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CATALYTIC REDUCTIVE CARBONYLATION OF AROMATIC NITRO COMPOUNDS TO URETHANES PROMOTED BY SUPPORTED PALLADIUM ACTIVATED WITH 1,10-PHENANTHROLINE DERIVATIVES

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Summary

A simple catalytic system, involving supported Pd and a phenanthroline in equimolar ratio, has been shown to be very active and selective in reductive carbonylation of nitroaromatic compounds to the corresponding urethanes when the reaction is conducted in anhydrous ethanol and in the presence of a catalytic amount of a weak non-esterifiable, Brönsted acid. The chelating nitrogen donor ligand plays the role taken in other systems by large amounts of Lewis acids involving activation of the supported metals, probably to favour a fragmentation process which gives active homogeneous species. The system works best at 170–190°C and CO pressures as low as 40 bars, with turnover numbers of up to 125 cycles per hour.

Introduction

In recent papers [1,2] we showed that 2,2′-bipyridine, 1,10-phenanthroline, and related ligands can activate the rhodium and ruthenium carbonyl clusters towards the catalytic reduction of nitrobenzene to aniline by the CO + H_2O system (eq. 1), in aqueous ethanolic media.

$$PhNO_2 + 3CO + H_2O \xrightarrow{cat} PhNH_2 + 3CO_2 \qquad (1)$$

We subsequently tested both Ru and Rh in the form of supported metals for this catalytic reaction (eq. 1), and we found that the nitrogen containing chelating ligands also activate these systems [3].

The nature of such catalytic systems, simply involving a supported metal and a phenanthroline in equimolar ratios, and their ability to activate CO prompted us to try them in a reaction more interesting than the reduction of nitrobenzene, namely reductive carbonylation, which should give the aromatic urethane when conducted in alcoholic media, and to this all that was necessary to remove the water from the medium and use anhydrous alcohol.

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The catalytic synthesis of aromatic isocyanates (eq. 2) and urethanes (eq. 3) from nitroaromatics and CO is of considerable

$$PhNO_2 + 3CO \xrightarrow{cat.} PhNCO + 2CO_2 \quad (2)$$

$$PhNO_2 + 3CO + ROH \xrightarrow{cat.} PhNHCOOR + 2CO_2 \quad (3)$$

industrial [4,5] as well as academic [5–12] interest, since it would open an attractive alternative route to these important intermediates. The synthetic process at present used is based on the phosgenation of aromatic amines (eq. 4), and so the reductive

$$PhNH_2 + COCl_2 \rightarrow PhNCO + 2HCl \quad (4)$$

carbonylation would prevent the reduction of nitroaromatics to amines and remove the need to use phosgene.

Although urethanes are employed as agricultural chemicals, the aromatic isocyanates are more needed by the chemical industry, especially for the synthesis of polyurethanes. However they are extremely reactive compounds [13], and therefore not easy to handle and store. Thus many processes are directed at the synthesis of the more stable urethanes [4b–4d,10,12] by carrying out the reactions in the presence of an alcohol instead of in a pure aprotic solvent. The isocyanates can be released from the urethanes as required by simple thermal cracking (eq. 5).

$$PhNHCOOR \xrightarrow{\Delta} PhNCO + ROH \quad (5)$$

Most of the reported catalytic systems consist of a noble metal, or salt or complex thereof, plus a Lewis acid as cocatalyst [4c,5,6,8,10]; the palladium based systems appear to be the most selective. A large excess of a tertiary amine (usually pyridine or Et_3N) is often required in order to improve selectivity [4c,5,10] and simplify the catalyst recovery [4c].

In the absence of a Lewis acid the supported Pd is inactive, even in the presence of an excess of pyridine [5], whereas under such conditions both $PdCl_2$ [4b] and Rh/Al_2O_3 [9] show appreciable activity. Complexes of the type $[Pd(py)_2Cl_2]$ and $[Rh(py)_3Cl_3]$ are active in aprotic solvents at low py/metal ratios [4a,11]. $PdCl_2$ is active even by itself, but under more severe conditions [7]. Recently a quite different catalytic system, based on $Ru_3(CO)_{12}$ plus a tetraalkylammonium salt as cocatalyst, has been reported [12]. Almost all these systems require elevated CO pressures, usually in the range 60–200 atm, and rather high temperatures, in the range 160–270°C; the most severe conditions are necessary to obtain activity from supported metals in the absence of Lewis acids [9] or from $PdCl_2$ alone [7].

