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Catalysis by palladium salts

XIII *. The reductive carbonylation of nitroaromatic compounds to isocyanates with Pd^{II} and Pd^0 complexes as homogeneous catalysts **

R. Ugo [a], R. Psaro [b], M. Pizzotti [a], P. Nardi [a], C. Dossi [a], A. Andreetta [c] and G. Capparella [d]

[a] *Dipartimento di Chimica Inorganica e Metallorganica dell'Universita', Via G. Venezian 21, 20133 Milano (Italy)*
[b] *Centro C.N.R., Via G. Venezian 21, 20133 Milano (Italy)*
[c] *Enimont Augusta Industriale, Via Reali 4, 20037 Paderno Dugnano (Italy)*
[d] *Montedipe S.p.A., Enichem Group, Via Rosselini 15/17, 20124 Milano (Italy)*

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Abstract

A study has been made of the reductive carbonylation of 2,4-dinitrotoluene (2,4-DNT) to 2,4-diisocyanotoluene (2,4-TDI) with catalysis either by [Pd(isoquinoline)$_2$Cl$_2$], in the presence of Fe_2O_3 and MoO_3 or of $Fe_2(MoO_4)_3$ as cocatalysts, or by Pd^0 complexes without cocatalysts. In the case of catalytic systems based upon [Pd(isoquinoline)$_2$Cl$_2$] the reaction can be carried out at about 200 °C and under 200 atm of CO to produce 2,4-TDI with high conversions and acceptable selectivities. With Pd^0 complexes as catalysts good conversions can be achieved at much lower temperatures (100–120 °C) but with a low selectivity when a higher pressure of CO is used (300 atm or more). An investigation of the reductive carbonylation of nitrobenzene to phenylisocyanate as a model system, together with a study of the thermal stability of [Pd(isoquinoline)$_2$Cl$_2$] in the presence of CO, has provided evidence that the actual active catalyst could be a reduced (probably zerovalent) form of palladium stabilised by the nitroaromatic substrate or by some of the products formed from it as ligands.

Introduction

Since 1962 reductive carbonylation of nitroaromatic compounds to give isocyanates has been the subject of several investigations owing to interest in a new industrial method for production of isocyanates avoiding the use of phosgene [1].

Originally the research was carried out mainly in industrial laboratories and so results were limited to the patent literature. Corporations such as American

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* For Part XII see R. Ugo, A. Chiesa, P. Nardi and R. Psaro, *J. Mol. Catal.*, 59 (1990) 23.
** Dedicated to the memory of Professor Piero Pino.

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Cyanamide [2], ICI [3], Olin Mathieson Corp. [4], Du Pont [5], and Shell [6] produced a series of patents between 1962 and 1969 describing different homogeneous and heterogeneous catalysts, in the latter case mainly supported noble metals such as palladium and rhodium. Only a little information appeared in scientific journals [7].

After 1969 the research was also undertaken in some academic laboratories and consequently many papers appeared in academic journals on the use of homogeneous catalysts involving palladium, rhodium and ruthenium [8,9]. Relatively little detailed information was published on homogeneous systems involving palladium catalysts [10], although in the patent literature, these, together with those of rhodium [1] were the first homogeneous catalysts studied in depth.

We report here the results of an extensive comparative study of some homogeneous catalytic systems involving Pd^{II} and Pd^0 for the reductive carbonylation of 2,4-dinitrotoluene (2,4-DNT) to give 2,4-diisocyanotoluene (2,4-TDI) together with two isomers of cyano nitrotoluene (NTI).

Experimental

Palladium complexes

The palladium complexes were prepared by published methods (see Table 5 for the meaning of DBA, BQ, AM):

$[Pd(isoquinoline)_2Cl_2]$ [11], $[Pd({}^tBuNC)_2Cl_2]$ [12], $[\{Pd({}^tBuNC)_2Cl\}_2](C_6H_5Cl)$ [12], $[Pd({}^tBuNC)_2]$ [13], [Pd(*o*-phenanthroline)DBA] [14], [Pd(*o*-phenanthroline)BQ] [14], $[Pd(\alpha,\alpha'\text{-dipyridile})AM]$ [15], $[Pd({}^tBuNC)_2AM]$ [16], $[Pd(DBA)_2]$ [17], $[Pd(\alpha,\alpha'\text{-dipyridile})DBA]$ [15], $[Pd(\alpha,\alpha'\text{-dipyridile})BQ]$ [15], $[Pd(PPh_3)_3CO]$ [18].

Cocatalysts

MoO_3 was prepared by decomposition of $(NH_4)_2MoO_4$ (reagent grade, obtained from Rudi Pont) at 500 °C for 12 h. Fe_2O_3 was obtained by precipitation of $Fe(NO_3)_3$ (100 g) (reagent grade from C. Erba) in 1 l of distilled water with 60 ml of 32% NH_3. The final pH was ca. 7. The hydroxide was filtered off, washed with a solution of 10 ml of aqueous NH_3 (32%), in 1 l of distilled water, dried at 130 °C for 4 h, and then was kept at 500 °C for 12 h.

$Fe_2(MoO_4)_3$ was prepared from $(NH_4)_2MoO_4$ (reagent grade from Rudi Pont); to a solution of 52.8 g of the latter in 150 ml of distilled water was added a solution of 80.8 g of $Fe(NO_3)_3$ (reagent grade from C. Erba) dissolved in 200 ml of distilled water, and aqueous NH_3 (32%) was added to give a pH of ca. 6. Water was then distilled off, the solid residue was dried at 130 °C for 12 h, and then kept at 500 °C for 12 h.

Reagents and solvents

Nitrobenzene and 2,4-DNT were obtained from Merck-Schuchardt, and respectively purified by distillation and crystallization from methanol. 1,2-Dichlorobenzene (C. Erba) was distilled twice before use. Carbon monoxide was carefully dried and freed from traces of hydrogen.

Catalytic runs with $[Pd(isoquinoline)_2Cl_2]$ as catalyst

Two different procedures were used.

(*a*) The solvent, the reagent and the catalyst were placed in the autoclave, which was then degassed, and heated to the chosen reaction temperature. Carbon monoxide was introduced and pressure was kept constant by continuous addition of CO. At the end of reaction (see Tables), the mixture was cooled and transferred at room temperature to a glass container, avoiding any contact with air. When this method was used, we always observed a strong and sudden increase of temperature immediately after the initial addition of CO, making it very difficult to control the reaction temperature. If the CO was introduced initially, before the warming, control of temperature was easier, but some reaction occurred during the warming process.

(*b*) All the reagents, including carbon monoxide, were introduced into the autoclave at room temperature, and the mixture was then quickly warmed to a temperature of about 50 ° C below the temperature needed for complete reduction of both nitro-groups of 2,4-DNT (about 200 ° C). The reaction mixture was kept at this temperature (about 150 ° C) for a chosen time (see Table 3) and the temperature was then raised to the value required for completion of the reaction (see Table 3). At the same time the CO pressure was kept at the chosen value by continuous addition of CO. At the end the reaction mixture was recovered as in (a). With this method control of temperature was quite satisfactory, and there was good reproducibility of the results.

Work-up of the reaction mixtures

At the end of the reaction a solution mixed with some precipitate was present. This precipitate was a mixture of $[Pd(isoquinoline)_2Cl_2]$ (which is not soluble at room temperature in 1,2-dichlorobenzene), metal oxides and salts, metallic palladium, and insoluble organic oligomers. The solids were filtered off under nitrogen and the solution analysed by GLC (see later). The palladium content of the solution was determined by atomic absorption spectroscopy.

The solid residue was washed with cold acetone to remove the organic oligomers and then continuously extracted with $CHCl_3$ in order to take up completely $[Pd(isoquinoline)_2Cl_2]$, which is insoluble in cold acetone. The amount of the complex in the $CHCl_3$ solution was determined by atomic absorption spectroscopy.

The insoluble material left after washing was extracted with acetone/ether mixtures, then dried and analysed for palladium. The amount of metallic palladium was determined by X-ray fluorescence spectroscopy or by dissolving the solid in concentrated HNO_3, evaporating the solution to dryness, dissolving the residue in 1.5% aqueous HCl, and analysing the solution by atomic absorption spectroscopy.

Catalytic reactions using $[Pd(^tBuNC)_2Cl_2]$ or $[\{Pd(^tBuNC)_2Cl\}_2] \cdot C_6H_5Cl$ or $[Pd(^tBuNC)_2]$ or other Pd^0 complexes as catalysts

All the reactions were carried out without the addition of a cocatalyst by the procedure (a), with work-up of the reaction mixture described above.

Investigation of the stability of the catalytic systems based upon $[Pd(isoquinoline)_2Cl_2]$

The reaction was carried out in a glass reactor which was pre-heated with an oil bath (150 ml; temperature control between 20 and 170 ° C; warming time, 10 min). The reagents and solvent were placed in the reactor, the mixture was warmed, and the system kept at the required temperature for a chosen time (usually 3 or 6 h). The suspension was filtered off while still warm. The solid was a mixture of [Pd(isoquinoline)$_2$Cl$_2$], metallic palladium, and some $Fe_2(MoO_4)_3$. The palladium complex was removed by continuous extraction with $CHCl_3$. The palladium content of the solution obtained after filtration and that in the $CHCl_3$ extract were determined by atomic absorption spectroscopy.

The solid residue left after the extraction was dissolved in concentrated HNO_3 as previously described, finally to give a solution in 1.5% aqueous HCl, the palladium content of which was determined by atomic absorption spectroscopy. The gas phase in the glass reactor was analysed (before and after the reaction) by gas chromatography.

