

Journal of Organometallic Chemistry, 428 (1992) 401–408
 Elsevier Sequoia S.A., Lausanne
 JOM 22603

$[\text{Rh}(\text{CO})_4]^-$, $[\text{Rh}_5(\text{CO})_{15}]^-$, and bimetallic clusters as catalysts for the carbonylation of nitrobenzene to methyl phenylcarbamate *

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(Received October 7, 1991)

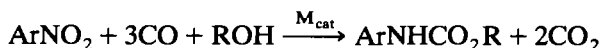
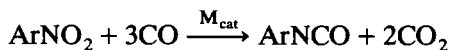
Abstract

Bimetallic clusters of the general formula $[\text{PPN}]_2[\text{MRh}_4(\text{CO})_{15}]$ ($M = \text{Fe}$, Ru , or Os ; $\text{PPN}^+ = (\text{PPh}_3)_2\text{N}^+$) are active catalysts in the presence of methanol for the carbonylation of nitrobenzene to methyl phenylcarbamate. The clusters are active even without co-catalyst, but the addition of bipy (2,2'-bipyridine) greatly enhances both rates and selectivities. In the absence of methanol the conversion was much lower, with a low selectivity in phenyl isocyanate.

Interchanging Fe , Ru , and Os has a negligible effect on the activity and a moderate effect on the selectivity, with ruthenium being best. However, the monometallic rhodium cluster $[\text{Rh}_5(\text{CO})_{15}]^-$ proved to be both more active and selective, and the monomer $[\text{Rh}(\text{CO})_4]^-$ was found to be even better. This last catalytic system has been optimized with respect to temperature, CO pressure and the bipy/ Rh ratio. The influence of solvent was also examined.

Introduction

The catalytic carbonylation of organic nitro-compounds is of paramount importance, since a series of industrially significant derivatives can be obtained by this reaction in a single step [1]. Among these, isocyanates ArNCO and carbamates ArNHCO_2R deserve particular attention, as these derivatives are final products and/or intermediates in the synthesis of pesticides and polyurethanes. Catalysis by transition metals is an interesting synthetic method.

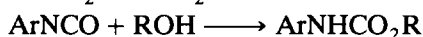
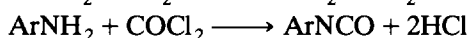
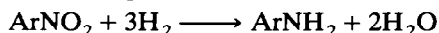


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* Dedicated to Professor Wolfgang Beck on the occasion of his 60th birthday.

Part of this work was presented at the OMCOS 6, Utrecht, 1991.

This avoids the use of the poisonous and corrosive phosgene, employed in the industrial process.



In previous works we have reported on the synthesis of carbamates and isocyanates *via* the catalytic route, using ruthenium [2,3], rhodium [3,4], or palladium [4], either as supported metals or as soluble complexes.

Despite growing interest in bimetallic catalysis, few examples have been reported in which a clearly defined bimetallic complex has been used as the catalyst. In the carbonylation of nitrobenzene, only heterogeneous catalysts derived from the decomposition of Fe–Pd or Mo–Pd clusters have been described [5,6]. However, the activity in this reaction of the original clusters has not been studied, and furthermore metal segregation was observed to occur during the catalytic reaction at least for the Fe–Pd derived catalyst [7].

Since rhodium is a very active catalyst for the carbonylation of nitrobenzene to methyl phenylcarbamate, we decided to investigate the activity of a series of related clusters $[\text{PPN}]_2[\text{MRh}_4(\text{CO})_{15}]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{or Os}$; $\text{PPN}^+ = \text{Ph}_3\text{P}=\text{N}=\text{PPh}_3^+$) and to compare them with the monometallic cluster $[\text{PPN}][\text{Rh}_5(\text{CO})_{15}]$ and with the mononuclear $[\text{PPN}][\text{Rh}(\text{CO})_4]$. Pentanuclear anionic clusters were chosen because they are known to be stable, at least under moderate CO pressures.

Results

Metal clusters of composition $[\text{MRh}_4(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{or Os}$) were found to be active and selective catalysts for the carbonylation of nitrobenzene in the presence of methanol yielding methyl phenylcarbamate (Table 1).

