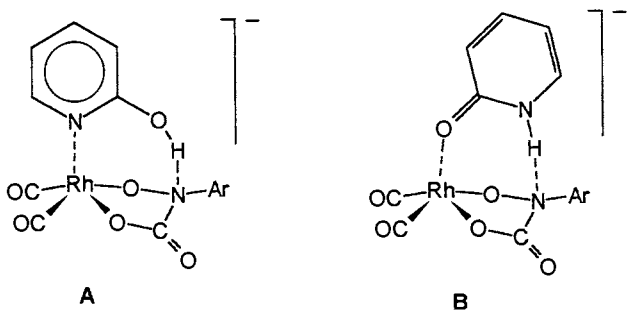


Fig. 1. Structures of the promoters used.



Scheme 3.



Scheme 4.

equilibria. With this knowledge in mind, the most reasonable explanation for the effect of pyridine, at least in the present reaction, is that this base can also coordinate to the fifth position of the rhodium complex in place of CO (Scheme 3).

Interestingly, 2-hydroxypyridine reacts with **1a** even in the absence of both CO and methanol. Clearly, the bifunctional nature of this reagent is essential in this case. Based on what was previously said about the interaction of methanol and pyridine with **1a**, an interaction of the kind shown in Scheme 4 can be proposed, where the possibility that the molecule is reacting in its pyridonic form has also been considered.

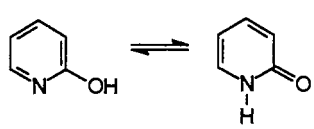
Iridium complexes in which the nitrogen atom of a 2-hydroxypyridine is bound to the metal and the hydroxylic hydrogen is interacting with another ligand have been isolated [13]. Independent of the separate use of CO/Py and methanol or of 2-hydroxypyridine, it appears that **1a** needs simultaneous activation by a coordinating group and an acid.

It should be noted that the proton in the 2-hydroxypyridine molecule has been shown as interacting with the nitrogen atom of the metallacycle, but this is not certain at this stage. To gain more information on this point, several experiments were performed by using some electrophiles other than protons, which could give an irreversible interaction with the most nucleophilic atom of **1a** and allow the atom responsible for the interaction with the hydroxylic group of 2-hydroxypyridine and methanol to be identified. We recall that previously reported experiments have excluded the two 'CO_2' oxygen atoms as the reactive sites [6].

Reaction with *p*-toluolyl chloride afforded the N-acylated product (Eq. (2)). Although it may be argued that the observed amide may derive from the intermediate formation of aniline as an intermediate, which would then be trapped by excess toluolyl chloride, the aprotic conditions employed suggest that the nitrogen atom was acylated as the first stage of the reaction. However, the source of the nitrogen-bound hydrogen atom remains uncertain, although a trace amount of *p*-methylbenzoic acid present even in the freshly distilled acyl chloride is the most likely candidate. The analogous reaction with acetic anhydride afforded both the N-acylated and the N,O-diacylated products, but again no O-monoacylated product was observed. Although we could not isolate the acylated complexes formed as intermediates, the identity of the isolated organic products represents a good indication, although not definitive evidence, that the nitrogen atom of the metallacycle is the most reactive site towards electrophiles.

The data reported in Tables 1 and 2 clearly show that 2-hydroxypiridine also accelerates the catalytic carbonylation reaction, but this does not a priori mean that this is due to the acceleration of the decomposition of **1**.

2-Hydroxypyridine is known to be in tautomeric equilibrium with its pyridonic form (Eq. (5)) and the position of the equilibrium depends on the solvent [14]. The equilibrium is known to favour the pyridonic form in polar solvent and at ambient temperature, but, to the best of our knowledge, no experimental study on the position of equilibrium (5) has been performed at high temperatures and in solution, so that the relative amounts of the two tautomers under the actual catalytic conditions are not known.