Autoclaves

We observed some corrosion when using AISI 316 or Inconel autoclaves so decided to use Hastelloy C. autoclaves. Experiments were carried out with a rocking autoclave (100 or 250 ml) equipped with a thermocouple, systems for gas injection and removal of liquids, and a manometer with a Hastelloy membrane. The temperature was kept constant with an oil bath.

Owing to the high exothermicity of the reaction:

$$\text{2,4-DNT} + 6CO \rightarrow \text{2,4-TDI} + 4CO_2 \qquad \Delta H = -228 \text{ kcal/mol}$$

poor temperature control was obtained with this kind of autoclaves. Furthermore use of a simple rocking process did not allow a satisfactory diffusion of CO from the gas into the liquid phase. Therefore, particularly in the reactions involving zerovalent palladium complexes as catalysts, we used a 500 ml Hastelloy C autoclave provided with magnetic stirring.

Analysis

The aromatic products in the reaction solutions were analysed by GLC with a Hewlett-Packard 5750 G gas chromatograph fitted with a thermal conductivity detector. Analyses were carried out with a 2 mm i.d. Hewlett-Packard UCC-W-982 column, 2 m long in the case of 2,4-DNT and 4 m long in the case of nitrobenzene. The conditions used for the analysis were: injection temperature 240 °C, detector temperature 150 °C, column temperature 160 °C (with 2,4-DNT) and 130 °C (with nitrobenzene). Helium was used as carrier gas (210 ml/h with 2,4-DNT and 120 ml/h with nitrobenzene).

The gas phase was analysed by gas chromatography using a Carlo Erba ADC/t instrument equipped with a thermistor detector operating with a current of 100 mA.

Further experimental details were as follows:

(*a*) For the analysis of CO and CO_2 after reactions, a 4 m long, 4 mm i.d. column filled with 20% dimethylsulfolane on Chromosorb P (30–60 mesh) was used at 20 °C with Helium (0.5 atm) as carrier gas.

(*b*) The purity of CO for reaction studies was checked by use of a 2 m long, 4 mm i.d. column filled with molecular sieves. The analysis was carried out at 58 °C with Ar (0.5 atm) as carrier gas.

Analysis for palladium was carried out by atomic absorption spectroscopy, with a Varian-Techtron AA-5 apparatus. Metallic palladium in the solid residue was determined directly by X-ray fluorescence spectroscopy using a Siemens SRS-I apparatus.

Results

1. Reductive carbonylation of 2,4-dinitrotoluene using [Pd(isoquinoline)$_2$Cl$_2$] as catalyst

One of the most efficient Pd^{II} homogeneous catalysts described in the patent literature appears to be [Pd(isoquinoline)$_2$Cl$_2$] with $Fe_2O_3 + MoO_3$ [4] or $Fe_2(MoO_4)_3$ [6] as cocatalysts. We first studied the stability and chemistry of one of these catalytic systems under various conditions.

1.1. The stability of the catalytic system

The stability of the system [Pd(isoquinoline)$_2$Cl$_2$] with $Fe_2(MoO_4)_3$ as cocatalyst was initially studied under one atmosphere pressure of CO. The palladium complex, which is stable under nitrogen up to 170 ° C, is reduced to metal to a small extent (1.5–3.5%) at 170 ° C, under one atmosphere of CO with 1,2 dichlorobenzene as solvent.

Upon addition of $Fe_2(MoO_4)_3$ the reduction to metal becomes significant even at 170 ° C (about 40%), although this process is independent on the excess of $Fe_2(MoO_4)_3$ (Fig. 1a).

Upon addition of an excess of nitrobenzene, some reduction to metallic palladium occurs; in this case the process is dependent on the amount of nitrobenzene present; the nitrobenzene remains quite unchanged because of the low CO pressure (see Fig. 1b).

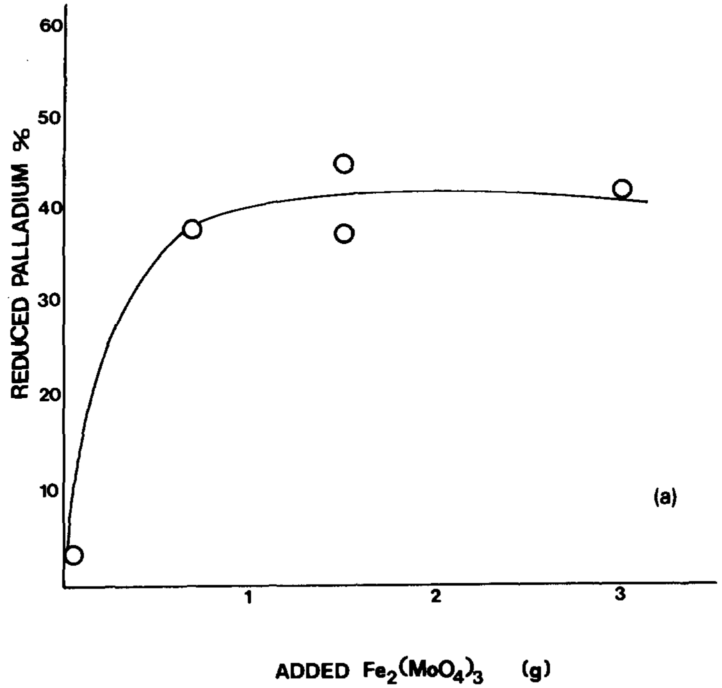
Upon addition of nitrobenzene and $Fe_2(MoO_4)_3$ together, the extent of reduction to metallic palladium is much larger than when only nitrobenzene is added, but is lower than that when only $Fe_2(MoO_4)_3$ is added. It appears that nitrobenzene activates, but at the same time stabilises the palladium catalyst. Under all the conditions used the extent of decomposition to palladium metal is dependent on the initial total quantity of nitrobenzene present (see Fig. 2).

We have observed that under the conditions used (for instance 3 h at 170 ° C, under 1 atm of CO), the $Fe_2(MoO_4)_3$ gives a blue colour with parallel formation of some CO_2. This colour change is a sign of some reduction of Fe^{III} to Fe^{II}, and this was confirmed analytically. When the same experiment was carried out for 6 h at 190 ° C and under 35 atm of CO pressure in the presence of only $Fe_2(MoO_4)_3$, the latter is again reduced to the blue form, with oxidation of CO to CO_2. Consequently, under CO pressure the real cocatalyst is probably the reduced form of $Fe_2(MoO_4)_3$.

In conclusion the action of a cocatalyst such as $Fe_2(MoO_4)_3$ is to increase the reactivity towards CO of [Pd(isoquinoline)$_2$Cl$_2$]. This complex is activated, although to a smaller extent, by the presence of a nitroaromatic species, which, however, at the same time stabilizes the catalytic system.

We also investigated, as a model system, the carbonylation of nitrobenzene using as catalyst the system [Pd(isoquinoline)$_2$Cl$_2$] with $Fe_2(MoO_4)_3$ as cocatalyst. The reaction was carried out at 160 ° C and under 200 atm of CO with 1,2-dichlorobenzene as solvent.

Figures 3 and 4 show both the extents of conversion of nitrobenzene and the yields of phenylisocyanate for two initial concentrations of nitrobenzene. At a high concentration of nitrobenzene, 90% conversion occurred in 420 min, whereas only 40 min are required for the same extent of conversion at the lower concentration; the selectivity towards isocyanate is greater for the lower concentration of nitro-



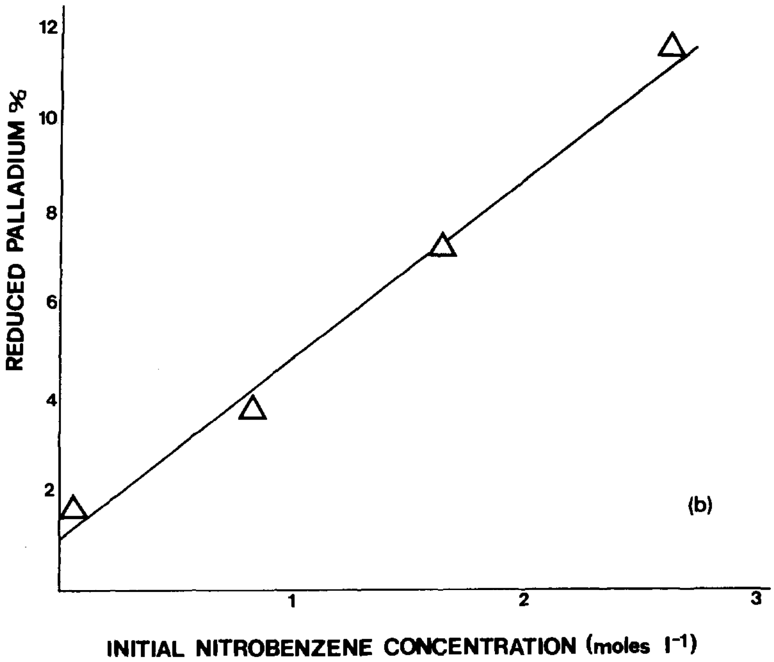


Fig. 1a. The reduction to palladium metal of [Pd(isoquinoline)$_2$Cl$_2$] with different amounts of $Fe_2(MoO_4)_3$ after 3 h at 170 °C and under 1 atm of CO; initial amount of [Pd(isoquinoline)$_2$Cl$_2$] is 1 g, the solvent is 1,2-dichlorobenzene (50 ml).

Fig. 1b. The reduction to palladium metal of [Pd(isoquinoline)$_2$Cl$_2$] with different amounts of nitrobenzene after 3 h at 170 °C and under 1 atm of CO; initial amount of [Pd(isoquinoline)$_2$Cl$_2$] is 1 g, the solvent is 1,2-dichlorobenzene (50 ml).