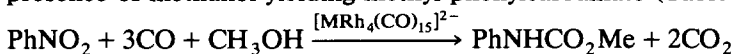


Table 1

Catalysis by mixed-metal clusters ^a

Catalyst	PhNO ₂ / catalyst ^b	bipy / catalyst ^b	MeOH (ml)	Conversion (%)	Selectivity (%) ^c		
					Carbamate	Aniline	Azoxybenzene
$[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$	400	0	1.4	66.3	82.7	12.7	0
$[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$	400	0 ^d	1.4	73.1	91.1	7.2	0
$[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$	400	8	1.4	98.5	87.9	7.5	0
$[\text{PPN}]_2[\text{OsRh}_4(\text{CO})_{15}]$	400	8	1.4	100	89.0	9.0	0
$[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$	400	8	0	20.6	– ^f	16.0	0
$[\text{PPN}]_2[\text{FeRh}_4(\text{CO})_{15}]$	1500	8	3	44.2	42.2	17.3	19.1
$[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$	1500	8	3	45.5	56.6	13.8	13.5
$[\text{PPN}]_2[\text{OsRh}_4(\text{CO})_{15}]$	1500	8	3	45.8	49.1	13.6	18.3
$[\text{PPN}][\text{Rh}_5(\text{CO})_{15}]$	1500	8	3	51.1	58.9	13.0	13.1
$[\text{PPN}][\text{Rh}(\text{CO})_4]$ ^e	300	8/5	3	56.2	61.1	11.9	18.7

^a Cluster = 0.025 mmol, THF = 8 ml, 60 atm, 170°C, 1.5 h. ^b Molar ratio. ^c Calculated with respect to consumed PhNO₂. ^d $[\text{Et}_4\text{N}]\text{Cl}$ (8/1 molar ratio with respect to the cluster) was used as co-catalyst. ^e $[\text{PPN}][\text{Rh}(\text{CO})_4] = 0.125$ mmol. ^f Phenyl isocyanate (27.5% selectivity) was detected.

The clusters are active even without co-catalyst, but bipy (2,2'-bipyridine) was found to greatly enhance the catalytic activity. On the other hand, $[\text{Et}_4\text{N}]\text{Cl}$ had only a moderate effect. The ammonium salt co-catalyst was essential for the catalytic carbonylations carried out with $[\text{Ru}_3(\text{CO})_{12}]$ as catalyst [2]. Working under the conditions given in Table 1 and with a molar ratio $\text{PhNO}_2/\text{cluster}$ of 400, selectivities of *ca.* 90% are achieved under non-optimized conditions. At this catalytic ratio, the only observable byproduct is aniline. Methanol does not simply trap the intermediate isocyanate, as, when it is absent, the conversion drops markedly and only a low selectivity in isocyanate is observed.

In order to better differentiate the activity of the various clusters, we have run some experiments with a high $\text{PhNO}_2/\text{cluster}$ molar ratio (1500/1). Under these conditions we were surprised to find relatively high quantities of azoxybenzene,

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 \uparrow
 $\text{PhN}=\text{NPh}$,

although azobenzene, $\text{PhN}=\text{NPh}$, was never present in more than trace amounts (except in the experiment in the absence of methanol). Azo- and azoxybenzene are only observed occasionally in these catalytic carbonylation reactions [1]. Changing the metal in the iron triad had only a negligible effect on the activity and a moderate effect on the selectivity, ruthenium giving the best. However, the monometallic cluster $[\text{PPN}][\text{Rh}_5(\text{CO})_{15}]$ proved to be both more active and selective, and the mononuclear $[\text{PPN}][\text{Rh}(\text{CO})_4]$ was found to be even better. We have thus started studying the catalytic activity of this last complex, and the results are reported in Table 2.

The products are the same as in the cluster-catalyzed reactions. Even with $[\text{PPN}][\text{Rh}(\text{CO})_4]$, never more than 1% azobenzene was observed. The quantity of azoxybenzene is linked to the amount of bipy present, increasing when the bipy/Rh ratio is changed from 0 to 8 (runs 1–5). 1,10-Phenanthroline is a less efficient co-catalyst, affording a much lower conversion and selectivity in carbamate (runs 2 and 6). With terpy (2,2',6',2''-terpyridine), in place of bipy, somewhat higher conversions could be achieved but with a slightly lower selectivity (runs 15 and 16). These small differences do not seem to justify the use of terpy for large-scale application in this catalytic system, as it is much more expensive than bipy.

Conversions and selectivities in carbamate increase with the temperature up to 200°C, while at 220°C a decrease of both is observed (runs 3 and 7–9). Toluene was found to be the best solvent (runs 3, 10 and 11) despite the fact that $[\text{PPN}][\text{Rh}(\text{CO})_4]$ is almost insoluble in it at room temperature. However, the reaction mixtures were completely homogeneous at the end of the reactions. The ideal CO pressure is 60 atm, higher and lower pressures resulting in lower conversions and selectivities (runs 11–13). A decrease in activity at high CO pressures is very common in this type of carbonylation reaction and is indicative of the need for a vacant coordination site on the metal at some stage of the reaction. The corresponding decrease in selectivity in carbonylated product is, however, unusual.

