

reaction takes place in the lowest excited singlet state. It is also to be noted that the α C-C cleavage process does not require very much higher activation barrier. The reported observation²⁵ of the α -cleavage process in cyclobutane dithione in its lowest excited singlet state is not surprising.

Results in Table I reveal that the calculated activation barriers for photodissociation into radicals on the lowest singlet or triplet ($n\pi^*$) surfaces obtained by the CNDO-CI procedure are approximately an order of magnitude higher than that obtained by the MINDO-CI procedure. But, both methods lead to approximately similar trend. It should be noted that ab initio calculations with geometry optimization in the lowest excited state also leads to very high activation barrier in most compounds. From the

present results and our previous observations,¹³ we tend to believe that the present MINDO-CI procedure leads to more realistic values of activation energies for the photochemical α -cleavage processes.

Conclusions

Although the activation barrier for the α -cleavage process in H_2CS is within the upper limit required for an unimolecular process to compete with phosphorescence, the nonobservation of photocleavage is due to the effective quenching of its triplet state by the ground state. In cyclopropenethiones the α -cleavage process can take place in its lowest triplet state with an activation barrier of about 12.5 kcal M^{-1} . In β -dithio lactones the similar process can take place in its lowest excited singlet state as its activation barrier is even lower.

Registry No. Formaldehyde, 50-00-0; thioformaldehyde, 865-36-1; cyclopropenethione, 69903-36-2; 3-mercapto-2,2,4-trimethylthio-3-pentenoic acid β -thiolactone, 10181-61-0.

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Ruthenium Carbonyl Catalyzed Reductive Carbonylation of Aromatic Nitro Compounds. A Selective Route to Carbamates

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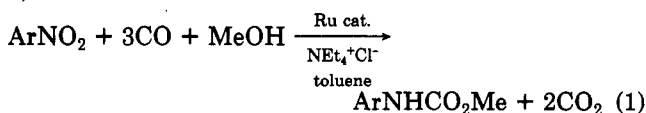
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$Ru_3(CO)_{12}$ (1) and $Ru(CO)_3(PPh_3)_2$ (2) catalyze the reductive carbonylation of nitrobenzene and of substituted aromatic mononitro compounds to give the corresponding methylcarbamates, in toluene-methanol, at 160–170 °C and 60 atm, with high selectivity, in the presence of $NEt_4^+Cl^-$ as cocatalyst. Compound 1 also catalyzes the conversion of 2,4-dinitrotoluene into the corresponding dicarbamate although less efficiently. The effects of CO pressure, reaction temperature, and amount and nature of the added alcohol and cocatalyst have been studied. The mechanism of the reaction catalyzed by 1 has been investigated by studying the reactivity and catalytic activity of possible intermediates.

Introduction

The catalytic carbonylation of aromatic nitro compounds is an area of current interest, both from an academic and an industrial viewpoint.^{1,2} Many important nitrogen-containing organic compounds such as isocyanates, carbamates, ureas, azo compounds, Schiff bases, amines, and heterocyclic derivatives can now be selectively obtained in this way. However, the potential utility of these reactions has not yet been fully explored and, for example, only very recently we reported that the carbonylation of 2-nitrostyrenes catalyzed by $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$ gives indoles in good yields.³ We also recently briefly reported that $Ru_3(CO)_{12}$ (1) and $Ru(CO)_3(PPh_3)_2$ (2) catalyze the reductive carbonylation of aromatic nitro compounds to the corresponding carbamates with high selectivity in the presence of $NEt_4^+Cl^-$ as cocatalyst (eq 1).⁴



We report here a full account of this work. Carbamates are important pesticides and, moreover, they can be transformed into isocyanates by thermal cracking (eq 2).²



They are usually obtained by reaction with alcohols of the corresponding isocyanates which, on the other hand, are obtained by reaction of phosgene with amines (eq 3).⁵



Thus the discovery of alternative syntheses of carbamates is of interest not only in view of the importance of these chemical products but would also give a phosgene-free route to isocyanates, which are of practical interest in the manufacture of polyurethanes. In the patent literature there are many reports on the synthesis of carbamates by reductive carbonylation of aromatic nitro compounds in the presence of alcohols catalyzed by heterogeneous, usually complex, catalytic systems.² One of these based on metallic palladium with iron(III) chloride and pyridine as cocatalysts has been considered of industrial interest.⁶

Homogeneous catalysts are also known for this reaction.² The catalytic system discovered by us works in relatively mild conditions, and it is one of the most selective reported

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so far. Other interesting routes to carbamates have been recently discovered: the oxidative carbonylation of aniline in the presence of alcohol catalyzed by metallic palladium and iodide⁷ or by $\text{Co}^{\text{II}}(\text{salen})$,⁸ the catalytic reaction of dimethyl carbonate⁹ with amines,¹⁰ and the carbonylation at atmospheric pressure of organic azides catalyzed by $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ heterogenized on a polymeric phosphine.¹¹

Experimental Section

All gases were high-purity grade. Dry solvents were used. They were degassed with dinitrogen before use and stored under a dinitrogen atmosphere. Nitrobenzene was distilled at reduced pressure under a dinitrogen atmosphere; 2,4-dinitrotoluene containing 10% water was crystallized from hot methanol. All the other reagents were commercial products and were used as received. $\text{Ru}_3(\text{CO})_{12}$,¹² $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$,¹³ $[\text{PPN}][\text{Ru}_4(\mu\text{-Cl})(\text{CO})_{13}]$,¹⁴ $\text{Rh}_3(\text{CO})_{16}$,¹⁵ $\text{Ru}_3(\text{CO})_{10}(\text{NPh})_2$,¹⁶ and $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ ¹⁶ were prepared by literature methods. In order to purify $\text{Ru}_3(\text{CO})_{12}$ from some ruthenium metal, the carbonyl was dissolved in hot toluene and the resulting solution was filtered through Celite 577. The carbamates used for GC analyses were prepared by standard literature methods.

The reactions at atmospheric pressure were carried out with magnetic stirring, under a dinitrogen or a carbon monoxide atmosphere. The reactions under high pressure were conducted in a glass-liner inside a stainless steel autoclave, equipped with a thermocouple to check the temperature of the solution during the reaction. The air in the autoclave was replaced with dinitrogen by 3 freeze-pump-thaw cycles, before the introduction of carbon monoxide at the desired pressure. The autoclave was heated by a thermoregulated oven and magnetic stirring was applied. At the end of the reactions the autoclave was cooled by an ice bath, and then it was blown off. IR spectra were taken on a Perkin-Elmer 1310 and on a Nicolet MX-1 FT-IR spectrophotometers. IR spectra under pressure were taken in the laboratories of the Department of Organic Chemistry of Florence University, on a Perkin-Elmer PE 580 spectrophotometer coupled to a Perkin-Elmer PE 5600 data station. In this case the reactions were carried out in a 100-mL stainless steel rocking autoclave, without glass-liner, linked by a stainless steel pipe to the cell.