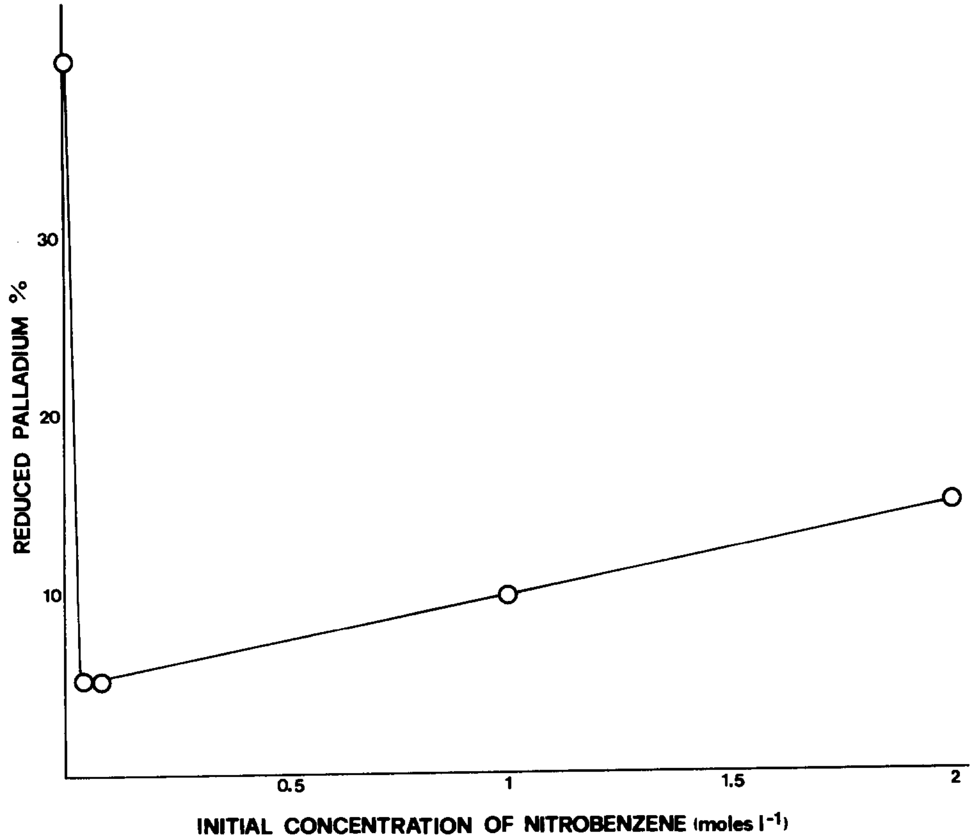


Fig. 2. The reduction to palladium metal of [Pd(isoquinoline)$_2$Cl$_2$] with different amounts of nitrobenzene after 3 h at 170 °C and under 1 atm of CO; initial amount of [Pd(isoquinoline)$_2$Cl$_2$] is 1 g and the solvent is 1,2-dichlorobenzene (50 ml); Fe$_2$(MoO$_4$)$_3$ is 15 g.

benzene. This behaviour can be attributed to increase in the extent of decomposition of the palladium(II) complex to metal with increase in the proportion of nitrobenzene. (In our study the molar ratio of the nitrobenzene and the palladium complex was increased from 10.6 to 26.5 (Fig. 5).)

In Fig. 6 the amount of unchanged [Pd(isoquinoline)$_2$Cl$_2$] (which is insoluble in cold 1,2-dichlorobenzene) is plotted against the extent of nitrobenzene conversion, together with the amount of metallic palladium produced, and that of an unidentified Pd-containing species soluble in cold 1,2-dichlorobenzene. As expected, the extent of decomposition of the palladium complex is large and already at low conversions, particularly with a high initial concentration of nitrobenzene. Similar features (Fig. 7) are observed when the same variables are plotted against time.

In conclusion it appears that under catalytic conditions the original palladium complex, which is thermally stable, is activated by both the cocatalyst and the nitroaromatic reagent, to give soluble, unidentified palladium species, accompanied by extensive decomposition to palladium metal. A plot of the concentration of this soluble species, which may be the active catalyst, against time or the extent of conversion is parabolic (Figs. 6 and 7), as expected for its fast formation of this

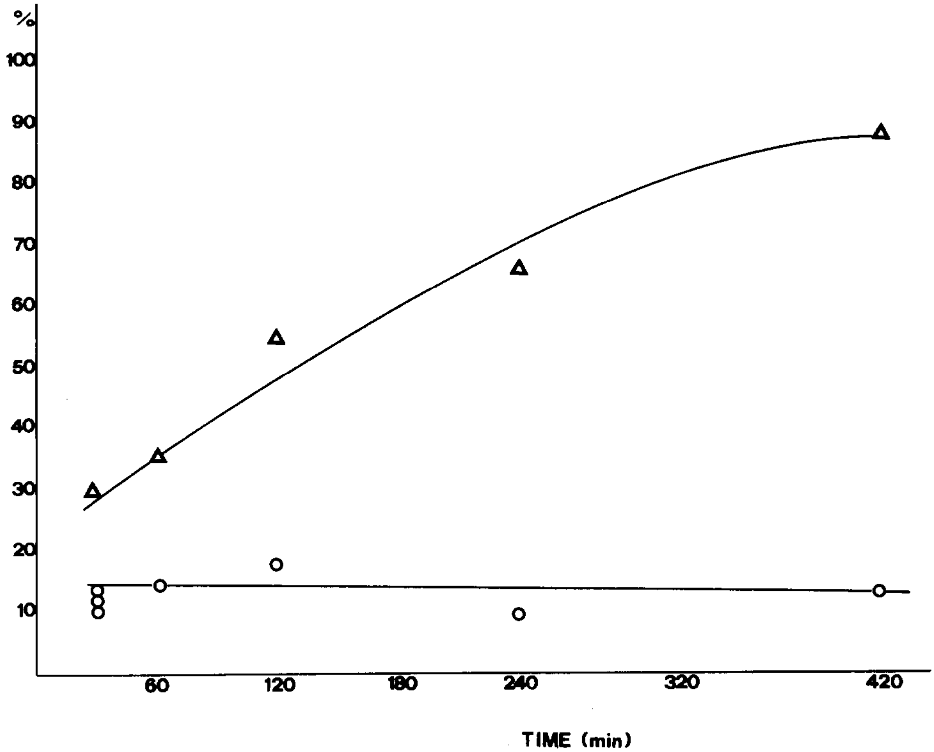


Fig. 3. Conversion of nitrobenzene at 160 °C and under 200 atm of CO; [Pd(isoquinoline)$_2$Cl$_2$] 0.8 g, $Fe_2(MoO_4)_3$ 1.2 g, nitrobenzene 6 g, solvent 1,2-dichlorobenzene (40 ml). All reagents are added at room temperature, the time to reach 160 °C is about 30 min. △, Nitrobenzene conversion; ○, phenylisocyanate yields.

complex followed by its decomposition to metal. We were unable to isolate and characterise this species owing to its low concentration in the reaction medium and its low stability.

The decomposition of the initial palladium(II) complex does not much depend on the amount of an excess of the cocatalyst (Fig. 8), or consequently, on the extent of nitrobenzene conversion (Fig. 9). The extent of formation of metallic palladium is strongly dependent on the extent of nitrobenzene conversion, being significant even at relatively low conversions (Fig. 10).

1.2. The reductive carbonylation of 2,4-DNT to 2,4-TDI with [Pd(isoquinoline)$_2$Cl$_2$] and Fe_2O_3 plus MoO_3 as the catalyst system

We first studied the reductive carbonylation of 2,4-DNT with the standard palladium complex [Pd(isoquinoline)$_2$Cl$_2$] as catalyst in the presence of Fe_2O_3 plus MoO_3 as cocatalyst. The reaction was carried out under CO pressures between 200 and 400 atm and at temperatures between 150 and 200 °C with 1,2-dichlorobenzene as solvent. The choice of this system was based on the observation that when $Fe_2(MoO_4)_3$ is added as cocatalyst the results were very difficult to reproduce owing to the lack of control of temperature (see later, and the Experimental section).

As expected, the reaction takes place in two steps: the first is the reduction of only one nitro group (see Scheme 1) to give two isomers (*ortho* and *para*) of nitro