In this paper we describe some of our work in this field, namely that on systems based on supported metals. Some preliminary results have already been reported [14].

Results and discussion

Some of the results obtained in the reduction of nitrobenzene with $CO + H_2O$, which prompted us to test our catalytic system in other reactions of carbon monoxide, are summarized in Table 1. They show the parallel between the effectiveness of carbonyl clusters and supported metals [15,16], as well as the importance of

TABLE 1

CATALYTIC REDUCTION OF NITROBENZENE TO ANILINE WITH CO + H_2O (Reaction conditions: $[Sub]/[M]_0$ 250, T 180°C, P(CO) (30 atm (r.t.); medium: EtOH 90% (50 ml))

Precursor, M	$[chel]/[M]_0$	Time (h)	Aniline (%)
$Rh_6(CO)_{16}$	–	1	0
$Rh_6(CO)_{16}$ + TMphen [a]	1	1	95.0
Rh/Al_2O_3 (5%)	–	2	4.0
Rh/Al_2O_3 (5%) + TMphen [a]	1	2	99.0
$Ru_3(CO)_{12}$	–	1	7.0
$Ru_3(CO)_{12}$ + Phen	1	1	94.0
Ru/Al_2O_3(5%)	–	2	38.0
Ru/Al_2O_3(5%) + Phen	1	2	93.0

[a] TMphen = 3,4,7,8-Me_4Phen.

the chelating ligand (chel) for activation of the systems *. In the absence of a phenanthroline both the clusters and the supported metals are inactive (or at best very weakly active in the case of ruthenium), while the presence of a chelating nitrogen donor ligand (chel/M = 1) in every case induces a significant activity.

In the tests of such systems in the reductive carbonylation of nitrobenzene, preliminary screening of the Group VIII transition metals showed that only palladium and, to a lesser extent, platinum were active under the conditions we used. Thus all the results presented refer to the palladium-based systems.

As can be seen from Table 2 the presence of a nitrogen donor chelating ligand is again essential for catalytic activity. The supported Pd by itself is inactive and it remains virtually so even in the presence of a large excess of a unidentate ligand as pyridine [5]. In contrast, addition of the chelating ligand, even at a chel to Pd ratio $\leqslant 1$, promotes the catalytic activity; this is still low when the ligand is flexible (Bipy) but becomes appreciable when it is rigid (Phen), and increases on going to a more powerfully σ donor, viz. 3,4,7,8-Me_4Phen. Nevertheless the selectivity for formation of urethane is still disappointing, the by-products being aniline and, mainly, azo- and azoxy-benzene.

In order to reduce the yield of condensation products, a Brönsted acid was added to the catalytic system (Pd/C + 3,4,7,8-Me_4Phen); the results were in the expected direction, but appropriate acid must be used. A weak organic acid such as acetic acid is very effective in increasing the selectivity (87.5%) and the activity (95.5% of conversion in 2 h), but it has to be used in large amounts ($CH_3COOH/Pd = 100$) since it is readily esterified; this reaction not only removes the acid but also produces water, and this increases the production of aniline via the reduction pathway (eq. 1).

Use of 2,4,6-trimethylbenzoic acid (2,4,6-TMBA) eliminates the possibility of esterification and so minimizes the water content; thus an increase in selectivity for urethane is obtained at the expense of aniline, and, since this acid is not consumed during the reaction it can be used in catalytic amounts.

In the light of these results the catalytic system formed by Pd/C + chel (chel =

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* Several other parallels between clusters and the corresponding supported metals have been demonstrated [3] (e.g. P(CO), chel nature, chel/M ratio...), but are not described here for the sake of brevity.