¹H and ¹³C NMR spectra were recorded on a Bruker VP-80 spectrometer, with SiMe_4 as internal standard.

Ruthenium analyses were performed on a Perkin-Elmer 4000 atomic absorption spectrophotometer and conductivity measurements were obtained on an Orion Research conductivity meter Model 101. Elemental analyses were carried out in the analytical laboratories of Milan University.

Reaction of $\text{Ru}_3(\text{CO})_{12}$ (1) with $\text{NEt}_4^+\text{Cl}^-$. $\text{Ru}_3(\text{CO})_{12}$ (1) (0.400 g, 0.626 mmol) and $\text{NEt}_4^+\text{Cl}^-$ (0.726 g, 4.49 mmol) were refluxed in toluene (25 mL) and methanol (5 mL) for 12 h, under a dinitrogen atmosphere. At the end of the reaction two phases separated: the overhanging colorless and the lower dark brown. By addition of methanol at the lower dark brown phase a yellow compound precipitated. It was filtered off and washed under

stirring with diethyl ether: mp 250–270 °C dec; IR in Nujol (cm^{-1}) $\nu(\text{CO})$ 2066 (w), 2006 (vs), 1933 (vs), 1719 (m); Λ_M 302 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in MeCN. Anal. Found: C, 28.69; H, 3.74; N, 2.45; Cl, 5.82; O, 17.45; Ru, 37.23. Calcd for $[\text{NEt}_4]^+[\text{Ru}_4(\mu\text{-Cl})(\text{CO})_{13}]^-$: C, 27.00; H, 2.14; N, 1.50; Cl, 3.80; O, 22.28; Ru, 43.28. Calcd for $[\text{NEt}_4]_2^+[\text{Ru}_4(\text{CO})_{12}\text{Cl}_2]^{2-}$: C, 31.06; H, 3.84; N, 2.68; Cl, 6.81; O, 16.87; Ru, 38.73. ¹H NMR in CD_3CN δ (ppm): 1.25 (tt), 3.20 (q). ¹³C NMR in CD_3CN δ (ppm): 10, 53, 198, 200. Repeated attempts to grow crystals of this material suitable for a X-ray structural determination were unsuccessful.

This yellow material (0.100 g) was allowed to react with PhNO_2 (0.040 g) in toluene (23 mL) and methanol (2 mL) under CO pressure (82 atm) at 170 °C, for 1.5 h. Gas chromatographic analysis of the resulting yellow solution showed the presence of PhNH_2 , but PhNHCO_2Me was absent.

Reaction of $\text{Ru}_3(\text{CO})_{10}(\text{NPh})_2$ (4) with $\text{NEt}_4^+\text{Cl}^-$. $\text{Ru}_3(\text{CO})_{10}(\text{NPh})_2$ (4) (0.100 g, 0.179 mmol) and $\text{NEt}_4^+\text{Cl}^-$ (0.290 g, 1.04 mmol) were refluxed in toluene (23 mL) and methanol (2 mL), under a carbon monoxide atmosphere, in the presence of hexamethylbenzene as internal standard for gas chromatographic analyses. The reaction was also followed by IR spectroscopy. After 30 min small amounts of PhNH_2 and $\text{Ru}_3(\text{CO})_{12}$ (1) were formed, while PhNHCO_2Me was absent. After 5 h two phases separated: the overhanging colorless and the lower dark brown. By addition of methanol to the dark brown phase, the yellow material described in the previous paragraph was obtained. The same reaction carried out under a dinitrogen atmosphere, quantitatively gave the yellow material after 4 h. The same reaction was carried out under CO pressure (82 atm, 170 °C, 1.5 h). PhNH_2 was detected in the yellow solution, while PhNHCO_2Me was absent; $\text{Ru}_3(\text{CO})_{12}$ (1) slowly precipitated from the yellow solution after some hours.

When compound 4 was refluxed in toluene-methanol under a carbon monoxide or a dinitrogen atmosphere, but in the absence of $\text{NEt}_4^+\text{Cl}^-$, we were unable to isolate well-defined inorganic or organic products.

Reaction of $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5) with $\text{NEt}_4^+\text{Cl}^-$. The reaction of $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5) (0.100 g, 0.135 mmol) with $\text{NEt}_4^+\text{Cl}^-$ (0.157 g, 0.95 mmol) was carried out in toluene (23 mL) and methanol (2 mL) at 170 °C, 82 atm of CO, for 1.5 h. The final yellow solution was shown to contain PhNH_2 by IR and gas chromatographic analyses, while PhNHCO_2Me and $\text{Ru}_3(\text{CO})_{12}$ (1) were absent.

Catalytic Reactions. An example of the catalytic reactions is reported below, by using $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, PhNO_2 as substrate, and $\text{NEt}_4^+\text{Cl}^-$ as cocatalyst. All the other catalytic reactions have been similarly carried out.

$\text{Ru}_3(\text{CO})_{12}$ (1) (0.100 g, 0.156 mmol), $\text{NEt}_4^+\text{Cl}^-$ (0.180 g, 1.09 mmol), and nitrobenzene (1.924 g, 15.64 mmol) were weighed in the glass-liner. Toluene (23 mL) and methanol (2 mL) were added. The glass-liner was put into the autoclave and carbon monoxide was admitted at 60 atm with the procedure described above. The reaction was carried out at 170 °C for 1.5 h from the start of the heating. In one case, at the end of the reaction, nitrobenzene (1.924 g) was added to the solution and the reaction was repeated, obtaining conversion and selectivity for the formation of PhNHCO_2Me similar to those observed at the end of the first cycle.

In one experiment carried out with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst, PhNO_2 as substrate, and $\text{NEt}_4^+\text{Cl}^-$ as cocatalyst, at the end of the reaction, after removal of the solvent, the oily residue was chromatographed on SiO_2 deactivated with 10% water. A brown product was separated [IR in Nujol (cm^{-1}): $\nu(\text{CO})$ 2049 (vs), 1977 (vs)]. This compound was used as catalyst with PhNO_2 as substrate and $\text{NEt}_4^+\text{Cl}^-$ as cocatalyst, at 170 °C, 82 atm of CO, for 7 h. A low conversion of nitrobenzene was observed (54%), giving the carbamate and aniline in 43% and 32% yields, respectively. This could be due to some transformations occurring to the active species present in solution during the workup procedure above described.

In the only case in which $[\text{Na}]^+[\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{Me})]^-$ (6) has been used as catalyst with nitrobenzene as substrate, the procedure was different. A solution of compound 6 in methanol, synthesized by a literature method,¹⁷ was transferred into the glass-liner inside the autoclave under CO, using a standard Schlenck apparatus; then nitrobenzene (1.924 g, 15.64 mmol) was added under CO and

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the usual procedure was followed.