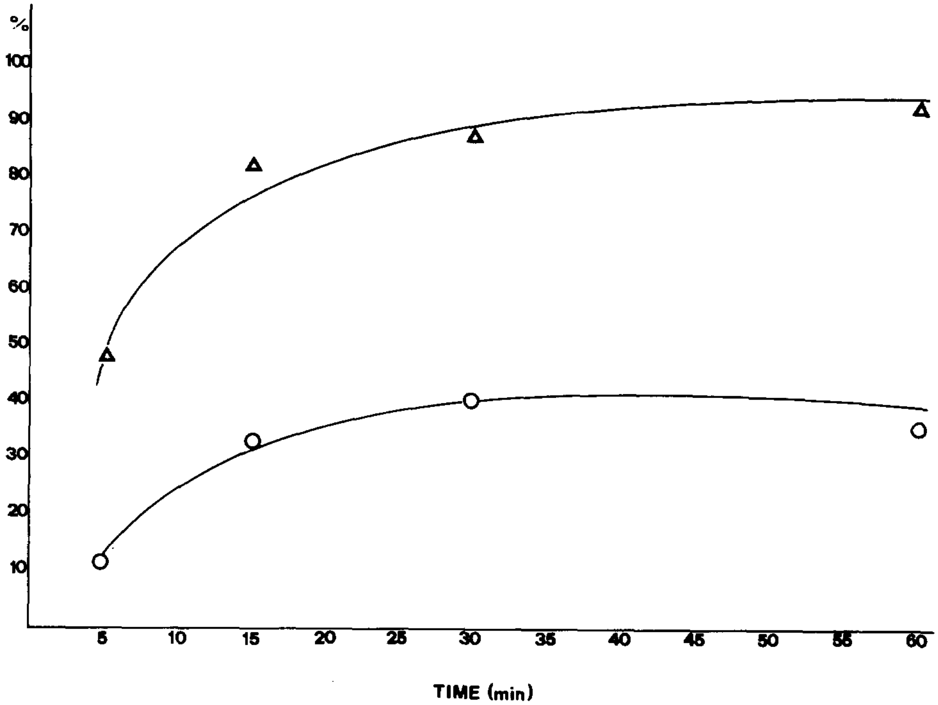
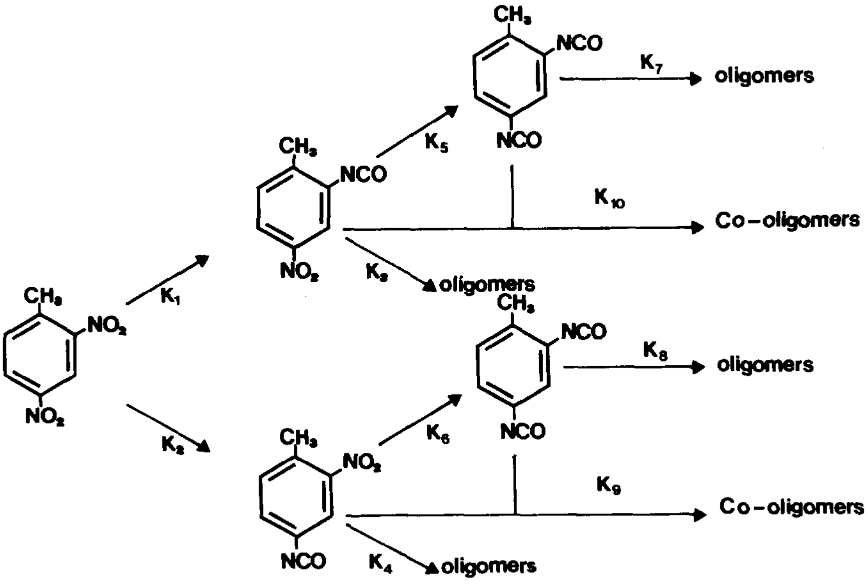


Fig. 4. Conversion of nitrobenzene at 160 °C and under 200 atm of CO; [Pd(isoquinoline)$_2$Cl$_2$] 0.8 g, $Fe_2(MoO_4)_3$ 1.2 g, nitrobenzene 2.4 g, solvent 1,2-dichlorobenzene (40 ml). All reagents are added at room temperature, the time to reach 160 °C is about 30 min. △, Nitrobenzene conversion; ○, phenylisocyanate yields.



Scheme 1. The series of reactions taking place in the catalytic solution.

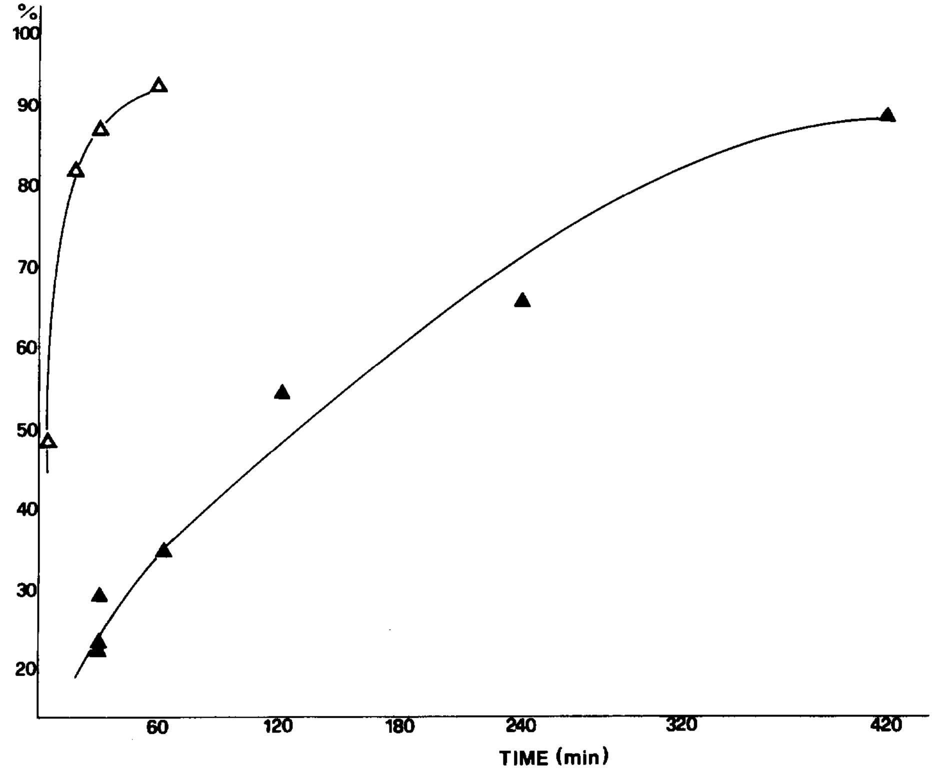


Fig. 5. Conversion of nitrobenzene at 160 °C and under 200 atm of CO; [Pd(isoquinoline)$_2$Cl$_2$] 0.8 g, $Fe_2(MoO_4)_3$ 1.2 g, solvent 1,2-dichlorobenzene (40 ml). All the reagents are added at room temperature, the time to reach 160 °C is about 30 min. △, Molar ratio nitrobenzene to palladium complex is 10.6; ▲, ratio is 26.5.

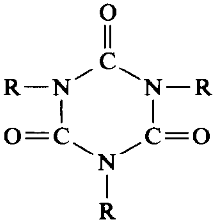
isocyanotoluene (NTI), and this is followed by the second step involving formation of 2,4-TDI (see Scheme 1).

Under many different reaction conditions conversion is quite high (Table 1), whilst selectivity towards 2,4-TDI depends on many variables.

The NTI isomers are generated quite quickly (see, for instance, Table 1 for a reaction complete in only 20 min); the product with the isocyano group in *ortho* position is formed more quickly than its *para* isomer (Table 2).

As expected the second nitro group is reduced and carbonylated more slowly, because the presence of an NCO group in the aromatic ring slows down the reductive carbonylation of that NO_2 group [19]. In order to achieve acceptable TDI yields it is necessary to work at high temperature and high CO pressure (Table 1).

At the same time the monoisocyano compounds are oligomerised to involatile products, probably cyclic species such as triphenylbiuret:



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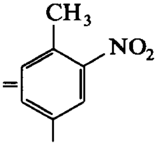

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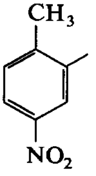


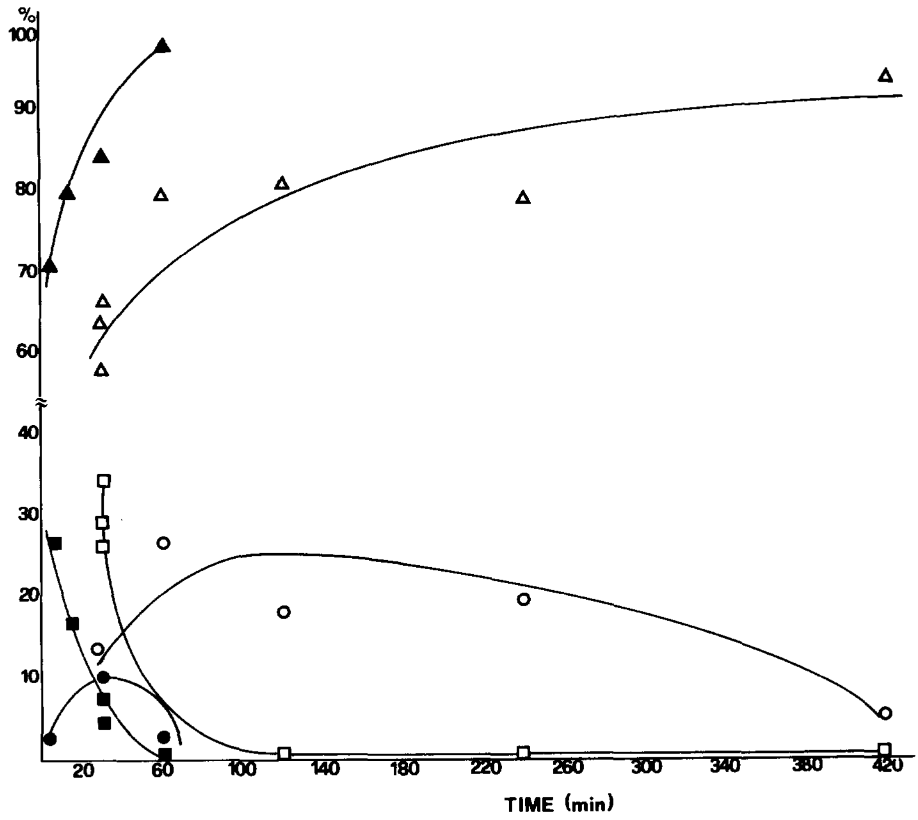


Fig. 6. Dependence from nitrobenzene conversion of the relative amount of $[Pd(isoquinoline)_2Cl_2]$ (□ and ■), of metallic palladium (△ and ▲) and of a soluble form of palladium (○ and ●). Conditions are: 160 ° C and under 200 atm of CO; $[Pd(isoquinoline)_2Cl_2]$ 0.8 g, $Fe_2(MoO_4)_3$ 1.2 g, solvent 1,2-dichloromethane (40 ml). All the reagents are added at room temperature, the time to reach 160 ° C is about 30 min. □, △, and ○ correspond to an initial molar ratio nitrobenzene to palladium complex of 26.5; ■, ▲, ● to a ratio of 10.6.