TABLE 2

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO (Catalyst precursor: Pd/C (5%)+chel) (Reaction conditions: $PhNO_2$: 0.01 mol (1 ml); $[PhNO_2]/[Pd]_0$ 125; *P*(CO) 40 bars (r.t.); *T* 180°C; medium: dry ethanol (25 ml))

Chel	$[chel]/[Pd]_0$	Conversion (%) (2 h)	Urethane (%) (2 h)	Selectivity
Py	300	traces	–	–
Bipy	1	10.0	5.0	50.0
Phen	1	38.5	23.0	59.5
3,4,7,8-Me_4Phen	1	42.5	22.0	51.5
3,4,7,8-Me_4Phen	0.5	32.5	24.2	74.5

3,4,7,8-Me_4Phen) + 2,4,6-TMBA was studied in greater detail, in order to optimize, both the catalytic activity and selectivity; these both increase as the volume of the alcohol medium is reduced (Fig. 1) and when the acid to Pd ratio is increased (Fig. 2), so that under optimal conditions (2,4,6-TMBA/Pd 8) the reaction is complete within 2 hours and has a selectivity $\geqslant$ 95%. But it can also be seen from Fig. 2 that even at acid to Pd ratios as low as 2, both conversion and selectivity are greater than 90% even within 2 hours.

Other hindered acids, such as the 2,6-dimethylbenzoic and 2,6-dimethoxybenzoic,

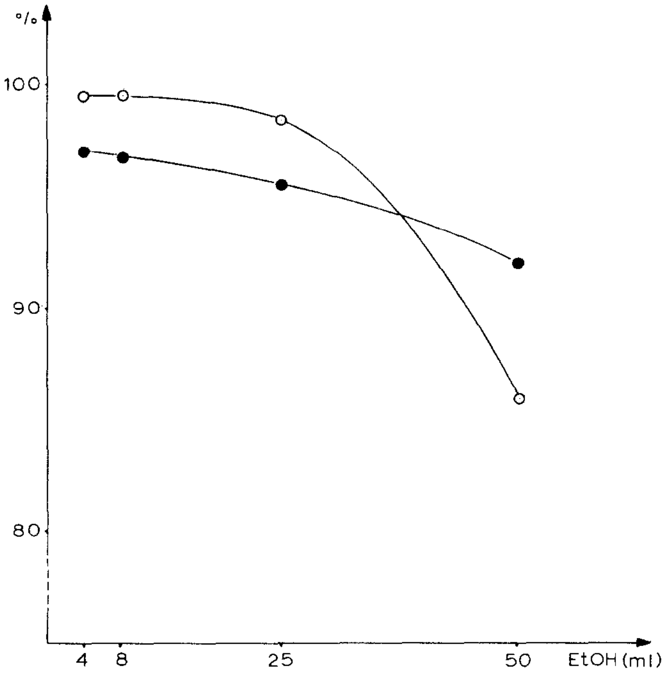

Fig. 1. Variation of the catalytic activity and selectivity with the volume of ethanol used. ○ = conversion, ● = selectivity, catalyst precursor: Pd/C(5% + 3,4,7,8-Me_4Phen + 2,4,6-TMBA, reaction conditions: $PhNO_2$: 0.01 mol (1 ml); $[PhNO_2]/[Pd]_0$ 125; $[3,4,7,8\text{-}Me_4Phen]/[Pd]_0$ 1; 2,4,6-TMBA/Pd_0 8; *P*(CO) 40 bars (r.t.), *T* = 180°C; medium: dry ethanol.