In a previous paper [4], we reported the use of the system $[\text{Rh}_4(\text{CO})_{12}]$ -bipy for the catalytic carbonylation of nitrobenzene to methyl phenylcarbamate. In comparison with the present system (run 17) under the same experimental conditions, $[\text{PPN}][\text{Rh}(\text{CO})_4]$ gives higher conversions and selectivities, although optimization of the $[\text{Rh}_4(\text{CO})_{12}]$ system under the same conditions should be carried out.

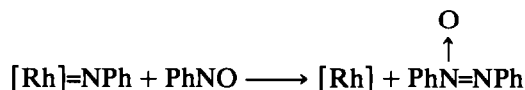
Table 2

Catalysis by [PPN][Rh(CO)₄]^a

Run	T (°C)	bipy/ Rh ^b	Solvent	Conversion (%)	Selectivity (%) ^c		
					Carbamate	Aniline	Azoxybenzene
1	170	0	THF	16.3	60.3	16.1	0
2	170	8/5	THF	56.2	61.1	11.9	18.7
3	170	3	THF	61.4	52.2	14.9	18.1
4	170	5	THF	56.4	46.7	16.4	24.3
5	170	8	THF	46.6	38.6	20.4	30.5
6	170	8/5 ^d	THF	25.2	24.0	25.3	26.7
7	180	3	THF	67.9	59.4	12.1	14.8
8	200	3	THF	76.9	76.1	6.9	3.6
9	220	3	THF	73.3	71.1	16.1	3.9
10	200	3	C ₆ H ₄ Cl ₂	69.9	85.9	11.9	1.0
11	200	3	Toluene	82.3	84.4	9.3	1.0
12 ^e	200	3	Toluene	68.4	68.1	12.3	0.8
13 ^f	200	3	Toluene	69.7	72.8	11.8	4.5
14 ^g	200	3	Toluene	100	88.0	14.6	0
15	200	2 ^h	Toluene	83.7	81.8	13.7	2.2
16	200	3 ^h	Toluene	88.3	79.1	15.1	2.6
17 ⁱ	200	3	THF	67.1	71.2	12.8	6.9

^a [PPN][Rh(CO)₄] = 0.125 mmol, molar ratio PhNO₂/Rh = 300, P_{CO} = 60 atm, MeOH = 3 ml, solvent = 8 ml, t = 1.5 h. ^b Molar ratio. ^c Calculated with respect to converted PhNO₂. Less than 1% azobenzene was also always detected except for runs 1 and 14. ^d 1,10-Phenanthroline was used instead of bipy. ^e P_{CO} = 40 atm. ^f P_{CO} = 80 atm. ^g PhNO₂/Rh = 80. ^h Terpy was used instead of bipy. ⁱ [Rh₄(CO)₁₂] (3.13 × 10⁻² mmol) was used in place of [PPN][Rh(CO)₄].

Azoxybenzene is not usually obtained in the catalytic carbonylation of nitrobenzene, but it has been reported that by reduction of nitrosobenzene at 75°C under CO, using [Ru(CO)₃(PPh₃)₂] [8] and [RhCl(1,5-C₈H₁₂)(PhNO)] [9,10] as catalysts, good yields of azoxybenzene could be obtained. The authors [9,10] suggest that this product arises from the trapping of a metal nitrene complex by free nitrosobenzene:



At higher temperatures and pressures, carbamate is also obtained, probably by trapping by CO of the same intermediate complex. Nitrosobenzene is always supposed to be an intermediate in the reductive carbonylation of nitrobenzene. However it cannot be usually observed (nor in the present case) because of its high reactivity, which prevents its accumulation in the reaction mixtures under the conditions under which nitrobenzene itself reacts. The fact that azoxybenzene is obtained only when a high concentration of nitrobenzene is present seems to support the conclusion that even in this case azoxybenzene derives from the reaction of a nitrene complex with nitrosobenzene (see below for discussion of the mechanism).