Table 1

Reductive carbonylation of 2,4-DNT to 2,4-TDI and to isomeric NTI (total isocyanates = TDI + Σ NTI). Reaction conditions: palladium catalyst $[Pd(isoquinoline)_2Cl_2]$ (2.4 g); solvent 1,2-dichlorobenzene (64 g); cocatalyst Fe_2O_3 (0.6 g) and MoO_3 (3 g); 2,4-DNT (6 g)

Reaction time (min)	Temperature [c] (° C)	Pressure (atm)	Conversion (%) 2,4-DNT	Molar yields TDI (%)	Yields total isocyanates (%)
90	185–200	200	100 (97.7) [b]	61.6 (16.2) [b]	61.8 (40.3) [b]
90	185–200	300	100	47.3	47.3
20 [a]	185–200	250	86.2	15.4	41.7
20	185–200	250	97.3	13.2	19.4
15	170–220	200	86	13.2	37.3
5	150–200	200	82	1.7	12.3
2	185–200	400	100	50.7	52.4

[a] Without cocatalyst. [b] Catalyst 0.5 g. [c] The control of temperature is difficult (see Experimental).

Table 2

Reductive carbonylation of 2,4-DNT to 2,4-TDI and to isomeric NTI (total isocyanates = TDI + Σ NTI). Reaction conditions: 2,4-DNT (6 g); palladium catalyst [Pd(isoquinoline)$_2$Cl$_2$] (1.2 g); solvent 1,2-dichlorobenzene (64 g); cocatalyst Fe$_2$O$_3$ (0.3 g) and MoO$_3$ (1.5 g); reaction time 90 min

Temperature [a] (°C)	Pressure (atm)	Conversion (%) 2,4 DNT	Molar yields (%)					Selectivity (%)	
			p-NTI	*o*-NTI	TDI	oligomers	total isocyanates	TDI	total isocyanates
150–153	200	44.7	5.5	24.5	1.7	7.6	31.7	3.9	71
170–174	200	71.2	9.6	35.8	13	19.5	58.4	18.3	82
195–206	200	99.0	1.4	6.2	64.7	9.5	72.3	68.0	73
195–200	100	93.2	5.1	18.0	16.5	8.7	39.6	17.7	42.5
196–209	300	96.8	0.4	2.1	58.3	11.4	60.8	60.3	62.8

[a] The control of temperature is difficult, but better than in experiments reported in Table 1 (see Experimental).

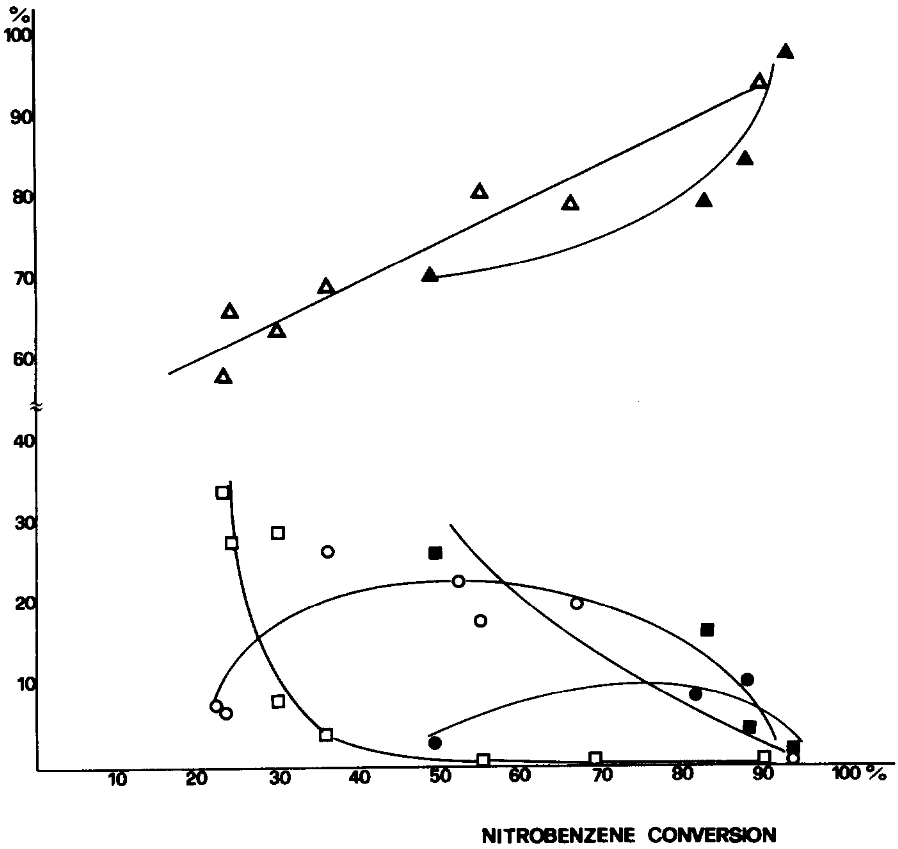


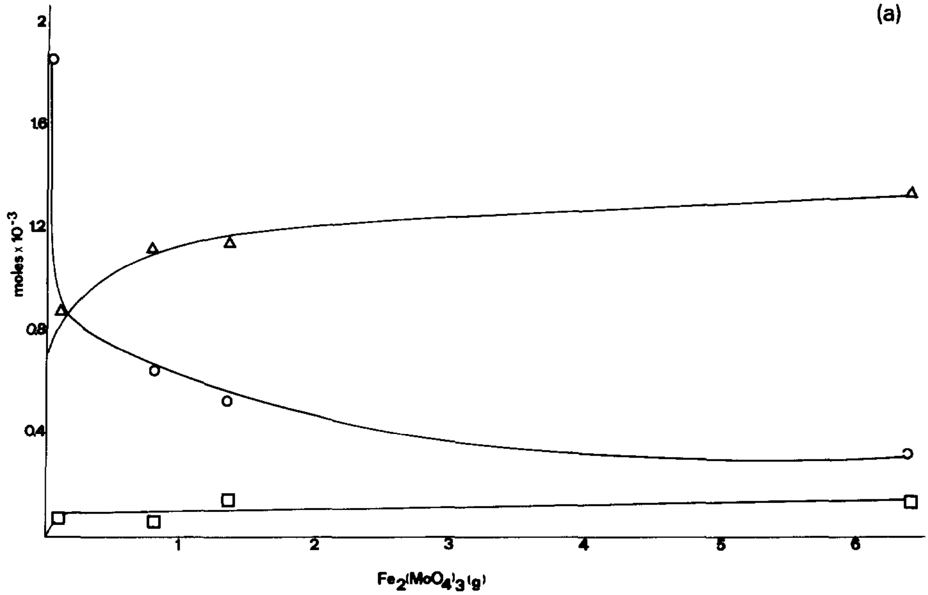
Fig. 7. Time dependence of the relative amount of [Pd(isoquinoline)$_2$Cl$_2$] (□ and ■), of metallic palladium (△ and ▲) and of a soluble form of palladium (○ and ●). Conditions are: 160 °C under 200 atm of CO; [Pd(isoquinoline)$_2$Cl$_2$] 0.8 g, Fe$_2$(MoO$_4$)$_3$ 1.2 g, solvent 1,2-dichloromethane (40 ml). All the reagents are added at room temperature, the time to reach 160 °C is about 30 min. □, △, ○ correspond to a molar ratio nitrobenzene to palladium complex of 26.5; ■, ▲, ● to a molar ratio of 10.6.

Table 3

Reductive carbonylation of 2,4-DNT to 2,4-TDI and to isomers of NTI (total isocyanates = TDI + Σ NTI). Reaction conditions: two-step reaction with t_1 and t_2 reaction times (see Experimental); temperature of the first step 150–152 °C, of the second step 195–197 °C; DNT (12 g); solvent 1,2-dichlorobenzene (100 ml); pressure 200 atm of CO; catalyst [Pd(isoquinoline)$_2$Cl$_2$] (2 g), cocatalyst Fe$_2$(MoO$_4$)$_3$ (3 g)

t_1 (min)	t_2 (min)	Conversion (%) 2,4-DNT	Molar yields (%)				Selectivity total isocyanates (%)
			TDI	*p*-NTI	*o*-NTI	total isocyanates	
60	105	97.5	51.2	1.7	11.1	64	65.5
60 [a]	150	99.5	68.5	0	0	68.5	69.0
60	210	94.5	67.5	0	0	67.5	71.5
60 [b]	120	99.5	68.0	0	0	68.0	68.5

[a] Fe$_2$(MoO$_4$)$_3$ (1.5 g). [b] [Pd(isoquinoline)$_2$Cl$_2$] (4 g), Fe$_2$(MoO$_4$)$_3$ (6 g).