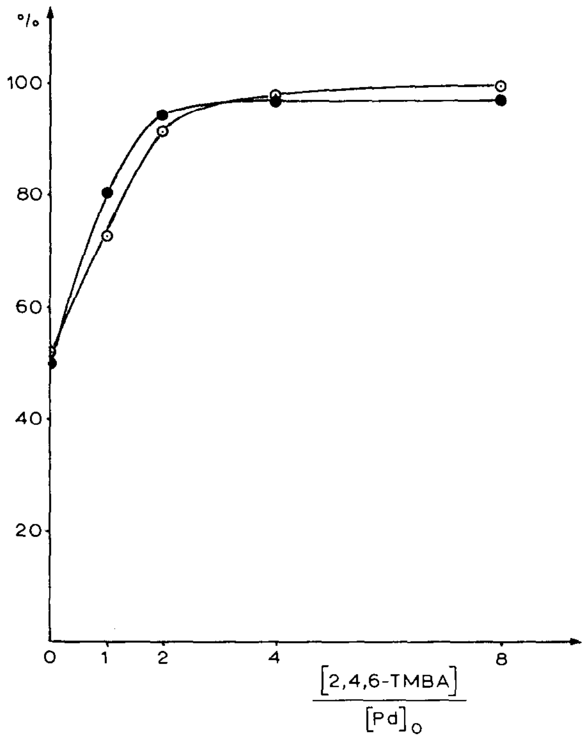

Fig. 2. Variation of the catalytic activity and selectivity with acid to palladium ratio. ○ = conversion, ● = selectivity, catalyst precursor: Pd/C(5%)+3,4,7,8-Me_4Phen+2,4,6-TMBA, reaction conditions: see Fig. 1, medium: dry ethanol (8 ml).

were examined for comparison with the 2,4,6-TMBA, with the objective of working at even lower acid/Pd ratios; the reactions were conducted at an acid to Pd ratio of 2 in order to show up possible differences between these systems but the results reveal no significant variations in activity or selectivity.

The dependence of the nature of the chel ligand was re-examined in the presence of acid and under the best catalytic conditions, (Table 3) and the results confirm the features noted above, namely: that the catalytic activity (i) depends on the presence of a chelating ligand, (ii) increases from a flexible to a rigid ligand, and (iii) increases

TABLE 3

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO. (CATALYST PRECURSOR: Pd/C(5%) + chel + 2,4,6-TMBA) (Reaction conditions: $PhNO_2$: 0.01 mol (1 ml); $[PhNO_2]/[Pd]_0$ 125; 2,4,6-TMBA/$[Pd]_0$ 8; P(CO) 40 bar (r.t.); T 180°C; medium: dry ethanol (8 ml))

Chel	[Chel]/$[Pd]_0$	Conversion (%) (2 h)	Urethane (%) (2 h)	Selectivity
Py	2	–	–	–
Bipy	1	21.0	20.5	97.6
Phen	1	78.6	73.1	93.0
3,4,7,8-Me_4Phen	1	99.3	95.9	96.6
2,9-Me_2Phen	1	4.8	3.6	75.0

TABLE 4

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO. (Catalyst precursor: Pd/C (5%)+3,4,7,8-Me_4Phen + 2,4,6 TMBA, for reaction conditions see Table 3)

$[Chel]/[Pd]_0$	Conversion (%) (1 h)	Urethane (%) (1 h)	Selectivity
0.5	31.1	30.3	97.4
1	77.5	75.2	97.0
2	97.6	95.0	97.3
3	97.5	94.1	96.5

with the donor power of the chel ligand, so that 3,4,7,8-Me_4Phen is the most effective. Furthermore (iv) steric hindrance near the nitrogen atoms (as in 2,9-Me_2Phen), is a powerful inhibiting factor, as previously observed [1,2].

With 3,4,7,8-Me_4Phen the influence of the chel/Pd ratio was also studied. The results shown in Table 4 show that the system is strongly influenced by this ratio and, although the activity is fairly high even for ratios < 1, it reaches a maximum value of 2. Further increase of the chelating ligand amount has no significant effect. In contrast, the selectivity is not influenced by the nature of the chel ligand or the Pd/chel ratio, but seems to depend only on the amount of acid present.

It is noteworthy, that for a chel/Pd ratio of 2 the reaction is almost complete within 1 hour, rather than 2, from the start of the heating, i.e. after about 30 minutes under the steady conditions, and always shows a a selectivity $> 95\%$. Under the conditions specified in Table 3, with a chel/Pd ratio of 2, 2 ml of nitrobenzene ($PhNO_2$/Pd 250) (i.e. twice the normal amount) are almost completely converted within 2 hours with the same selectivity.