Analyses of the Products of the Catalytic Reactions. Quantitative analyses were carried out on a Carlo Erba HRGC Fractovap 4160 gas chromatograph equipped with an "on-column" injector and coupled with a Perkin-Elmer LCI-100 data system or on a DANI 3600 gas chromatograph coupled with a Perkin-Elmer Sigma 10B data system.

In the second case, sometimes phenyl isocyanate was also present in the gas chromatographic analyses (10% with respect to the carbamate). However, it originated from the thermal cracking of the carbamate due to the high temperature in the injector of the gas chromatograph.

Results

Efficiency of the Catalytic Systems. The ruthenium carbonyl complexes $\text{Ru}_3(\text{CO})_{12}$ (1) and $\text{Ru}(\text{CO})_5(\text{PPh}_3)_2$ (2) are very efficient homogeneous catalysts, in toluene-methanol, at 170 °C and 60 atm of carbon monoxide (room temperature pressure), in the reductive carbonylation of nitrobenzene to give methyl phenyl carbamate, when an alkylammonium salt as tetraethylammonium chloride is used as cocatalyst (eq 1) (Table I, entries 7 and 8). During the reactions, the pressure in the autoclave increases up to 80–85 atm. In the absence of the cocatalyst and of methanol (entries 1 and 2, Table I), both complexes gave a low conversion of nitrobenzene, with aniline as the main product. No significant amounts of PhNCO could be detected, while catalyst 1 gave significant amounts of diphenylurea (see the paragraph on Reaction Mechanism for the possible routes to this compound). At the end of the reaction this catalyst was present in solution as the bis-nitrene complex 5. Similar results were obtained when the cocatalyst was used in toluene as solvent (entries 3 and 4). However with 1 as catalyst, aniline was only a minor product, while significant amounts of diphenylurea precipitated at the end of the reaction, in mixture with a black, oily ruthenium carbonyl complex (IR evidence). The conversions of nitrobenzene and the amounts of diphenylurea increased when $\text{NBu}_4^+\text{Cl}^-$ and PPN^+Cl^- , which are more soluble in toluene than $\text{NEt}_4^+\text{Cl}^-$, or when $\text{NEt}_4^+\text{Cl}^-$ in toluene-acetone were used as cocatalysts (entries 9–11). Moreover, in one experiment nitrobenzene was carbonylated in toluene at 220 °C, with $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst (entry 12, Table I). A complete conversion was achieved, with diphenylurea as the main product. The IR spectrum of the solution at the end of the reaction showed the presence of $\text{Ru}_3(\text{CO})_{12}$ (1) in a mixture with $\text{Ru}(\text{CO})_5$.

With methanol in the reaction medium but without the cocatalyst (entries 5 and 6, Table I), again a low conversion was observed with both catalysts. Aniline was the main product, but significant amounts of PhNHCO_2Me were also formed.

Finally, in the presence of both methanol and the cocatalyst (entries 7 and 8), a complete conversion of PhNO_2 was achieved, with a high selectivity on PhNHCO_2Me . Compound 1 was more selective and even more active, since a much lower reaction time was necessary in order to obtain a complete conversion, with respect to the 7 h required by catalyst 2. One hour and a half was enough for catalyst 1 to achieve a 100% conversion of nitrobenzene, with a substrate/catalyst ratio of 100, but also 200. However, in the latter case, a much lower selectivity was observed. At the end of the catalytic reactions, catalyst 1 slowly precipitated from the solutions left at atmospheric pressure. On the other hand, catalyst 2 had been transformed into a new carbonyl complex ($\nu(\text{CO})$ 2049 (vs), 1977 (vs) cm^{-1} , in Nujol), which showed a catalytic activity lower than that of compound 2 (see Experimental Section). In two experiments, at the end of the reactions with the two catalysts 1 and 2, a further amount of nitrobenzene was

Table I. Effects of Methanol and of the Cocatalyst in the Reductive Carbonylation of Nitrobenzene at 170 °C and 60 atm^a

	1	2	3	4	5	6	7	8	9	10	11	12 ^c
conversion (%)	21	26	19	41	26	36	100	100	96	100	54	100
aniline (%) ^b	46	7 ^c	15 ^c	traces ^c	32	34	10	6	17 ^c	7 ^c	c, d	9 ^f
PhNHCO_2Me (%) ^b					20	22	85	93				
catalyst	2	1	2	1	2	1	2	1	1	1	1	1
cocatalyst			$\text{NEt}_4^+\text{Cl}^-$	$\text{NEt}_4^+\text{Cl}^-$			$\text{NEt}_4^+\text{Cl}^-$	$\text{NEt}_4^+\text{Cl}^-$	$\text{NBu}_4^+\text{Cl}^-$	$\text{NEt}_4^+\text{Cl}^-$	PPN^+Cl^-	
mol cocat./mol cat.			3	7			3	7	7	7	7	
reactn time (h)	7	5	5	5	7	5	7	5	5	5	5	5
solvent (mL)	25 (toluene)	25 (toluene)	25 (toluene)	25 (toluene)	23 (toluene) + 2 (MeOH)	23 (toluene) + 2 (MeOH)	23 (toluene) + 2 (MeOH)	23 (toluene) + 2 (MeOH)	25 (toluene)	20 (toluene) + 5 (acetone)	25 (toluene)	25 (toluene)

^a mol PhNO_2 /mol cat. = 100; for entry 1 this ratio is 50. ^b Calculated as a percentage of the converted nitrobenzene, thus representing selectivity. ^c Significant amounts of diphenylurea were detected. ^d Significant amounts of phenyl isocyanate were detected by gas chromatographic and IR analyses of the solution. ^e Reaction carried out at 220 °C. ^f Diphenylurea (ca. 46%) precipitated from the solution.

Table II. Effect of the Nature and of the Amount of Alcohol in the Reductive Carbonylation of Nitrobenzene at 170 °C and 60 atm of CO • Ru₃(CO)₁₂ (1) as Catalyst^a

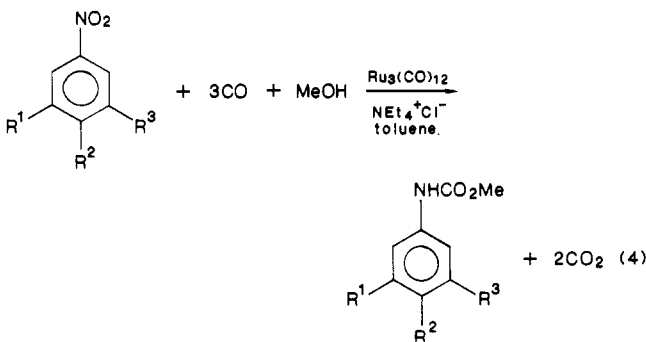
	entry						
	1	2	3	4	5 ^c	6 ^d	7
alcohol (mL)	EtOH (5)	MeOH (5)	MeOH (2)	MeOH (1)	EtOH (25)	PhOH (e)	MeOH (2) ^f
convsn (%)	100	100	100	100	100	93	100
aniline (%) ^b	14	11	6	11	45	traces ^f	69
PhNHCO ₂ R (%) ^b	63	88	93	85	31	4 ^f	0

^a mol PhNO₂/mol cat. = 100; mol NEt₄⁺Cl⁻/mol cat. = 7; reaction time, 5 h; solvent, toluene (25 - x mL) + ROH (x mL). ^b Calculated as a percentage of the converted nitrobenzene, thus representing selectivity. ^c Reaction time 7 h. ^d Reaction time 3 h. ^e 4.6 g. ^f 48% of diphenylurea was obtained. ^g 2 mL of water were also added.

added and the reactions were repeated. In both cases a complete conversion was again obtained. In one experiment with 1 as catalyst, water (2 mL) was added to the reaction medium. A 100% conversion was obtained, but aniline was the main product (see later, Table II).