(5)

Moreover, 2-hydroxypyridine is more acidic than methanol [15]. Given this knowledge, one may wonder if either the existence of a tautomeric equilibrium or the acidity of 2-hydroxypyridine (or both) is responsible for the observed effect. To study this question, the promoting effect of 4-hydroxypyridine, which has a similar acidity and for which the same tautomeric equilibrium

exists as for 2-OH isomer [15,16], was tested. However, 4-hydroxypyridine completely inhibited the reaction (run 9, Table 2). The onset of a tautomeric equilibrium by itself is unlikely to justify such a strong inhibiting effect and the origin of the deactivation must lie in the acidity of the phenolic group. This result implies that the acidity even of the 2-OH isomer must severely deactivate the catalytic system and that another positive effect that overwhelms the first must be present in this case. This effect can only be ascribed to the proximal position of the basic and acidic sites and can be attributed to some form of bifunctional activation. The negative effect of an acidic proton is also indicated by a comparison between the results obtained by using 2-hydroxypyridine and the ones obtained with the more acidic 2-thiopyridine, 2-hydroxyquinazoline and hydroxypyrimidine. The same conclusion is supported by the fact that picolinic acid completely inhibited the reaction, despite its geometry being very close to that of 2-hydroxymethylpyridine, which promotes the reaction to approximately the same extent as pyridine. Why acids inhibit the reaction is not obvious. It should be noted that acids have been found to promote, rather than inhibit, the activity of the related palladium–phenanthroline catalytic system [17], despite the fact that the mechanism of the two catalytic cycles presents many similarities [18]. One possibility is that acids promote the aggregation of anionic mononuclear species into catalytically inactive polynuclear ones by rendering them neutral. We have previously shown that the size of the countercations of $[Rh(CO)_4]^-$ and $[Ir(CO)_4]^-$ has a dramatic effect in determining the nuclearity of the products in reactions with organic halides [19].

At this point, the problem of the identity of the bifunctional effect responsible for the acceleration of the catalytic reactions must be addressed. Although the use of bifunctional promoters was originally suggested by the results of the stoichiometric decomposition reactions of **1**, the data collected in order to determine the role of this reaction in the catalytic cycle indicates that the acceleration of the stoichiometric reaction is not relevant to that of the catalytic reactions. Indeed, if the role of 2-hydroxypyridine is to replace both CO and methanol, a decrease in the concentration of this latter reagent should maximise its effect, which is not the case. Moreover, if the decomposition of **1a** were rate determining in the catalytic cycle, the reaction rate should not be influenced by the addition of aniline, which is again contrary to what is observed. This does not mean that the interaction between **1** and 2-hydroxypyridine does not occur under catalytic conditions, but only that the decomposition of **1** is not rate determining and its possible acceleration is not influential. Thus it appears that there must be at least two bifunctional effects of 2-hydroxypyridine. The data reported in Table 3 indicate that the rate-determining step of the cycle involves aniline and is likely to be its attack on a carbomethoxy complex. There are several ways in which this step may be accelerated by 2-hydroxypiridine. Pyridine and substituted pyridines are known to promote several carbonylation reactions. In the case of the carbonylation of ethylene to methyl acetate, catalysed by cobalt carbonyls, evidence has been reported that the effect is due to the nucleophilic attack of pyridine on the carboethoxy group of $(CO)_4CoC(O)OEt$, generating a reactive $[PyC(O)OEt]^+$ intermediate [20]. Alternatively, the bifunctional nature of 2-hydroxypyridine may allow for an assisted proton transfer between the incoming aniline molecule and a carbomethoxy group. Unfortunately, the failure to isolate any rhodium carbomethoxy complex in our reactions prevented us from testing the validity of these hypotheses and the detailed nature of this second effect remains uncertain, although an increase in the rate of the catalytic reactions is evident.

4. Conclusions

We have investigated the effect of several bifunctional reagents on the $[Rh(CO)_4]^-$-catalysed carbonylation of nitrobenzene and some related stoichiometric reactions. The results clearly indicate that some effects are present that can only be ascribed to the bifunctional nature of the reagents employed, but it has not been possible to identify unequivocally the catalytically relevant effect. The addition of 2-hydroxypyridine or 2-hydroxyquinoline to the catalytic system remarkably increases the rates and selectivity under the suitable conditions, but the acidity of these molecules also has negative effects and these predominate under some circumstances. On the other hand, since the first discovery of the acceleration effects described here, we have also tested the use of 2-hydroxypyridine as a promoter in the related reduction reaction of 2-nitrostyrenes by CO to afford arylindoles, again catalysed by $[PPN][Rh(CO)_4]$. In this last case, a positive effect on both rate and selectivity was observed under all the conditions employed [21]. Even in this case, 4-hydroxypyridine had an inhibiting effect on the reaction.