The dependence of the activity and selectivity of the system on the temperature is shown in Table 5. There is a maximum at 180°C, and while the loss of activity at lower temperatures was expected, that at higher ones was less predictable; it may be attributed to a displacement of the ligand from the active species and consequent shift of the equilibria towards the inactive metal.

As for the CO pressure, 40 bars at room temperature seems to be the most suitable for this system under our conditions; lower pressures reduce the rate and lower the selectivity while higher ones have no positive influence of the activity (Table 6). This feature might appear unusual when compared with data for other catalytic systems, which almost always require far higher pressures for a good

TABLE 5

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO (Catalyst precursor: Pd/C (5%) + 3,4,7,8-Me_4Phen + 2,4,6-TMBA) (For reaction conditions see Table 3 [3,4,7,8-Me_4Phen]/$[Pd]_0$ 1)

Temperature (°C)	Conversion (%) (1 h)	Urethane (%) (1 h)	Selectivity
160	48.6	45.4	93.4
170	59.2	55.0	93.0
180	77.5	75.2	97.0
190	75.5	71.1	94.2

TABLE 6

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO (Catalyst precursor: Pd/C(5%)+3,4,7,8-Me_4Phen+2,4,6-TMBA) (For reaction conditions see Table 5)

P(CO) (atm)	Conversion (%) (1 h)	Urethane (%) (1 h)	Selectivity
20	40.0	34.2	85.7
30	59.0	52.8	89.5
40	77.5	75.2	97.0
50	71.3	68.6	96.2

TABLE 7

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO (Catalyst precursor: Supported Pd+3,4,7,8-Me_4Phen+2,4,6-TMBA) (Reaction conditions: $PhNO_2$: 0.01 mol (1 ml); $[PhNO_2]/[Pd]_0$ 125; $[3,4,7,8\text{-}Me_4Phen]/[Pd]_0$ 1; $[2,4,6\ TMBA]/[Pd]_0$ 2; T 180°C; P(CO) 40 bar (r.t.); medium; dry ethanol (8 ml))

Precursor	Conversion (%) (2 h)	Urethane (%) (2 h)	Azo + Azoxybenzene (%) (2 h)	Selectivity
Pd/C (5%)	91.0	85.5	1.2	94.0
Pd/$BaSO_4$ (5%)	99.7	91.5	6.6	91.7
Pd/Al_2O_3 (5%)	98.3	70.5	25.7	71.8
Pd/Al_2O_3 (10%)	98.1	80.5	16.1	81.9

TABLE 8

SYNTHESIS OF PHENYLURETHANE FROM NITROBENZENE AND CO (Catalyst precursor: M/C (5%)+3,4,7,8-Me_4Phen+2,4,6-TMBA) (Reaction conditions see Table 5)

Precursor	Conversion (%) (2 h)	Urethane (%) (2 h)	Selectivity
Ru/C 5%	8.0	–	–
Rh/C 5%	1.2	1.1	–
Pd/C 5%	99.3	95.9	96.6
Pt/C 5%	9.5	5.7	60.0

activity, and it must depend on competition between CO and the chelating ligand for the coordination to the metal centre previously noted for our systems [2]. Since the presence of the ligand is essential for catalytic activity, high CO pressures can have an unfavourable effect on the overall outcome because they can reduce the formation of the active species at the same time as promoting the various steps of the reaction.

All the reported experiments were conducted with palladium supported on carbon; the choice of this system is justified by the results obtained with the other carriers (Table 7), these were only tested for an acid to Pd ratio of 2.

Pd on $BaSO_4$ shows a higher activity than Pd on carbon, but this was counterbalanced by a lower selectivity. The use of alumina in this case is very unfavourable; entry 4 in Table 7 reveals that the loss of selectivity obtained with Pd/Al_2O_3 (entry

3) is ascribable to the support, since the smaller the amount of alumina used and the lower is the percentage of condensation products. These differences may depend not only on the deposition methods and therefore on the size of the metal particles and their positions on the carrier, but also on the special properties of the support especially on the presence of acidic or basic groups; alumina in particular is more basic than the other supports examined.