Finally in one experiment aniline was used as substrate instead of nitrobenzene with 1 as catalyst, and no catalytic reaction was observed.

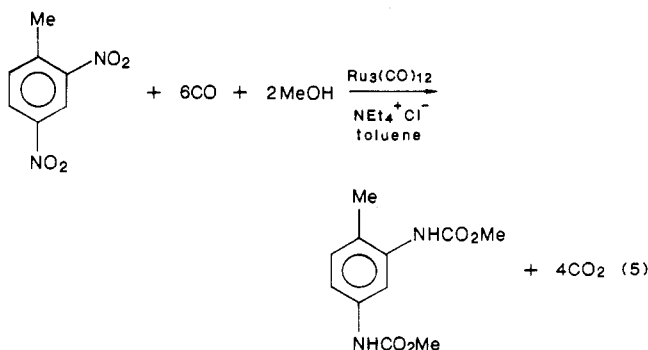
The more active Ru₃(CO)₁₂ (1) was also used as catalyst with a series of substituted aromatic nitro compounds (eq 4, see paragraph about supplementary material).



(R¹ = R² = H, R³ = Me, CF₃; R¹ = R³ = H, R² = Me, CO₂Me; R¹ = R² = Cl, R³ = H; R¹ = R³ = Cl, R² = H; R¹ = Cl, R² = Me, R³ = H)

The reaction conditions tolerate a variety of substituents on the aromatic nucleus of the nitro compound. Good yields (73–88%) were always obtained in the synthesis of these carbamates, some of which are used as pesticides. The corresponding amines were the usual byproducts.

Compound 1 was also used as catalyst for the reductive carbonylation of 2,4-dinitrotoluene (DNT) (eq 5).



Under the reaction conditions used for the mononitro derivatives, decomposition of the catalyst was observed. A black, glassy material precipitated from the solution ($\nu(\text{CO})$ 2010 (s), 1940 (s) cm⁻¹, in Nujol). This material showed a poor catalytic activity in the reductive carbonylation of DNT. The formation of this ruthenium-containing decomposition product was avoided by increasing the amount of methanol (5 mL of MeOH and 20 mL of toluene). However, with a ratio DNT/catalyst = 50, a 100% conversion was achieved only after 7 h of reaction.

The selectivity in the biscarbamate was 45–50%. No 2,4-diaminotoluene or the two possible nitroanilines was formed. Unknown byproducts were obtained, together with the mononitro monocarbamate derivatives. Catalyst 2 proved to be much less active than catalyst 1 in the reaction with DNT.

The homologous carbonyl complexes, M₃(CO)₁₂ (M = Fe, Os) and Fe(CO)₃(PPh₃)₂ were also tested as catalysts with NEt₄⁺Cl⁻ as cocatalyst, in the reductive carbonylation of nitrobenzene, but very small conversions were observed. In the case of Fe₃(CO)₁₂, a gas bubbling was noted when PhNO₂ and the solvent containing methanol were added to the solid catalyst-cocatalyst mixture.² However even when the autoclave was charged with the reactants at -70 °C and under a dinitrogen atmosphere, no significant catalytic activity was noted.

Negative results were also obtained when the metal carbonyls, Ni(CO)₂(PPh₃)₂, Mo(CO)₄(Ph₂PCH₂CH₂PPh₂), and Mo(CO)₂(Ph₂PCH₂CH₂PPh₂)₂, were used as catalysts. By using *cis*-Ru(CO)₂(PPh₃)₂Cl₂ as catalyst, a 33% conversion of nitrobenzene was obtained, but aniline was the main product. A 100% conversion of nitrobenzene was achieved when Rh₆(CO)₁₆ (3) was used as catalyst, under the reaction conditions reported in Table I, entry 8. The carbamate was obtained in 78% yield, while aniline was 17%. Reducing the reaction time to 1.5 h, a 78% conversion of nitrobenzene was observed. At the end of the reactions, a black-brown precipitate (purple in THF) was filtered off from the solutions. Its IR spectrum was similar to the one reported for [Rh₁₂(CO)₃₀]²⁻.¹⁸

Screening of the Cocatalysts. With Ru(CO)₃(PPh₃)₂ (2) as catalyst (see paragraph about supplementary material), LiX compounds (X = F, Cl, I) were not selective cocatalysts in this reaction. Significant conversions of nitrobenzene with the carbamate as the main product were obtained only when alkylammonium salts were used as cocatalysts. Activity and selectivity are strongly influenced not only by the nature of anion but also of the cation of the cocatalyst used. Our results suggest that the activity follows the order F⁻ > Cl⁻ > Br⁻ ≈ I⁻, and NEt₄⁺ > NMe₄⁺ > NBu₄⁺ ≈ PBu₄⁺ > NEt₃(CH₂Ph)⁺ > NEt₃H⁺ > Li⁺. The selectivity follows the order Cl⁻ > Br⁻ ≈ I⁻ and NEt₄⁺ > NBu₄⁺ ≈ NMe₄⁺ > PBu₄⁺ > Li⁺ > NEt₃(CH₂Ph)⁺ ≈ NEt₃H⁺. The best combination being NEt₄⁺Cl⁻.