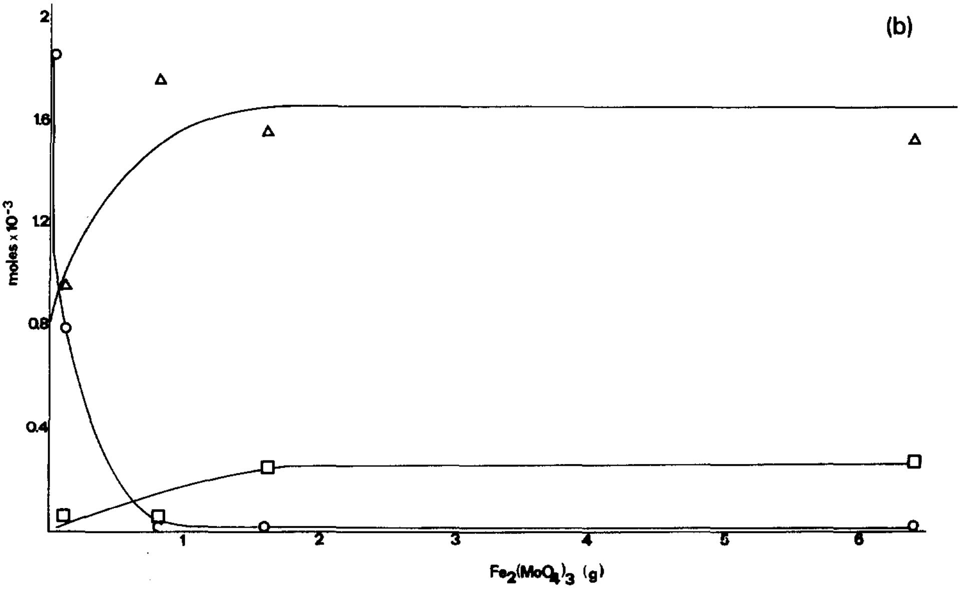


Fig. 8a. Influence of the amount of cocatalyst added on the decomposition of the initial complex [Pd(isoquinoline)$_2$Cl$_2$]; △, metallic palladium; □, soluble form of palladium; ○, [Pd(isoquinoline)$_2$Cl$_2$]. Conditions are: reaction time 30 min, temperature 160 °C, 200 atmospheres of CO pressure, [Pd(isoquinoline)$_2$Cl$_2$] 1.835×10^{-3} mol, solvent 1,2-dichlorobenzene (40 ml). Initial concentration of nitrobenzene 1.08 mol l^{-1}, final concentration of nitrobenzene 0.54 mol l^{-1}.

Fig. 8b. Influence of the amount of cocatalyst added on the decomposition of the initial complex [Pd(isoquinoline)$_2$Cl$_2$]; △, metallic palladium; □, soluble form of palladium; ○, [Pd(isoquinoline)$_2$Cl$_2$]. Conditions are as in Fig. 8a. Initial concentration of nitrobenzene 0.43 mol l^{-1}, final concentration of nitrobenzene 0.087 mol l^{-1}.

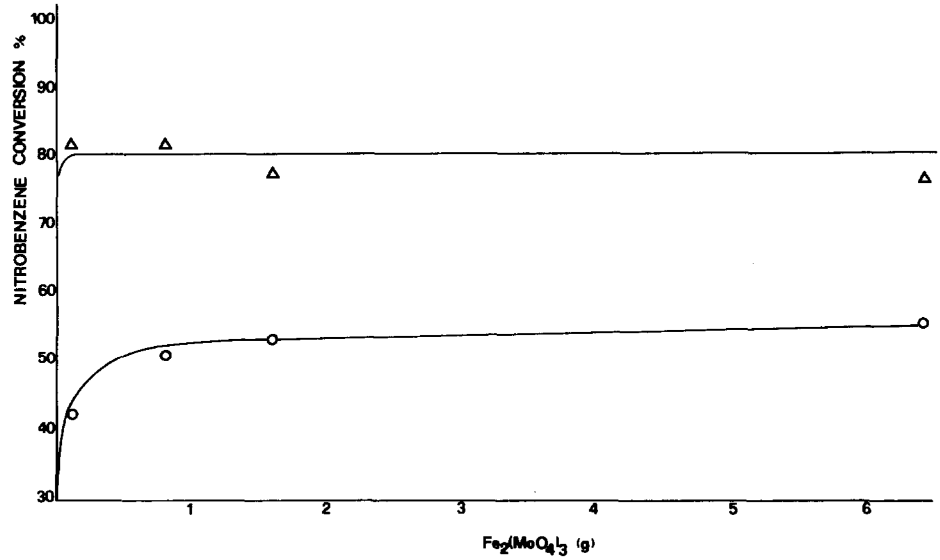


Fig. 9. Influence of the amount of cocatalyst on the conversion of nitrobenzene. Conditions are: reaction time 30 min, temperature 160 °C, 200 atm of CO pressure, [Pd(isoquinoline)$_2$Cl$_2$] 1.835×10^{-3} mol, solvent 1,2-dichlorobenzene (40 ml). ○, Initial concentration of nitrobenzene 1.08 mol l^{-1}; △, initial concentration of nitrobenzene 0.43 mol l^{-1}.

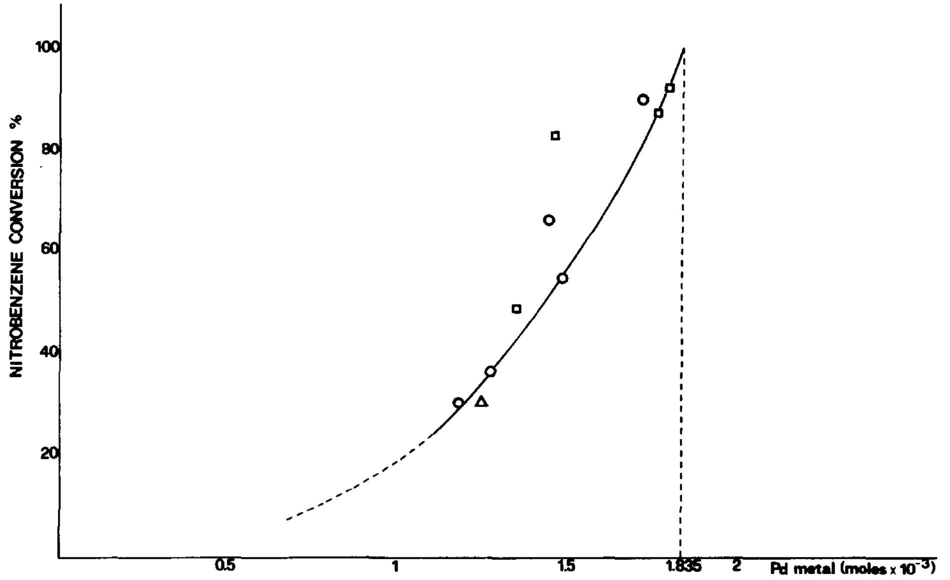


Fig. 10. Reduction of [Pd(isoquinoline)$_2$Cl$_2$] to metal as a function of initial nitrobenzene conversion. Conditions are: [Pd(isoquinoline)$_2$Cl$_2$] 1.835×10^{-3} mol, $Fe_2(MoO_4)_3$ 1.2 g, solvent 1.2-dichlorobenzene (40 ml), temperature 160 °C, 200 atm of CO pressure. □, Initial concentration of nitrobenzene 0.43 mol l^{-1}; ○, initial concentration of nitrobenzene 1.08 mol l^{-1}; △, initial concentration of nitrobenzene 2.16 mol l^{-1}.

This suggestion is to some extent supported by the IR spectra, which show the typical absorptions of NO_2, NCO and C=O groups. Furthermore, catalytic reduction of the nitro groups occurs readily.

This concurrent cyclic oligomerisation of isocyano compounds, which is not well reproducible, lowers the overall selectivity toward isocyanate formation and also (but to a lesser extent) to 2,4-TDI.

In order to increase yields of 2,4-TDI it is necessary to carry out reactions above ca. 200 ° C. For instance, the production of monoisocyano compounds is satisfactory even at 150 ° C. However, when the temperature is increased the overall selectivity towards isocyanates falls, due to the cyclic oligomerisation which is by higher temperatures favoured. A similar fall in selectivity occurs when the CO pressure is increased, probably because of a high rate of decomposition and deactivation of the catalytic system. In agreement with this suggestion, the overall selectivity remains satisfactory for reactions at high CO pressures but with very short reaction times (see Table 1). As expected, the reaction is not much affected by the amount of the cocatalyst and it even takes place in the total absence of a cocatalyst (Table 1).

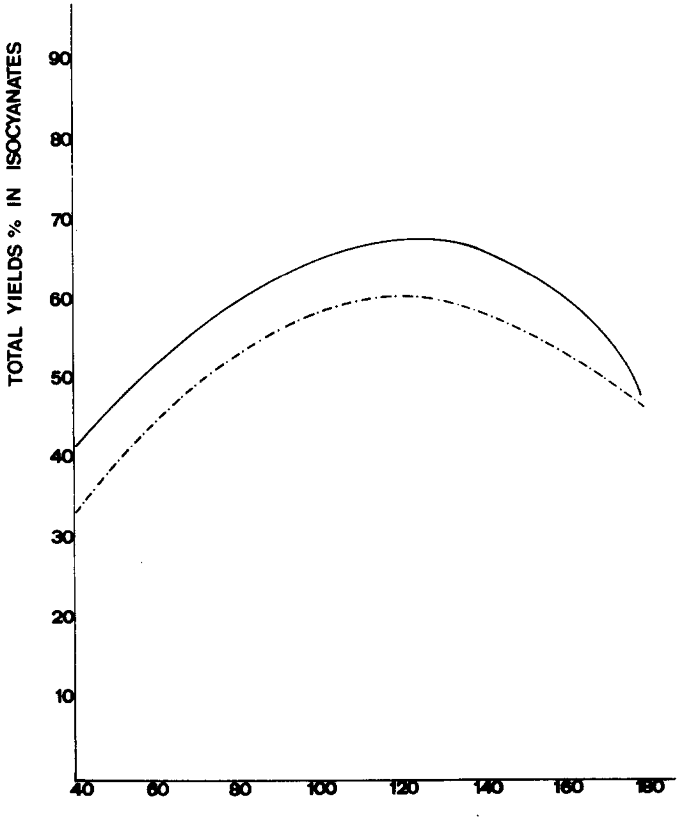


Fig. 11. Total yields in isocyanates as function of the time of the second step; reaction conditions are those standard of Table 3. ——— with 4 g of [Pd(isoquinoline)$_2$Cl$_2$] and 24 g of 2,4-DNT; –·–·–·– with 1 g of [Pd(isoquinoline)$_2$Cl$_2$] and 24 g of 2,4-DNT.