Although a final clarification of the origin of the effects observed must await for an in situ study under catalytic conditions, it is interesting to note that 2-hydroxypyridine has also been found to promote the rhodium-catalysed hydrogenation of CO to ethyleneglycol and ethanol [22]. For these last reactions, it was proposed that the promoting effect derived from the ability of this reagent to supply an anion with a delocalised charge. However, the results reported here, indicate that 2-hydroxypyridine has some more specific properties that may be responsible for the acceleration of even these other reactions.

5. Experimental

5.1. General procedure

All reactions were conducted under a dinitrogen or CO atmosphere using either standard Schlenk apparatus or an autoclave (see below). Solvents were dried by standard procedures. [PPN][$Rh(CO)_4$] was synthesised by the method reported in the literature [23]. This complex is air sensitive even in the solid state and has to be weighed under an inert atmosphere. 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. All other reagents were commercial products and were used as received. Gas chromatographic analyses were performed on a Perkin–Elmer 8420 gas chromatograph (PS 255 capillary column) for quantitative analysis, or on a Hewlett–Packard 5890 gas chromatograph equipped with a 5971 A mass-selective detector for confirmation of product identities. HPLC analyses were performed on a Hewlett–Packard 1050 instrument equipped with a Purospher® RP-18 e (5 μm) column. NMR spectra were recorded on a Bruker AC 200 FT (200 MHz) or on a Bruker AC 300 FT (300 MHz) spectrometer at room temperature (r.t.). IR spectra were recorded on a FTS-7 Bio Rad FT-IR spectrometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

5.2. Synthesis of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (**1a**)

3,4-$Cl_2C_6H_3NO_2$ (350 mg, 1.82 mmol) was added at −78°C to a solution of [PPN][$Rh(CO)_4$] (905 mg, 1.26 mmol) in THF (15 ml) under a CO atmosphere. The resulting yellow suspension was stirred for 30 min during which time the temperature of the reaction was allowed to increase to r.t. Then the reaction mixture was analysed by IR spectroscopy and the spectrum showed that [PPN][$Rh(CO)_4$] had been completely consumed and, in the carbonyl region, only the absorptions attributed to **1a** (2050(s), 1973(s), 1638(m) cm^{-1}) were present. The flask was evacuated and filled with dinitrogen, *n*-hexane (20 ml) was added to the yellow mixture to yield a yellow microcrystalline solid that was collected by filtration, washed with *n*-hexane (5 ml) and dried in vacuo (86%). Contrary to the previously reported procedure [6], the formation of a black solid was not observed. The elemental analysis and spectroscopic data are in agreement with those previously reported by us [6].

5.3. Reaction of **1a** with methanol and pyridine

A total of 0.12 ml of CH_3OH and 0.050 ml of pyridine were added at r.t. to a THF (15 ml) solution of complex **1a** (142 mg, 0.144 mmol) under a dinitrogen atmosphere. The resulting brown solution was stirred at r.t. for 1 h and 30 min and at 50°C for 1 h. During this time the reaction mixture was analysed by IR spectroscopy. The absorptions attributed to **1a** (2050(s), 1973(s), 1638(m) cm^{-1}) disappeared and four new absorptions (2048(s), 2028(s), 2018(s), 1969(s) cm^{-1}) were observed in the carbonyl region of the spectrum. The solvent was evaporated to dryness in vacuo and *n*-hexane (20 ml) was added to the black residue. The resulting black solid was collected, washed with more *n*-hexane and dried in vacuo (70 mg). Consistent elemental analyses could not be obtained for this material. The formation of 3,4-$Cl_2C_6H_3NH_2$ was evidenced by gas-chromatographic analysis.