With Ru₃(CO)₁₂ (1) as catalyst, similar results were observed. However, when a cryptand such as Kryptofix-222 was added to the reaction carried out with KCl as cocatalyst, the catalytic system became selective in the formation of the carbamate, a result which emphasizes the importance of the cation in this reaction. Tetraethylammonium chloride was again the best combination, while the reduced selectivity of NEt₄⁺F⁻ must be in part attributed to the high hygroscopic character of this compound. Neutral ligands such as pyridine and triphenyl-

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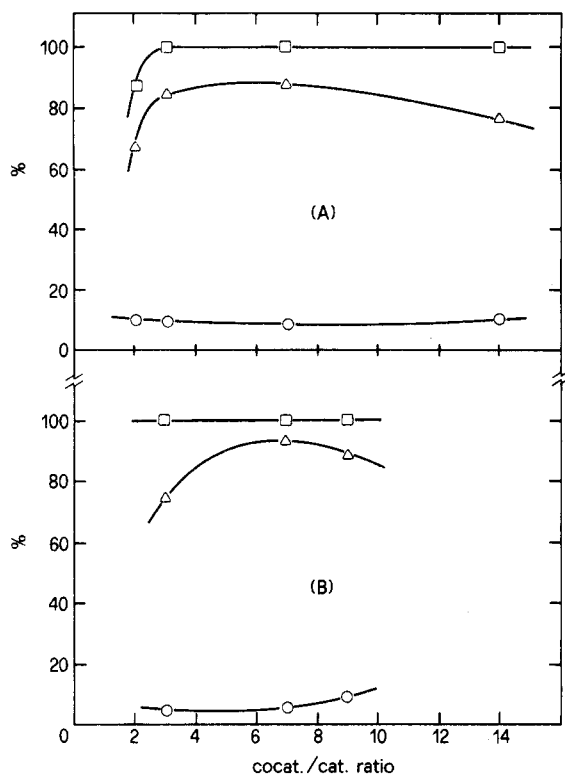


Figure 1. Effect of the cocatalyst/catalyst ratio in the reductive carbonylation of nitrobenzene at 170 °C, $P_{\text{CO}} = 60$ atm, cocatalyst = $\text{Et}_4\text{N}^+\text{Cl}^-$, mol PhNO_2 /mol cat. = 100, solvent = toluene (23 mL) + MeOH (2 mL), for (A) cat. = $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2), reaction time = 7 h; and (B) cat. = $\text{Ru}_3(\text{CO})_{12}$ (1), reaction time = 5 h: (—□—) conversion of PhNO_2 ; (—△—) yield in PhNHCO_2Me (see note b in Table I); (—○—) yield in PhNH_2 (see note b in Table I).

phosphine have practically no effect on the reaction.

The effect of the cocatalyst/catalyst ratio was also studied. With $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst, the highest activity and selectivity were obtained with this ratio ranging from 3 to 7 (Figure 1A). A lower ratio gave a noncomplete conversion, while a higher ratio reduced the selectivity. With $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, the optimum ratio observed was 7 (Figure 1B).

Effects of the Nature and of the Amount of Alcohol Added to the Catalytic System in Toluene as Solvent. $\text{NEt}_4^+\text{Cl}^-$ as Cocatalyst. With $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst, the use of 2-propanol did not give a complete conversion (see supplementary material). A 100% conversion was reached with ethanol. By using methanol a longer reaction time was necessary in order to achieve a complete conversion. However, the latter was more selective for the formation of the carbamate. A dramatic effect was observed when the amount of methanol was decreased from 5–2 mL to 1 mL. In the latter case only traces of carbamate were obtained, while aniline was the predominant product. The stoichiometric quantity of methanol needed for the reaction was about 0.5 mL. With catalyst 1, methanol and ethanol were compared as reagents (Table II). Again the reaction was more selective when methanol was used (entries 1 and 2). Lowering the amount of methanol from 5 to 2 mL improved the selectivity (entry 3). When the alcohol was reduced to 1 mL (entry 4), we did not observe the dramatic effect shown by catalyst 2 and only a lowering of the selectivity was induced. On the other hand when pure ethanol was used as solvent for the catalytic reaction, aniline became the predominant product (entry 5). In the absence of the cocatalyst and in pure methanol as solvent, a low con-

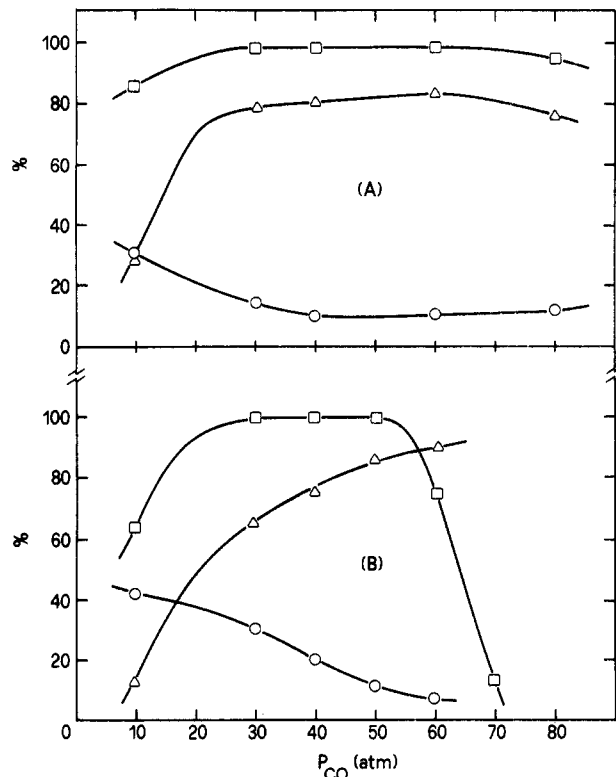
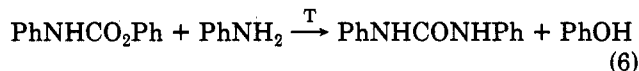


Figure 2. Effect of the pressure of carbon monoxide in the reductive carbonylation of nitrobenzene at 170 °C, mol PhNO_2 /mol cat. = 100, solvent = toluene (23 mL) + MeOH (2 mL), for (A) cat. = $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2), reaction time = 7 h, mol $\text{Et}_4\text{N}^+\text{Cl}^-$ /mol cat. = 3; and (B) cat. = $\text{Ru}_3(\text{CO})_{12}$ (1), reaction time = 1 h, mol $\text{Et}_4\text{N}^+\text{Cl}^-$ /mol cat. = 7: (—□—) conversion of PhNO_2 ; (—△—) yield in PhNHCO_2Me (see note b in Table I); (—○—) yield in PhNH_2 (see note b in Table I).

version of PhNO_2 was observed (34% for a 5-h reaction); aniline was the main product, and the carbamate was formed only in trace amounts. Phenol was also used as hydroxylic reagent (entry 6). In this case diphenylurea was the predominant product. The phenyl phenylcarbamate, PhNHCO_2Ph , was also formed. However, we experienced some difficulties in the gas chromatographic analyses of this carbamate, which is more labile than the carbamate derived from the aliphatic alcohols. The large amount of diphenylurea observed among the products in this case, together with the absence of aniline, may be due to a subsequent reaction between the carbamate and the amine, formed by reduction of nitrobenzene during the catalytic reaction (eq 6). In conclusion, with both catalysts 1 and



2 the use of methanol gave the best results. Water is a severe poison for this reaction, as shown by the fact that its presence leads mainly to the formation of aniline (entry 7).