1.3. The reductive carbonylation of 2,4-DNT to 2,4-TDI with $[Pd(isoquinoline)_2Cl_2]$ and $Fe_2(MoO_4)_3$ as the catalyst system

We subsequently studied the reductive carbonylation of 2,4-DNT using $[Pd(isoquinoline)_2Cl_2]$ in the presence of $Fe_2(MoO_3)_4$, but working under reaction conditions giving greater reproducibility (see Experimental section). In this latter case the reaction must be carried out in two separate stages in order to ensure good control of the temperature. The first stage occurs at temperatures which are ca. 50 ° C lower than those used in the previous experiments (see Experimental section and Tables 1 and 2). Under these conditions mainly monoisocyano derivates (NTI) are formed. After an appropriate time the CO pressure is restored and the temperature rapidly raised to the final value of ca. 200 ° C. This second step of reaction is also carried on for a specific time (see Table 3). In this way satisfactory control of reaction temperatures is achieved. Some relevant results are reported in Table 3.

Conversions and selectivities towards isocyanates are almost independent on the total amount of cocatalyst and on the time allowed for the second stage. However the selectivity towards 2,4-TDI depends on both the time of the second step and the amount of palladium catalyst.

Since this catalytic system is very active, the oligomerisation can be completely avoided, so that good yields of isocyanates can be obtained (see Table 3). A plot of the total yields of isocyanates against time shows a maximum, suggesting that some oligomerisation does occur, but only at longer times (Fig. 11).

In addition, a high initial concentration of 2,4-DNT gives rise to lower conversions (Fig. 12); this confirms the positive effect of the concentration of the initial nitroaromatic compounds on the stability of the catalytically inactive $[Pd(isoquinoline)_2Cl_2]$ complex.

2. The reductive carbonylation of 2,4-DNT to 2,4-TDI with Pd^0 complexes as catalysts or with Pd^{II} complexes in presence of a reducing agent as the catalyst system

Our previous studies have shown that the role of the cocatalyst is to activate the palladium(II) complex, probably to generate in situ a reduced palladium complex soluble in the reaction solvent (in our case 1,2-dichlorobenzene).

We studied the reductive carbonylation of 2,4-DNT to 2,4-TDI using Pd^{II}, Pd^I and Pd^0 complexes containing the same ligand, namely $[Pd(^tBuNC)_2Cl_2]$, $[\{Pd(^tBuNC)_2Cl\}_2]$ and $[Pd(^tBuNC)_2]$. The reaction was carried out in the absence of cocatalyst in order to avoid any effect on the oxidation state of palladium.

Only the zerovalent palladium complex is active, and its activity is limited by extensive and fast decomposition to metal (Table 4). This observation suggested that the actual palladium catalyst may be in the zerovalent state, and so we extended our investigation to a series of zerovalent palladium complexes (Table 5).

These all are quite active as catalysts; their stability and selectivity to isocyanates are increased by the presence of a bidentate nitrogen donor ligand such as 1,10-phenanthroline or α,α'-dipyridyl [20]. However, in all cases the catalytic activity falls, more or less rapidly, as metallic palladium separates.

Owing to the high activity of these complexes the reaction can be carried out at 100–120 ° C (temperatures between 150–200 ° C are required with the Pd^{II} complex we used). When a higher initial temperature (195 ° C) is used, there is total conversion in only 7–8 min, but the temperature control is very poor. The selectivity towards isocyanates (both isomers of NIT, and 2,4-TDI) is acceptable at very low

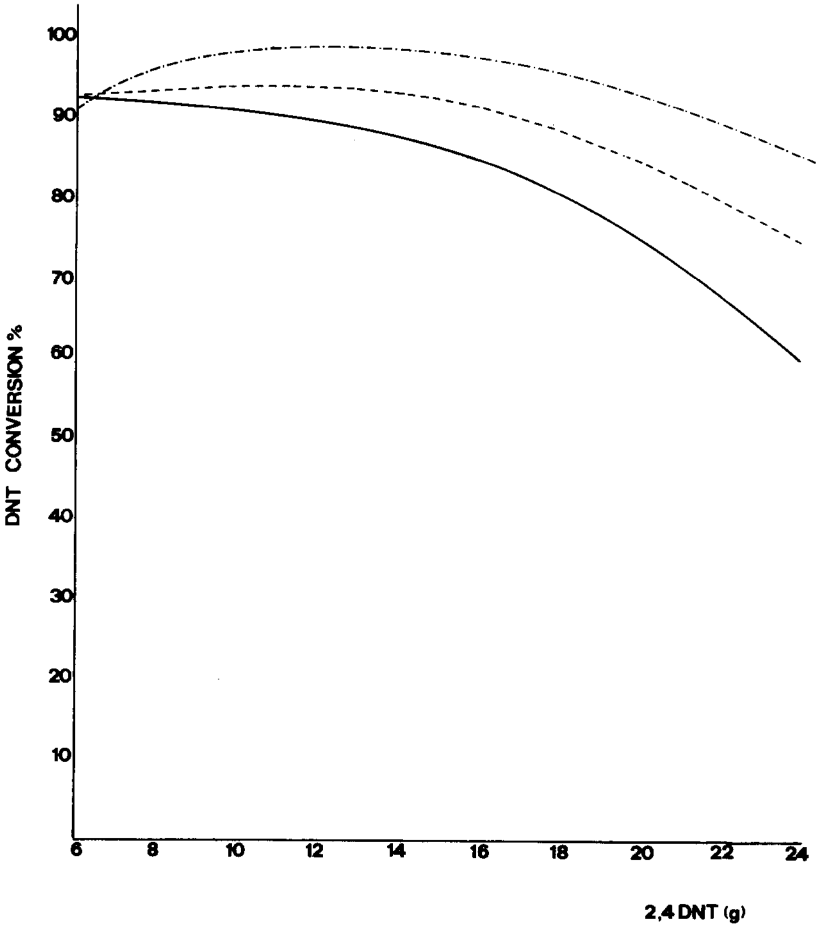


Fig. 12. Conversion of 2,4-DNT as a function of its initial total amount; reaction conditions are those standard of Table 3. –·–·–·–: with 1 g of [Pd(isoquinoline)$_2$Cl$_2$] and 180 min for the second step of reaction; ------: with 1 g of [Pd(isoquinoline)$_2$Cl$_2$] and 120 min for the second step of reaction; ———: with 1 g of [Pd(isoquinoline)$_2$Cl$_2$] and 40 min for the second step of reaction.

Table 4

Reductive carbonylation of 2,4-DNT to 2,4-DTI and to isomers of NTI (total isocyanates = TDI + Σ NTI); reaction conditions: reaction time 60 min, initial temperature 150 °C; DNT (6 g); pressure 290 atm of CO

Catalyst	Conversion 2,4-DNT (%)	Molar yields total isocyanates (%)
[Pd[^{t}BuNC]$_2$Cl$_2$] [a]	0 [d]	0
[{Pd(^{t}BuNC)$_2$Cl}$_2$]C_5H_5Cl [b]	0 [e]	0
[Pd(^{t}BuNC)$_2$] [c]	42 [f]	2.1

[a] Pd corresponding to 372 mg, 1,2-dichlorobenzene (15 ml). [b] Pd corresponding to 281 mg, 1,2-dichlorobenzene (48 ml); free ^{t}BuNC (0.2 ml). [c] Pd corresponding to 764 mg, 1,2-dichlorobenzene (52 ml); free ^{t}BuNC (0.7 ml). [d] Catalyst recovered unaltered. [e] Catalyst decomposes to [Pd(^{t}BuNC)$_2$Cl$_2$] and metallic palladium. [f] Catalyst decomposes to metallic palladium.

Table 5

Reductive carbonylation of 2,4-DNT to 2,4-TDI and NTI (total isocyanates = TDI + Σ NTI), using a series of Pd^0 complexes as catalysts. Reaction conditions: 2,4-DNT (13 g); solvent 1,2-dichlorobenzene (40 ml); pressure 250 atm of CO; time 20 min

Catalyst [a]	Ratio DNT to Pd (mol/mol)	Temperature [b] (°C)	Conversion (%) 2,4-DNT	Molar yields (%)		Selectivity total isocyanates (%)
				TDI	Σ NTI	
[Pd(*o*-phenanthroline)DBA]	60	120–130	23	0.15	3.2	15
[Pd(α,α′-dipyridile)DBA]	60	120–128	19	0.1	5	28
[Pd(α,α′-dipyridile)BQ]	60	120–124	11	0.12	0.9	9
[Pd(*o*-phenanthroline)BQ]	50	120–136	16	0.1	3.6	8
[Pd(TMEDA)BQ]	60	120–127	19	0.16	2.7	15
[Pd(^{t}BuNC)$_2$AM]	11	120–126	7	0	0.5	7
[Pd(*o*-phenanthroline)AM]	40	120–125	15	0.16	3.6	25
[Pd(DBA)$_2$]	60	120	0	0	0	0
[Pd(PPh$_3$)$_3$(CO)]	11	120	20	0	0	0
[Pd(α,α′-dipyridile)DBA] [c]	140	150	4	0	3.1	80

[a] DBA = dibenzilidene acetone; BQ = benzoquinone; AM = maleic anhydride; TMEDA = tetramethyl ethylendiamine. [b] The control of temperature, is difficult; only the range of temperatures is reported. [c] Solvent toluene (40 ml), time 7 min.