The choice of palladium is also justified by comparison with other similar systems under optimal reaction conditions (Table 8). The outstanding activity of palladium is not surprising since it is one of the metals most commonly specified in the patent literature for this reaction, and seems to give the best results [5].

As for the mechanism of formation of isocyanides some authors propose initial deoxygenation of nitrobenzene to a nitrene, followed by CO insertion to give the product [7,9]; this route would also account for the by-products commonly formed. In one case the deoxygenation step is rate determining [8], where as in another the CO insertion step is believed to be so [9].

The synthesis of the urethanes can be assumed to follow this route up to formation of the isocyanate, which would then immediately react with the solvent alcohol to give the final product [13]; indirect evidence of similar behaviour is found in the catalytic carbonylation of aromatic azides, which in aprotic solvents, under mild conditions give the corresponding isocyanate [17,18], whereas in the presence of ethanol or aniline they give the urethane or diphenylurea, respectively [19].

To our knowledge, only in one case has a mechanism been proposed for the reductive carbonylation to urethanes, and this did not take into account the possible formation of the isocyanate [12]. On the other hand, at the present moment, the evidence we have argues in favour of a mechanism involving isocyanate formation; when an aprotic solvent such as benzene is used instead of ethanol under very similar reaction conditions, high yields of phenyl isocyanate are obtained [20].

When the reaction is monitored chromatographically no formation of nitrosobenzene can be detected and so deoxygenation of such an intermediate seems unlikely to be rate determining, though the observation does not rule out the possibility that deoxygenation of nitrobenzene to nitrene takes place in a single step, as previously proposed [8], without going through a nitroso intermediate.

In our opinion the CO insertion is more likely to be rate determining provided that the intermediate is sufficiently stabilized by coordination; multi-site coordination of nitrene moieties to iron and ruthenium clusters has been observed [21–24], and proposed to be relevant in the synthesis of isocyanates on a rhodium surface [9].

We have not direct information yet on the nature of the active species, but some results lead us to believe that it must be a palladium complex with the chelating ligand, probably in a 1/1 ratio, active in the homogeneous phase and possibly in equilibrium with the metal. The visible absorption spectra of the solutions extracted from the autoclave at the end of the runs, shown in Fig. 3 support this view, that solutions always have an orange-red colour even when the substrate is absent. From Fig. 3 it is clear that the spectra have a maximum in the visible region whose position depends on the nature of the added chelating ligand; of particular interest is the bathochromic shift associated with 4,7-Ph_2Phen. These charge transfer bands indicate that some palladium must be present in the liquid phase and that it is complexed with the chelating ligand, since the maximum varies with the ligand. Thus the chelating ligand must promote the catalytic activity by inducing a disaggregation