We tried to shift the reaction towards azoxybenzene, but without success (Table 3). Indeed, lowering the temperature to 150°C and/or the pressure to 20 atm, resulted only in a much slower reaction and a lower selectivity in carbamate (runs

Table 3^a
 Attempted improvement in the synthesis of azoxybenzene

Run	<i>T</i> (°C)	<i>t</i> (h)	Solvent	MeOH (ml)	Conversion (%)	Selectivity (%) ^b		
						Carbamate	Aniline	Azoxybenzene
1 ^c	160	1.5	THF	3	36.6	44.6	30.7	9.6
2	150	1.5	THF	3	23.6	28.1	26.2	27.1
3	170	5	THF	3	86.5	13.5	59.7	15.3
4	170	5	THF	1	74.0	50.8	4.0	26.0
5	170	5	THF	1 ^d	36.3	40.5	10.0	12.5
6	170	5	Toluene	1	74.0	63.9	5.1	20.1
7	170	5	Toluene	0 ^e	11.4	– ^f	traces	traces
8	170	5	Toluene	0	3.4	– ^g	traces	traces

^a Experimental conditions as in Table 2 except bipy/Rh = 8. ^b With respect to converted nitrobenzene. Less than 1% azobenzene was also always detected. ^c $P_{\text{CO}} = 20$ atm. ^d 2-Propanol was used in place of methanol. ^e 2,4,6-Trimethylbenzoic acid (1.875 mmol) was also added. ^f Phenyl isocyanate was detected in a trace amount. ^g No phenyl isocyanate was detected.

1 and 2). The amount of aniline in the products increased markedly, but the selectivity towards azoxybenzene remained approximately constant.

Lowering the amount of methanol to 1 cm³ also resulted in a lower conversion, although in this case a somewhat higher selectivity towards azoxybenzene was obtained (run 4). The amount of azoxybenzene is in any case lower when longer reaction times are used in order to afford higher conversions. Neither did a more hindered alcohol (2-propanol) increase the yield (run 5). In the complete absence of alcohol, the reaction is virtually completely suppressed (run 8). As with the reactions reported in Table 2, in none of these reactions was more than 1% azobenzene detected. It is clear that this catalytic system, as do most of the systems for the carbonylation of nitrobenzene, requires a proton source to afford high conversions, even if the proton is not present in the final product. When studying the catalytic system Pd–phenanthroline for the carbonylation of nitrobenzene to phenylisocyanate [4] we discovered that a hindered acid (2,4,6-trimethylbenzoic acid, TMBA) could be used as a proton source in place of methanol, without remaining incorporated into the final product. In the present case use of TMBA resulted only in a small increase of the conversion (run 7) and only traces of products were observed.

Unfortunately, the 1800–2200 cm⁻¹ region of the IR spectrum of the solutions at the end of the reactions contains strong bands due to the organic products. Thus no information regarding the metal-containing species could be obtained.

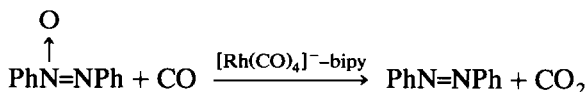
We have also undertaken a mechanistic study of these reactions [11], though some preliminary results can now be reported.

By reaction of [PPN][Rh(CO)₄] with an excess of bipy (10/1 molar ratio) in refluxing dichlorobenzene under dinitrogen, a new complex is rapidly formed (in 5 min) with two $\nu(\text{CO})$ stretching bands at 2061(m) and 1982(s) cm⁻¹. By further heating the solution, the intensity of these bands decreases. We tentatively assign these absorptions to [PPN][Rh(CO)₂(bipy)], which then yields [PPN][Rh(bipy)₂] by further reaction with bipy.

Both [PPN][Rh(CO)₄] and [PPN][Rh(CO)₂(bipy)] react smoothly with nitrobenzene (20/1 molar ratio) in dichlorobenzene at 40°C under dinitrogen. The product

of the reaction with $[\text{PPN}][\text{Rh}(\text{CO})_4]$ is a complex with two $\nu(\text{CO})$ stretching bands, at 2053(m) and 1973(s) cm^{-1} . On the other hand, after reaction of the bipy-containing complex with PhNO_2 , only a weak $\nu(\text{CO})$ band at 1973 cm^{-1} was observed in solution. This band is too weak to account for all of the reaction product, so other compounds, not containing CO, are probably formed at the same time. Attempts to isolate and characterize these products are in progress.

Before discussing the mechanism of these reactions three further points must be considered. (i) When azoxybenzene was used as a starting material (molar ratio azoxybenzene/Rh = 150, experimental conditions as run 1 in Table 3) an almost complete conversion was obtained (99.6%):



The main product was azobenzene (75.2%) with small amounts of carbamate (2.7%) and aniline (11.5%). (ii) Under the same experimental conditions, azobenzene proved to be much less reactive. Only 12.3% conversion was achieved with carbamate (15.6%) and aniline (29.2%) as the only detectable products. (iii) Azobenzene and nitrobenzene do not react with each other to any detectable extent under the usual experimental conditions, either in the presence or in the absence of the $[\text{PPN}][\text{Rh}(\text{CO})_4]$ -bipy system.