Effect of the CO Pressure. $\text{NEt}_4^+\text{Cl}^-$ as Cocatalyst. With $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst, increasing the CO pressure from 10 to 30 atm increased the activity and the selectivity in the formation of the carbamate (Figure 2A). From 30 to 60 atm a slight increase in the selectivity was observed. However, at high pressure (80 atm), the conversion was not complete and a slight drop in selectivity was found.

With $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, which is inactive at atmospheric pressure, increasing the CO pressure from 10 to 30 atm increased both the activity and the selectivity

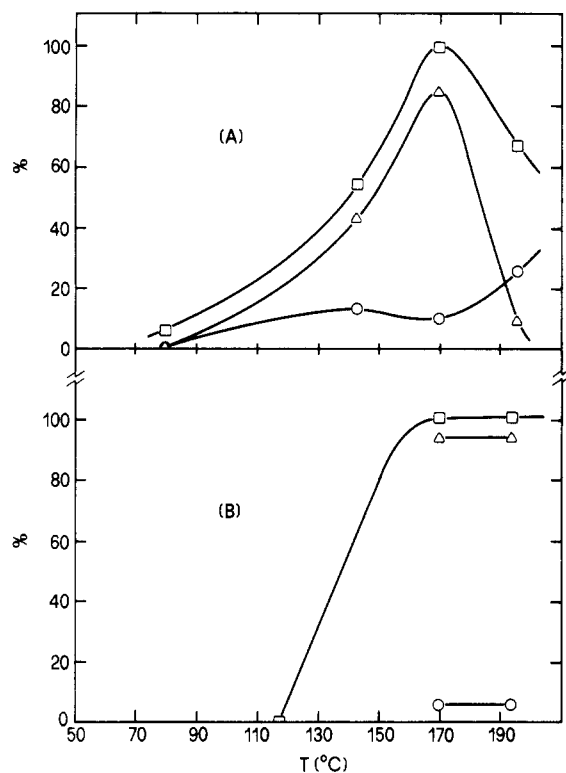


Figure 3. Effect of the temperature in the reductive carbonylation of nitrobenzene at $P_{\text{CO}} = 60$ atm, mol PhNO_2 /mol cat. = 100, solvent = toluene (23 mL) + MeOH (2 mL), for (A) cat. = $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2), reaction time = 7 h, mol $\text{Et}_4\text{N}^+\text{Cl}^-$ /mol cat. = 3, and (B) cat. = $\text{Ru}_3(\text{CO})_{12}$ (1), reaction time = 1.5 h, mol $\text{Et}_4\text{N}^+\text{Cl}^-$ /mol cat. = 7: (—□—) conversion of PhNO_2 ; (—△—) yield in PhNHC_2Me (see note b in Table I); (—○—) yield in PhNH_2 (see note b in Table I).

(Figure 2B). Increasing the CO pressure to 40 and 50 atm significantly increased the selectivity. The selectivity was even better at 60 atm, but a negative effect on the reaction rate was observed (76% conversion was obtained). At 70 atm, the conversion dropped to 15%. However, at this pressure, a longer reaction time gave a complete conversion, with a selectivity greater than 93%. Thus the selectivity regularly increases with increasing the CO pressure, which on the other hand has a marked negative effect on the reaction rate above about 50 atm. The best compromise seems to be a CO pressure of 60 atm, with a slightly longer reaction time (1.5 h).

Effect of the Temperature. $\text{NEt}_4^+\text{Cl}^-$ as Cocatalyst.

The effect of the temperature was particularly relevant for the activity of the catalysts and the selectivity of the reaction (the temperatures reported below are referred to the temperatures set on the heating system).

With $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst and with a CO pressure of 60 atm, practically no reaction was observed at 80 °C (Figure 3A). Activity and selectivity both increased when the temperature was raised to 143 °C (complete conversion not yet reached) and to 170 °C (complete conversion and high selectivity). However, at 196 °C, the conversion again was lower than 100%, and even the selectivity was very poor. Thus a narrow range of temperatures around 170 °C has to be used in order to obtain good results.

With $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, the negative effect of the temperature higher than 170 °C was not observed (Figure 3B), while the catalyst was practically inactive below 120 °C.

An interesting effect was observed when the temperature of the reaction medium inside the autoclave and with

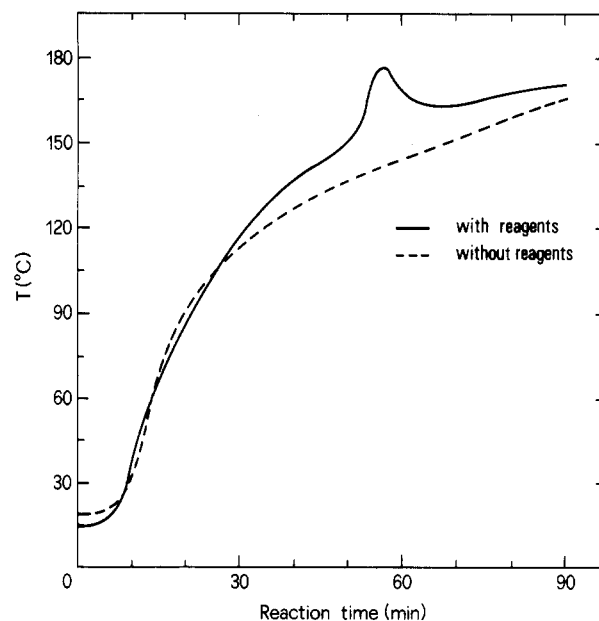


Figure 4. Catalyst $\text{Ru}_3(\text{CO})_{12}$ (1), mmol $\text{Et}_4\text{N}^+\text{Cl}^-$ /mmol cat. = 7, mmol PhNO_2 /mmol cat. = 100, $P = 60$ atm, solvent = 23 mL toluene + 2 mL MeOH.

$\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst was followed starting from the initial minutes of heating (Figure 4). The profile of the curve in the initial 30 min, the time required to reach about 120 °C in the reactor, was very close to the one obtained in a blank experiment. In the following 30 min of heating, the temperature inside the reactor was greater than that observed in the blank experiment, with a marked peak at around 60 min of heating. In the following 30 min of heating the curve corresponding to the catalytic reaction was again very close to the curve corresponding to the blank experiment. The carbonylation of nitrobenzene to give phenyl isocyanate and the reaction of phenyl isocyanate with methanol to give methyl phenylcarbamate are both exothermic.² Thus reaction 1 has a largely negative enthalpy. What we have observed suggests that most of the exothermic reaction occurs in about 20–30 min, starting only when the temperature inside the reactor reaches 120 °C. In one experiment the reaction was immediately stopped after the exothermic peak, observing a complete conversion of nitrobenzene. From these data we can roughly calculate that about 400 mol of nitrobenzene are converted per mole of catalyst per hour, considering only the time during which the carbonylation reaction occurs.