5.4. Reaction of **1a** with 2-hydroxypyridine

2-Hydroxypyridine (26 mg, 0.27 mmol) was added to a CH_2Cl_2 (15 ml) solution of **1a** (248 mg, 0.25 mmol) at r.t. under a dinitrogen atmosphere. The resulting brown solution was stirred at r.t. for 1 h. During this time the reaction mixture was analysed by IR spectroscopy. The absorptions attributed to **1a** (2059(s), 1982(s), 1628(m) cm^{-1}) disappeared and two new absorptions (2057(s), 1984(s) cm^{-1}) were observed in the carbonyl region of the spectrum. The solvent was evaporated to dryness and Et_2O (20 ml) was added to the brown residue. The resulting brown solid was collected, washed with more *n*-hexane and dried in vacuo (160 mg). Consistent elemental analyses could not be obtained for this material. The formation of 3,4-$Cl_2C_6H_3NH_2$ was evidenced by gas-chromatographic analysis.

5.5. Reaction of **1a** with p-toluolyl chloride

p-Toluolyl chloride (0.021 ml, 0.16 mmol) was added to a THF (10 ml) solution of **1a** (158 mg, 0.160 mmol) at r.t. under a dinitrogen atmosphere. The resulting brown solution was stirred at r.t. for 1 h. During this time the reaction mixture was analysed by IR spectroscopy. The absorptions attributed to **1a** (2059(s), 1982(s), 1628(m) cm^{-1}) disappeared and two new absorptions (2054(s), 1974(s) cm^{-1}) were observed in the carbonyl region of the spectrum. The reaction mixture was concentrated to one third of its original volume in vacuo and Et_2O (20 ml) was added to precipitate a brown solid. The mother liquor was analysed by GC–MS spectroscopy to identify 4-$CH_3C_6H_4C(O)NH$(3,4-$Cl_2C_6H_3$), whereas the brown precipitated solid was collected, solubilised in THF and identified by IR spectroscopy as [PPN][$Rh(CO)_2Cl_2$] [24].

5.6. Reaction of **1a** with acetic anhydride

Acetic anhydride (17 μl, 0.18 mmol) was added to a THF (10 ml) solution of **1a** (151 mg, 0.153 mmol) at

−78°C under a dinitrogen atmosphere. The resulting brown solution was stirred for 30 min during which time the temperature of the reaction was allowed to increase to r.t. During this time the reaction mixture was analysed by IR spectroscopy. The absorptions attributed to **1a** (2059(s), 1982(s), 1628(m) cm^{-1}) disappeared and new absorptions (2054(s), 1972(s), 1621(m) cm^{-1}) were observed in the carbonyl region of the spectrum. The resulting brown solution was stirred at r.t. for 1 h. The reaction mixture was evaporated to dryness and Et_2O (20 ml) was added to the residue. The resulting yellow powder was collected and recrystallization from THF–*n*-hexane gave crystals suitable for X-ray analysis, showing it to be $[Rh(CO)_2(CH_3COO)_2][PPN]$. The mother liquor was evaporated to dryness and the organic products were separated by flash chromatography (4:1 ethyl acetate–*n*-hexane) to obtain $Cl_2C_6H_3NHC(O)Me$ (A) and $Cl_2C_6H_3N(C(O)Me)OC(O)CH_3$ (B) in 37 and 30% yield, respectively. ^{1}H-NMR ($CDCl_3$, 200 MHz, 298 K) δ, ppm: (A) 7.74 (s, 1H); 7.34 (s, 1H, NH); 7.33 (m, 2H); 2.18 (s, 3H). (B) 7.59 (s, 1H); 7.48 (d, 1H, $J = 8.6$ Hz); 7.34 (d, 1H, $J = 8.6$ Hz); 2.17 (s, 3H); 2.12 (s, 3H).

5.7. Reaction of **1a** with aniline

Aniline (74 μl, 0.82 mmol) was added to a THF (10 ml) solution of **1a** (203 mg, 0.226 mmol) at r.t. under a CO atmosphere. The resulting brown solution was stirred for 4 h, during which time the reaction mixture was analysed by IR spectroscopy. The absorptions attributed to **1a** (2059(s), 1982(s), 1628(m) cm^{-1}) disappeared and an absorption (1896(s) cm^{-1}) due to $[Rh(CO)_4]^-$ was observed in the carbonyl region of the spectrum. PhNHC(O)NHPh and 3,4-$Cl_2C_6H_3NHC(O)NHPh$ were also present in the reaction mixture in a 41:9 ratio (HPLC analysis).