Discussion and conclusions

Considering all these results, we now propose a tentative mechanism for the catalytic cycle.

The first step must be the interaction of nitrobenzene with $[\text{Rh}(\text{CO})_4]^-$ (or with a complex such as $[\text{Rh}(\text{bipy})(\text{CO})_2]^-$ or $[\text{Rh}(\text{bipy})_2]^-$). The products of this step are probably nitrosobenzene and CO_2 , while the catalyst is reformed. Nitrosobenzene is known to react with metal complexes much more readily than nitrobenzene [1]. Its reaction with $[\text{Rh}(\text{CO})_4]^-$ gives rise to a complex which may be a simple adduct, but is more probably different derivative. By reaction of $[\text{PPN}][\text{Rh}(\text{CO})_4]$ with a stoichiometric quantity of nitrosobenzene at room temperature, we indeed observed the formation of a carbonyl complex with two $\nu(\text{CO})$ stretching bands, at 2055(m) and 1977(s) cm^{-1} , and some CO_2 evolved. We are currently trying to characterize better this complex and to study its reactivity. All the data on the selectivities are best explained by supposing a metal-nitrene intermediate. Direct carbonylation of this intermediate in the absence of methanol, seems to be very difficult, as the reaction does not proceed in its absence. A second metal seems to play a significant role in this case, since some isocyanate was indeed formed when Ru was also present (Table 1). Evidence for the exact role of the alcohol cannot be obtained from our data.

The nitrene intermediate may abstract hydrogen atoms from the solvent or from the alcohol, to afford aniline. The amount of alcohol seems to be especially important, as shown by a comparison between runs 3 and 4 in Table 3.

The nitrene complex may also react with the intermediate nitrosobenzene to afford azoxybenzene. Finally it should be noted that the reaction of the catalyst with PhNO_2 must be faster than the reaction with azoxybenzene, since the latter is not competitively reduced when the former is present.

After submission of this paper, a related paper on the carbonylation of nitrobenzene using $[\text{PPN}][\text{Rh}(\text{CO})_4]$ as catalyst was published [12]. This work agrees with our finding that a high level of alcohol gives high quantities of aniline. The authors succeeded in avoiding this problem by using $t\text{-BuOH}$, which cannot dehydrogenate, but at the expense of a much slower reaction. The promoting effect of bases such as bipy was not investigated.

Experimental

All solvents were dried, distilled and stored under dinitrogen before use. Nitrobenzene was washed with H_2SO_4 , dried with CaCl_2 , distilled under reduced nitrogen pressure and stored under dinitrogen. Phenanthroline was dried by dissolving it in CH_2Cl_2 , drying the resulting solution with CaCl_2 and evaporating the solvent *in vacuo*. All other organic reagents were commercial products used as received. $[\text{PPN}][\text{Rh}(\text{CO})_4]$ [13], $[\text{PPN}][\text{Rh}_5(\text{CO})_{15}]$ [14], $[\text{PPN}]_2[\text{FeRh}_4(\text{CO})_{15}]$ [15], $[\text{PPN}]_2[\text{RuRh}_4(\text{CO})_{15}]$ [16] and $[\text{PPN}]_2[\text{OsRh}_4(\text{CO})_{15}]$ [17] were made by methods reported in the literature. Gas-chromatographic analyses were conducted on a Perkin-Elmer 8420 gas chromatograph equipped with a PS 255 column (for the analysis of all the products except phenyl isocyanate) or on a Dani 8520 gas-chromatograph equipped with a QF1 column and coupled to a Hewlett-Packard HP 3396 integrator (for the analysis of phenyl isocyanate). IR spectra were recorded on a Beckmann 4210 spectrophotometer.

Catalytic reactions

The catalytic reactions were performed in a glass liner, placed inside a stainless steel autoclave fitted with a magnetic stirrer. All the catalysts are very air-sensitive and were weighed under dinitrogen. Nitrobenzene and the co-catalyst were weighed in air inside the reaction liner. The liner was placed in a large Schlenk tube under dinitrogen and frozen in dry ice-acetone before the addition of the catalyst. Finally, the solvent and the alcohol were added and, after complete freezing of the mixture, the liner was quickly transferred to the autoclave. Air was immediately pumped off and replaced by dinitrogen. The autoclave was charged to the desired pressure and placed in a thermoregulated oil bath, previously heated to the required temperature. At the end of the reaction, the autoclave was cooled in an ice bath, vented and the solution was analyzed by gas-chromatography (using hexamethylbenzene as the internal standard).

Acknowledgements

Thanks are due to the Italian CNR, Progetto Finalizzato Chimica Fine II, and to the Istituto G. Donegani for financial support.

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