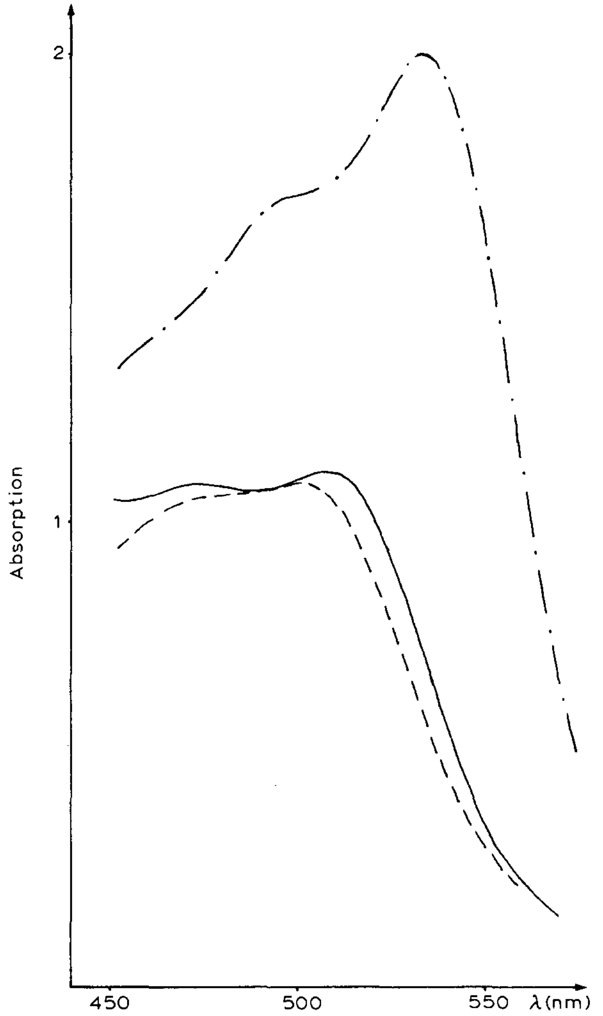

Fig. 3. Absorption spectra in the visible region of the solutions withdrawn from the autoclave. -·-·- 4,7-Ph_2Phen, ——— Phen, - - - - - - 3,4,7,8-Me_4Phen, Catalyst precursor: Pd/C(5%)+chel+2,4,6-TMBA, reaction conditions: see Table 5.

of the metallic surface; during this process the palladium may change its oxidation state, becoming palladium(I) or palladium(II). This oxidation step could be favoured by the presence of the Brönsted acid, through an oxidative addition of a proton; it must be remembered that the acid not only has a favourable effect on the selectivity but also greatly increases the catalytic activity.

The poor π back-bonding ability of palladium(II) complexes, which should lead to activation of the coordinated CO towards nucleophilic attack by making it a more acidic centre [25], is another feature which favours the view that the active species involves Pd in a high oxidation state. Whatever the oxidation state, if the proposal of an homogeneous activity species is valid, then the use of an appropriate palladium complex containing the chelating ligand should increase the catalytic activity, since the disaggregation process, which for certain metals has a high activation energy, would be avoided. Use of complexes in different oxidation states should give a more reliable guide to the actual oxidation state of the active species and possibly even allow isolation and characterization of these species. We have already obtained some results in this area, and they will be presented in a forthcoming paper.

Conclusions

The simple catalytic system described brings about reductive carbonylation of nitrobenzene to the corresponding urethane with a high selectivity and catalytic activity (at least comparable to those described in the patent literature) at relatively low CO pressures and, most importantly avoiding the presence of large amounts of anhydrous Lewis acids and/or tertiary amines which are usually employed to activate the metallic surfaces: Preliminary results show that the catalytic system also shows a good activity and selectivity in the reductive carbonylation of 2,4-dinitrotoluene [26].

The second aspect of this work concerns the nature of the activation of supported noble metals by the chelates. The fragmentation suggested probably occurs also in the presence of carbon monoxide alone, but they could only be revealed with difficulty mainly because it would occur to such a slight extent that any catalytic activity might be assigned to the metallic surface even if homogeneous species are partly responsible.

The addition of the nitrogen donor chelating ligands not only shifts the fragmentation equilibria towards active homogeneous species of low nuclearity but also reveals their existence through the appearance of strong charge transfer bands in the visible region. That these or related species are active is indicated by various features, which are inconsistent with a completely heterogeneous active system.

The use of an appropriate chelating ligand may, in addition to being used to promote catalytic activity, also provide a diagnostic method for determining whether the metal surface or a homogeneous species (or both) is the active system.

Experimental

Chemicals

Nitrobenzene (Carlo Erba) was shaken three times with 0.1 *M* KOH, then washed with water, shaken overnight with anhydrous Na_2SO_4, distilled under vacuum, and stored under argon in a sealed vial over silica gel.

The ethanol was dried as follows: commercial absolute ethanol (Carlo Erba) (50 ml) was refluxed for 2–3 hours with 5 g of magnesium (activated by a little sublimed I_2) then a further 950 ml were added. The mixture was refluxed for a further 5 h then distilled under argon, and stored under argon in a sealed bottle.

Each sample of nitrobenzene and of ethanol was withdrawn under a stream of argon.

The supported metals (Fluka), the hindered acids (Fluka), and the chelating ligands (Janssen, Fluka) were used as supplied.