Reaction Mechanism. The mechanism of the reaction catalyzed by $\text{Ru}_3(\text{CO})_{12}$ (1) has been investigated. We have studied this catalyst since several possible intermediates of the catalytic reaction have already been isolated (vide infra). In the preliminary communication of this work,⁴ we have proposed a reaction mechanism mainly based on literature data. The main observations were the following: (i) it is known that $\text{Ru}_3(\text{CO})_{12}$ (1) reacts with nitrobenzene in refluxing benzene to give the phenylimido complexes $\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4) and $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5) with the nitrene ligand(s) triply bridging the three metal atoms;¹⁶ (ii) Alper has shown that in the presence of sodium methoxide and of the $\text{M}_3(\text{CO})_{12}$ ($M = \text{Fe}, \text{Ru}$) metal carbonyls, the carbonylation of aromatic nitro compounds leads to carbamate esters, ureas, formamides, and amines, probably via the $[\text{M}_3(\text{CO})_{11}\text{CO}_2\text{Me}]^-$ and $[\text{M}_3(\text{CO})_9(\text{CO}_2\text{Me})(\text{NPh})]^-$ species;¹⁹ (iii) Alper has also reported that

(19) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* 1981, 103, 6514.

tetrabutylammonium fluoride can catalyze the reduction of nitrobenzenes to anilines by $\text{Fe}_3(\text{CO})_{12}$, suggesting the attack of fluoride ion on coordinated carbon monoxide followed by reaction with water and elimination of CO_2 from the labile iron-carboxylic acid, producing the $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$ cluster anion;²⁰ (iv) we have observed that the activity of $\text{Ru}_3(\text{CO})_{12}$ (1) is not significantly modified when $\text{NEt}_4^+\text{BF}_4^-$ is used as the cocatalyst (see supplementary material); (v) in the absence of alcohol no significant amounts of phenyl isocyanate are formed in the reaction catalyzed by $\text{Ru}_3(\text{CO})_{12}$ (1) (Table I). Thus the formation of the key intermediate, $\text{Ru}_3(\text{CO})_9(\text{CO}_2\text{Me})(\text{NPh})$, was proposed to originate from the nucleophilic attack of Cl^- on $\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4), followed by reaction with methanol. Reductive elimination from this intermediate in the presence of CO should produce the carbamate PhNHCO_2Me with regeneration of the catalyst $\text{Ru}_3(\text{CO})_{12}$ (1).

The importance of the cocatalyst in the reductive carbonylation of nitrobenzene was confirmed by using the nitrene complex $\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4) as catalyst (Table III).

Without any cocatalyst, in the presence (entry 1) or in the absence (entry 2) of methanol, a low conversion was observed, with aniline as the main product. In the latter case, only small amounts of phenyl isocyanate were detected by gas chromatographic analysis. Strangely enough, in the former case no carbamate was obtained. When $\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4) was used as catalyst for the carbonylation of nitrobenzene, in the presence of methanol and with $\text{NEt}_4^+\text{Cl}^-$ as cocatalyst (entry 3), good conversion and selectivity for the synthesis of the carbamate were observed, entirely comparable with those obtained with $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst (Table I, entry 8). At the end of the reaction with 4 as catalyst, $\text{Ru}_3(\text{CO})_{12}$ (1) was recovered from the solution. The bisnitrene complex $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5) was slightly less active and less selective as catalyst in this reaction (Table III, entry 4).

A high conversion of nitrobenzene with a good selectivity was also observed when the yellow product obtained from the reaction of $\text{Ru}_3(\text{CO})_{12}$ (1) with $\text{NEt}_4^+\text{Cl}^-$ in toluene-methanol (see Experimental Section) was used as catalyst (entry 6). Much less selective proved to be the product of the reaction between $\text{Ru}_3(\text{CO})_{12}$ (1) and PPN^+Cl^- , $[\text{PPN}][\text{Ru}_4(\mu\text{-Cl})(\text{CO})_{13}]^-$ (7) (entry 7). In both cases, no $\text{Ru}_3(\text{CO})_{12}$ (1) was formed at the end of the catalytic reactions. Moreover, when the yellow product of the reaction between $\text{Ru}_3(\text{CO})_{12}$ (1) and $\text{NEt}_4^+\text{Cl}^-$ was used as catalyst without the addition of the cocatalyst (in principle not necessary being the alkylammonium cocatalyst already present in the catalytic system), a very low conversion of nitrobenzene was observed, with a poor selectivity for the synthesis of the carbamate (entry 5). Finally the carbomethoxy complex anion $[\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{Me})]^-$ (6) was also used as catalyst (entry 8). Again a low conversion of nitrobenzene with a very poor selectivity was observed, and no $\text{Ru}_3(\text{CO})_{12}$ (1) was present at the end of the catalytic reaction.

The results above reported suggest that the arylimido complex $\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4) is the only possible intermediate to be considered. However, several stoichiometric reactions carried out on compound 4 failed to confirm at the moment the intermediate formation of this derivative in the reactions carried out with 1 as catalyst. Thus when compound 4 was treated with CO and methanol at reflux in toluene, with or without $\text{NEt}_4^+\text{Cl}^-$, only aniline was the

Table III. Reductive Carbonylation of Nitrobenzene at 170 °C and 60 atm^a with Various Catalysts Derived from $\text{Ru}_3(\text{CO})_{12}$ (1)

catalyst	entry							
	1	2 ^c	3	4	5	6	7	8 ^e
$\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4)	$\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4)	$\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4)	$\text{Ru}_3(\text{CO})_{10}(\text{NPh})$ (4)	$\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5)	yellow product ^d	yellow product ^d	$[\text{PPN}][\text{Ru}_4(\mu\text{-Cl})(\text{CO})_{13}]^-$ (7)	$[\text{Na}][\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{Me})]^-$ (6)
mol $\text{NEt}_4^+\text{Cl}^-$ /mol cat.	0	0	7	7	0	7	7	0
conversion (%)	19	12	100	96	13	99	100	45
aniline (%) ^b	34	7	9	16	37	9	42	51
PhNHCO_2Me (%) ^b	0		91	74	19	90	39	2

^a mol PhNCO_2 /mol cat. = 100; solvent, toluene (23 mL) + MeOH (2 mL); reaction time, 1.5 h. ^b Calculated as a percentage of the converted nitrobenzene, thus representing selectivity. ^c Solvent, toluene (25 mL); PhNCO was detected by gas chromatographic analysis. ^d Product of the reaction between $\text{Ru}_3(\text{CO})_{12}$ (1) and $\text{NEt}_4^+\text{Cl}^-$ (see Experimental Section). ^e MeOH (25 mL) as solvent.

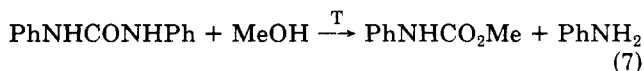
organic product identified. The same result was obtained when the stoichiometric reaction in the presence of methanol and of $\text{NEt}_4^+\text{Cl}^-$ was carried out on 4 and even on compound 5 at 170 °C and 60 atm of carbon monoxide. However, the latter experiment was not conclusive, since we know that the reaction only occurs at temperatures above 120 °C.