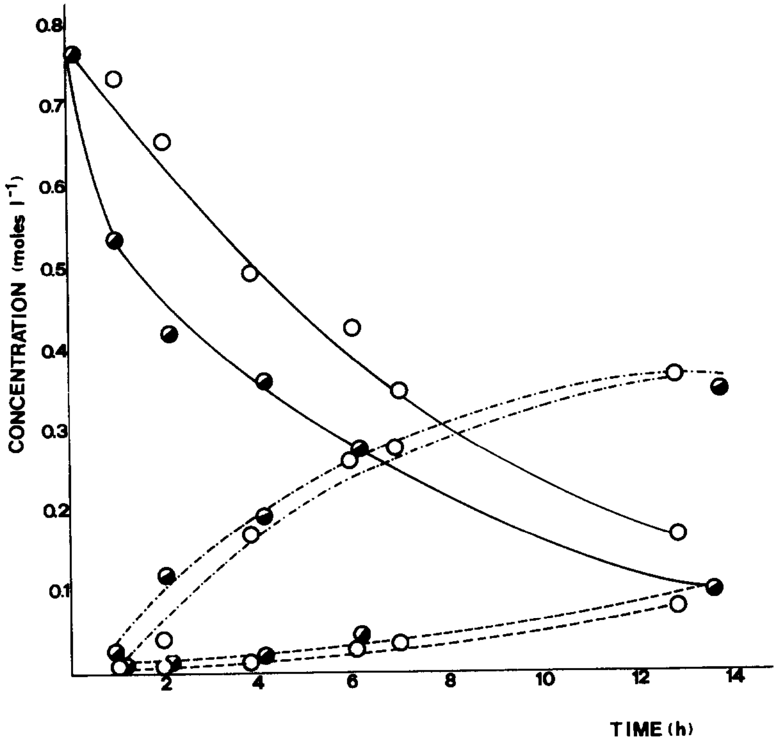


Fig. 13. Reductive carbonylation of 2,4-DNT in the absence or presence of water. Reaction conditions are: 2,4-DNT 60 g, [Pd(isoquinoline)$_2$Cl$_2$] 1.5 g, temperature 190 °C, pressure of CO 300 atm, solvent 1,2-dichlorobenzene 400 ml. ○, experiments in dry 1,2-dichlorobenzene; ◐, experiments in wet 1,2-dichlorobenzene (H_2O 2.1 g l^{-1}); ———: 2,4-DNT; –·–·–·–: Total NTI; ------: 2,4-DTI.

conversions (< 5%) but very low at higher conversions. In this latter case, by-products of the ureic type are formed. Both the activity and selectivity of the original complex can be increased by using high CO pressures (about 300–400 atm) and a very efficient phase-transfer process (good stirring) in order to maintain a high CO concentration in solution. It follows that CO can act not only as a reducing agent, but also as a ligand which stabilises the low oxidation state palladium catalyst.

Finally we investigated the effect of the addition of small quantities of reducing agents such as H_2O + CO, H_2 or HCOOH to the standard catalytic system [Pd(isoquinoline)$_2$Cl$_2$] plus cocatalyst [21]. In the presence of H_2 or HCOOH rapid reduction to metallic palladium occurs. In presence of H_2O the carbonylation of 2,4-DNT is faster but less selective towards formation of isocyanates, as is the case when a Pd^{II} complex is easily reduced to a Pd^0 complex (see Fig. 13).

In conclusion, although we established that zerovalent complexes of palladium are very active catalysts, their ready decomposition and their relatively low selectivities towards isocyanate formation do not indicate that they will find practical use. When we tried to stabilise the zerovalent state by adding a tertiary phosphine when Pd(CO)(PPh$_3$)$_3$ was used as catalyst, the formation of isocyanates was completely inhibited (see Table 5). It follows that to be active the palladium species must be not only in a low oxidation state but also have potentially vacant coordination sites.

Discussion and conclusion

We have confirmed that even with one of the best catalytic systems reported in patent literature, namely [Pd(isoquinoline)$_2$Cl$_2$], reduction to metal occurs with the concomitant deactivation of the catalytic system. However, under appropriate conditions (e.g. using a two-stage process involving two temperature steps and under high CO pressure), reasonable high yields of isocyanates with a good selectivity towards 2,4-TDI from 2,4-DNT can be achieved. Under conditions which favour a high formation of the two isomers of NTI, the yields of 2,4-TDI fall, and consequently also the total yields to isocyanates, since both NTI isomers oligomerise much more rapidly than 2,4-TDI.

During the investigation of the stability of the standard catalyst [Pd(isoquinoline)$_2$Cl$_2$] we found that a cocatalyst such as $Fe_2(MoO_4)_3$ or Fe_2O_3 plus MoO_3 activates the palladium complex through reduction of Pd^{II} to low oxidation state palladium, which probably involves an intermediate role of a reduced form of iron and oxidation of CO to CO_2.

Direct reduction of the original Pd^{II} complex by CO to form a low oxidation state palladium complex does not take place readily unless water or a strong reducing agent, such as H_2, is present.

In conclusion, our work suggests that the catalytic entity is a palladium complex in a low oxidation state. This is in line with recent findings that in the catalytic carbonylation of nitroaromatics the first step is a single electron transfer, which is favoured by low oxidation state metal complexes [22]. A further investigation involving only Pd^{II}, Pd^{I} and Pd^{0} complexes, all with the same ligands, confirms that the real catalyst is probably a soluble zerovalent complex of palladium. The nitro-aromatic substrate or one of its reaction products must play a role as ligand in this complex; we observed that the nitroaromatic substrates activate the original Pd^{II} complex but at the same time stabilise the system towards reduction to palladium metal.

Our suggestion is in line with some recent reports of isolation and characterisation of a metallacyclic palladium complex from the reaction of nitrobenzene and CO using a Pd^{II}–*o*-phenanthroline system known to produce isocyanate or carbamates catalytically [23]. In this complex, which gives some isocyanate or the corresponding carbamate upon reaction with CO, phenyl nitrosobenzene is involved in the cycle, together with two molecules of CO. It is obvious that CO must act as a ligand, since the CO pressure plays a role on both stability and activity of our catalytic system.

The activity, selectivity and stability of the catalytic system are directly related to the nature of the coordination sphere of the zerovalent palladium atom. If it is too ligand-deficient, deactivation to metal quickly occurs, but if the coordination sphere is too firmly filled the reaction and the synthesis of isocyanates are completely inhibited probably there is no interaction with the nitro-derivative.

Our interpretation of the experimental evidence provides an explanation of why a higher stability of the palladium catalytic system and a higher conversion to 2,4-TDI are observed when an excess of pyridine is added to [Pd^{II}(pyridine)$_2$Cl$_2$] [10b]. The excess of ligand stabilises the coordination sphere of the reduced palladium complex. Unfortunately an excess of nitrogen donor ligand cannot be used in practice because it catalyses the concurrent oligomerisation of isocyanates [24].

We suggest that the role of the cocatalyst is to induce the *in situ* production of a very active, probably coordinatively rather unsaturated, reduced palladium species that is soluble in the reaction medium. Both CO and the nitro substrate or its reaction products, which act as ligand, stabilise this reduced form towards decomposition to metal. When Pd^0 complexes are used as catalysts, the addition of a cocatalyst is not necessary. We thus suggest the following series of reactions, involving the original palladium catalytic complex:

$$\begin{tikzcd} \text{Pd(ligand)Cl}_2 \arrow[r, "\text{CO}", "\text{step A}"'] & \text{Pd}^0\ \text{ligand} \arrow[r, leftrightharpoons, "\text{step B}"'] \arrow[d, shift left] & \text{Pd}^0\ \text{ligand}\ \text{L}^*_n \\ & \text{Pd metal} \arrow[u, shift left] & \end{tikzcd}$$

L^* = a ligand originated from the nitrosubstrate and CO.

Step A is favoured by the addition of a cocatalyst or of a reducing agent; the actual catalyst must be the species stabilised by the step B. In addition, the low valent species formed in step A could also be active, although very unstable towards decomposition.

The mechanism of formation of the isocyanate group is not yet well understood; kinetic investigations of the carbonylation of nitrobenzene with $[Pd(pyridine)_2Cl_2]$ as catalyst [10c] and of 2,4-DNT with the same catalyst [10b] suggest that there is coordination or interaction, such as an oxidative addition, of the nitro-derivative to an active palladium species. Nitrene-type complexes, clusters, and metallacycles have been proposed as key intermediates [22,23,25].

Our suggestion that the active palladium species is stabilized by the nitro-derivative is consistent with the involvement of this reagent in the key active species in the catalytic system.

We have confirmed that a palladium(II) catalyst, when used under appropriate conditions, can give acceptable yields and selectivities in the reductive carbonylation reaction of 2,4-DNT to 2,4-TDI.

From our work it is clear that good selectivities can be achieved only with relatively low concentrations and at low extents of conversion of the nitro-derivative. Unfortunately, these conditions can be met only in the carbonylation of nitrobenzene to phenylisocyanate or of 2,4-DNT to the two isomers of NTI, because in the carbonylation of 2,4-DNT to 2,4-TDI it is impossible to work at low conversions to NTI.

The real catalytic entity, a low oxidation state Pd species generated *in situ*, is intrinsically unstable under the reaction conditions.

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