5.8. Catalytic reactions

In a typical reaction, nitrobenzene and, if required, aniline and the organic promoter (see the Tables for amounts) were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth, frozen at dry ice temperature, evacuated and filled with dinitrogen, after which $[PPN][Rh(CO)_4]$ (separately weighed under dinitrogen) and the solvents were added. After the solvent was also frozen, the liner was closed with a screw cap having a glass-wool-filled open mouth that allows for exchange of gaseous reagents and rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at r.t. at the required pressure and the autoclave was immersed in an oil bath preheated to the required temperature. 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 internal standard).

References

[1] M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857.
[2] M. Shibasaki, H. Sasai, T. Arai, Angew. Chem. Int. Ed. Engl. 36 (1997) 1236.
[3] E.K. van der Beuken, B.L. Feringa, Tetrahedron 54 (1998) 12985.
[4] F. Ragaini, S. Cenini, A. Fumagalli, C. Crotti, J. Organomet. Chem. 428 (1992) 401.
[5] S. Cenini, F. Ragaini, Catalytic Reductive Carbonylation of Organic Nitro Compounds, Kluwer, Dordrecht, 1997.
[6] F. Ragaini, S. Cenini, F. Demartin, Organometallics 13 (1994) 1178.
[7] J.D. Gargulak, W.L. Gladfelter, J. Am. Chem. Soc. 116 (1994) 3792.
[8] F. Demartin, personal communication.
[9] A. Fulford, N.A. Bailey, H. Adams, P.M. Maitlis, J. Organomet. Chem. 417 (1991) 139.
[10] F. Ragaini, M. Macchi, S. Cenini, J. Mol. Catal. A. 127 (1997) 33.
[11] F. Ragaini, A. Ghitti, S. Cenini, Organometallics in press.
[12] G. Mestroni, A. Camus, G. Zassinovich, J. Organomet. Chem. 65 (1974) 119.
[13] E. Peris, J.C. Lee Jr., J.R. Rambo, O. Eisenstein, R.H. Crabtree, J. Am. Chem. Soc. 117 (1995) 3485.
[14] J.M. Rawson, R.E.P. Winpenny, Coord. Chem. Rev. 139 (1995) 313.
[15] A. Albert, J.N. Phillips, J. Chem. Soc. (1956) 1294.
[16] J. Frank, A. Katritzky, J. Chem. Soc. Perkin Trans. 2 (1976) 1428.
[17] (a) P. Wehman, L. Borst, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Mol. Catal. A 112 (1996) 23. (b) P. Wehman, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (Cambridge) (1996) 217.
[18] (a) F. Ragaini, S. Cenini, 11th Int. Symp. Homogeneous Catalysis, St. Andrews, UK, 1998. (b) E. Gallo, F. Ragaini, S. Cenini, F. Demartin, J. Organomet. Chem. 586 (1999) 190.
[19] (a) F. Ragaini, F. Porta, A. Fumagalli, F. Demartin, Organometallics 10 (1991) 3785. (b) F. Ragaini, F. Porta, F. Demartin, Organometallics 10 (1991) 185. (c) F. Porta, F. Ragaini, S. Cenini, M. Pizzotti, F. Demartin, Organometallics 9 (1990) 929.
[20] N.S. Imyanitov, N.M. Bogoradovskaya, T.A. Semenova, Kinet. Katal. 19 (1978) 573 [Engl. transl. in Kinet. Catal. 19 (1978) 452].
[21] F. Ragaini, S. Tollari, S. Cenini, E. Bettetini, J. Mol. Catal. A 111 (1996) 91.
[22] B.D. Dombek, Adv. Catal. 32 (1983) 325.
[23] L. Garlaschelli, R. Della Pergola, S. Martinengo, Inorg. Synth. 28 (1990) 211.
[24] L.M. Vallarino, Inorg Chem. 4 (1965) 161.