Procedure

All reactions were carried out in a Berghof stainless steel autoclave (100 ml), equipped with a Teflon liner, magnetic stirrer, manometer, heating mantle, and temperature controller.

In a typical reaction, the supported metal, chelating ligand, and hindered acid were placed in the liner, and the alcohol and nitrobenzene were placed in a two necked flask connected to the autoclave through a PTFE tube. The whole apparatus was purged with CO for 20 min before the solution was transferred to the autoclave. The autoclave was then charged to the appropriate CO pressure and heated to the required temperature (Thermal equilibrium was usually reached in about 30 min). At the end of the run the autoclave was cooled and its contents were filtered to remove the supported metal from the solution. The products were analyzed by use of a DANI 6800 gas chromatograph (10% SE 30; 3 m) equipped with a Shimadzu C-R1A data processor.

The visible absorption spectra were recorded on a Cary 219 spectrophotometer.

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References

1 E. Alessio, F. Vinzi and G. Mestroni, J. Mol. Catal., 22 (1984) 327.
2 E. Alessio, G. Clauti and G. Mestroni, J. Mol. Catal., in press.
3 E. Alessio, G. Clauti and G. Mestroni, XVII National Symposium of Inorganic Chemistry, Cefalu, 1984.
4 (a) Mizoguchi et al., 1975, U.S. Patent 3,903,125; (b) Zajacek et al., 1976, U.S. Patent 3,993,685; (c) Hirai et al. 1980, U.S. Patent 4,186,269; (d) S. Cenini et al., 1983, Italian Patent 21951 A/83.
5 P. Braunstein, R. Bender and J. Kervennal, Organometallics, 1 (1982) 1236 and ref. therein.
6 W.B. Hardy and R.P. Bennet, Tetrahedron Lett., 11 (1967) 961.
7 F.J. Weigert, J. Org. Chem., 38 (1973) 1316.
8 K. Unverferth, R. Hontsch and K. Schwetlick, J. Prakt. Chemie, 321 (1979) 86; 321 (1979) 928.
9 B. Elleuch, Y. Ben Taarit, J.M. Basset and J. Kervennal, Angew. Chem. Int. Ed. Engl., 21 (1982) 687.
10 Y. Watanabe, Y. Tsuji and N. Suzuki, Chem. Lett., (1982) 105.
11 S.P. Gupta and R.C. Chaudhari, J. Mol. Catal., 24 (1984) 197.
12 S. Cenini, M. Pizzotti, C. Crott, F. Porta and G. La Monica, J. Chem. Soc., Chem. Comm., (1984) 1286.
13 R.G. Arnold, J.A. Nelson and J.J. Verbanc, Chem. Rev., 57 (1957) 47.
14 E. Alessio and G. Mestroni, J. Mol. Catal., 26 (1984) 337.
15 E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, Chem. Rev., 79 (1979) 91.
16 R. Ugo and R. Psaro; J. Mol. Catal., 20 (1983) 53 and ref. therein.
17 J.P. Collman, M. Kubota and J.W. Hosking, J. Am. Chem. Soc. 89 (1967) 4809.
18 S. Cenini and G. La Monica; Inorg. Chim. Acta Rev., 18 (1976) 279.
19 G. La Monica and S. Cenini, J. Organomet. Chem., 216 (1981) C35.
20 E. Alessio and G. Mestroni, unpublished results.
21 M.A. Andrews and H.D. Kaesz; J. Am. Chem. Soc., 99 (1977) 6763.
22 S. Aime, G. Gervasio, L. Milone, R. Rossetti and P.L. Stanghellini, J. Chem. Soc. Dalton Trans., (1978) 534.
23 F.L'Eplattenier, P. Matthys and F. Calderazzo, Inorg. Chem., 9 (1970) 342.
24 S. Bhaduri, K.S. Gopalkrishnan, G.M. Sheldrick, W. Clegg and D. Stalke, J. Chem. Soc. Dalton Trans., (1983) 2339.
25 F. Calderazzo and D. Belli Dell'Amico, Inorg. Chem., 20 (1981) 1310.
26 E. Alessio and G. Mestroni, 1984, Italian Patent 21401 A/84.