Thus it could be that during the heating from room temperature to the temperature useful for the reaction, another reaction took place on compound 4 giving aniline. Very recently methyl phenylcarbamate was produced from nitrene-methoxycarbonyl coupling when a methoxycarbonyl iron nitrene cluster was heated in methanol solution, a result which supports the suggestion of the intermediacy of nitrene-methoxycarbonyl ligated species in the catalytic reactions.²¹

We also attempted to follow several catalytic reactions by IR spectroscopy under pressure. However, we experienced some difficulties in obtaining IR spectra of good quality, since the solvent (toluene in the presence of methanol) was not well balanced in the 1950–1700 cm^{-1} region. These IR data have shown the well-known equilibrium²² between $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{CO})_5$ even under our experimental conditions. However, they did not exclude the participation of the trimeric arylimido complex (4) to the catalytic cycle, nor they proved that monomeric instead of cluster complexes are the true catalytic species in this reaction. This hypothesis is the usual problem which has to be considered when cluster compounds are used as catalysts. Moreover, in our case, the fact that even $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) is active as catalyst in this reaction was a further indication of this possibility.

It is interesting to note that when the reductive carbonylation of nitrobenzene with $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst was carried out at 170 °C without methanol, diphenylurea was obtained and the bisnitrene complex $\text{Ru}_3(\text{CO})_9(\text{NPh})_2$ (5) was the only metal carbonyl complex detected in solution when the conversion was not complete (see the paragraph on the efficiency of the catalytic systems). On the other hand when the reductive carbonylation of nitrobenzene with $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst in the presence of methanol and $\text{NEt}_4^+\text{Cl}^-$ was carried out in a way that the conversion was not complete (141 °C, 60 atm, for 50 min; conversion 25%, aniline 45%, PhNHCO_2Me 24%), only $\text{Ru}(\text{CO})_5$ was detected in solution when the autoclave was opened.

Thus the participation as a key intermediate of compound 5 in the synthesis of diphenylurea is strongly suggested, in agreement with what has been already proposed.² We finally noted that diphenylurea has never been detected among the products in the catalytic reactions carried out in the presence of methanol. This, however, is readily explained by the fact that under the reaction conditions, diphenylurea reacts with methanol to give aniline and the carbamate (eq 7). (170 °C, 60 atm of CO, 1.5 h, in toluene



(21) Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936.

(22) (a) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137. (b) Bor, G. *Pure Appl. Chem.* **1986**, *58*, 543.

(23 mL) + MeOH (2 mL); conversion % 96, giving aniline and PhNHCO_2Me in 1:1 ratio)

Thus the byproduct of reaction 1 could be in fact the urea and not the aromatic amine. However, it seems unlikely to suppose that the urea is the main product, since in the experiments carried out in the absence of alcohols we did not obtain amounts of urea comparable to those of the carbamate.

Conclusions

The reductive carbonylation of aromatic nitro compounds catalyzed by $\text{Ru}_3(\text{CO})_{12}$ (1) [and less efficiently by $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2)] in the presence of $\text{NEt}_4^+\text{Cl}^-$ as cocatalyst in toluene-methanol represents a simple and selective method for the synthesis of a variety of carbamates, starting from readily available substrates. These are important chemicals being used as pesticides. The optimization study of this reaction has led to rather mild reaction conditions (60 atm of carbon monoxide and 160–170 °C). However, even milder conditions can be used (30 atm for example) if a particularly high selectivity is not required.

Our work has also shown the extreme importance of the appropriate cocatalyst, in order to achieve a reasonable selectivity in the desired product. More generally, the reductive carbonylation of nitro compounds can now be considered a general method for the synthesis of a variety of important chemical products.^{1–3}

Recently, some catalytic systems operating at atmospheric pressure have been discovered,^{2,23} and this has greatly simplified the study of the reaction mechanisms, a problem which has not yet been fully solved for the catalytic system here reported.

Acknowledgment. Thanks are due to the Italian C. N.R. (Progetto Finalizzato Chimica Fine e Secondaria) for the financial support and to Prof. F. Piacenti and P. Frediani (Florence University) for the help in the registration of the IR spectra under pressure.

Registry No. 1, 15243-33-1; 2, 14741-36-7; 4, 51185-99-0; 5, 51233-18-2; $\text{NEt}_4^+(\text{RuCl}(\text{CO})_{13})^-$, 112531-86-9; PhNO_2 , 98-95-3; PhNHCO_2Me , 2603-10-3; PhNH_2 , 62-53-3; 3- $\text{MeC}_6\text{H}_4\text{NO}_2$, 99-08-1; 3- $\text{F}_3\text{CC}_6\text{H}_4\text{NO}_2$, 98-46-4; 4- $\text{MeC}_6\text{H}_4\text{NO}_2$, 99-99-0; 4- $\text{MeO}_2\text{CC}_6\text{H}_4\text{NO}_2$, 619-50-1; 3,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2$, 99-54-7; 3,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2$, 618-62-2; 3- $\text{Cl}_4\text{MeC}_6\text{H}_3\text{NO}_2$, 121-86-8; 3- $\text{MeC}_6\text{H}_4\text{NHCO}_2\text{Me}$, 39076-18-1; 3- $\text{F}_3\text{CC}_6\text{H}_4\text{NHCO}_2\text{Me}$, 18584-93-5; 4- $\text{MeC}_6\text{H}_4\text{NHCO}_2\text{Me}$, 5602-96-0; 4- $\text{MeO}_2\text{CC}_6\text{H}_4\text{NHCO}_2\text{Me}$, 94563-12-9; 3,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{NHCO}_2\text{Me}$, 1918-18-9; 3- $\text{Cl}_4\text{MeC}_6\text{H}_3\text{NHCO}_2\text{Me}$, 22133-20-6; 3,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{NHCO}_2\text{Me}$, 25217-43-0; 2,4-(O_2N) $_2\text{C}_6\text{H}_4\text{Me}$, 121-14-2; 2,4-(MeO_2CNH) $_2\text{C}_6\text{H}_3\text{Me}$, 6935-99-5.

Supplementary Material Available: Table of conversions and yields in the reductive carbonylation of substituted aromatic mononitro compounds, using $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, table of the screening of the cocatalysts in the reductive carbonylation of nitrobenzene using $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst, table of the screening of the cocatalysts in the reductive carbonylation of nitrobenzene using $\text{Ru}_3(\text{CO})_{12}$ (1) as catalyst, and table of the effects of the nature and of the amount of alcohol in the reductive carbonylation of nitrobenzene using $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (2) as catalyst (6 pages). Ordering information is given on any current masthead page.

(23) Schwetlick, K.; Unverferth, K.; Hoentsch, R.; Pfeifer, M. German (East) Patent 121 509, 1977; *Chem. Abstr.* **1977**, *87*, 39143v.