Palladium and silver reductive catalyzed carbonylation of nitrobenzene to methyl N-phenylcarbamate

Roberto Santi *, Anna Maria Romano *, Francesco Panella, Claudio Santini

EniChem, Istituto G. Donegani, via Fauser, 4, 28100 Novara, Italy

Abstract

Methyl N-phenylcarbamate has been synthesized by reductive carbonylation of nitrobenzene. Homogeneous catalytic systems based on palladium and silver salts, 1,10-phenanthroline (phen) and p-toluensulfonic acid (PTS) were found highly active and selective yielding nitrobenzene conversion up to 96%. The effect of Ag/Pd molar ratio has been studied. Copper (II) and mercury (II) acetates as cocatalysts in palladium based bimetallic systems also behaved satisfactorily. © 1997 Elsevier Science B.V.

Keywords: Reductive carbonylation; Nitrobenzene; Palladium; Silver; Copper; Mercury

1. Introduction

The direct carbonylation of nitroaromatics into the corresponding isocyanates (or carbamates, if an alcohol is present) is an important target reaction, from an industrial viewpoint, as it provides a phosgene- and aromatic amines-free route for the synthesis of these commercially important intermediates.

Industrially aromatic isocyanates are manufactured by phosgenation of the aminocompounds, deriving from the catalytic reduction of the corresponding nitroderivatives.

Reductive carbonylation of nitroderivates, occurring through

$$ArNO_2 + 3CO \rightarrow ArNCO + 2CO_2, \qquad (1)$$

is an attractive route as it eliminates the toxic phosgene, the carcinogenic amines and the hydrochloric acid co-product. The reaction, although thermodynamically favoured ($\Delta H_r^0 = -130$ kcal/mol), does not occur in the absence of a catalyst [1]. More conveniently, such a reaction can be carried out in an alcoholic medium to afford urethanes,

$$ArNO_2 + 3CO + ROH \rightarrow ArNHCOOR + 2CO_2 \qquad (2)$$
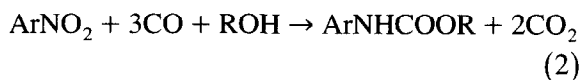
Usually, the catalytic systems for such a reaction are based on palladium [2–5], rhodium [6–8] or ruthenium [9–12] complexes.

The most reactive and selective systems reported up to date are those based on palladium catalysts. Drent and Van Leeuwen claimed high catalytic activity in carbonylation of nitroderivates when a chelating nitrogen ligand-based palladium catalyst is used [13].

* Corresponding author. Tel.: +39-32-1447532; fax: +39-32-1447425.

Catalytic systems based on palladium complexes in the presence of a Lewis acid have been used in the synthesis of isocyanates (Eq. (1)). All the active cocatalysts were Lewis acid [14] containing redox-active metals, like iron [15,16], vanadium [17,18] or molybdenum [19–21] salts, or their mixture.

In this paper, we report the results of methyl-N-phenylcarbamate synthesis by reductive carbonylation of nitrobenzene in the presence of a bimetallic system, based on homogeneuos palladium and silver compounds.

2. Results and discussion

The promotional effect of silver salts, such as AgF, Ag(OAc), Ag(tfa) (OAc = acetate; tfa = trifluoroacetate) in reductive carbonylation of nitrobenzene with the homogeneous $Pd(OAc)_2$-1,10-phenanthroline (phen) and p-toluenesulfonic acid (PTS) catalyst are summarized in Table 1.

Particularly, the catalytic system containing $Pd(OAc)_2$ and either Ag(OAc) or AgF (molar ratio Pd/Ag = 1/1) showed higher nitrobenzene conversion and selectivity into carbamate in comparison to the experiment conduced with $Pd(OAc)_2$ alone (run 2 and 3 vs. 1). In all experiments, diphenylurea was the major by-product; it arises from palladium(II) catalyzed

reaction of nitrobenzene, carbon monoxide and aniline [22]. The latter probably originates from reduction of nitrobenzene with CO and trace of water [23], although 2,2′-dimethoxypropane (DMP) was added as dehydrating agent.

On the other hand, using Ag(tfa) as cocatalyst (run 4) we observed an increase in the selectivity to urethane, while the conversion was a bit lowered.

The use of $Pd(tfa)_2$ alone gave a similar result to $Pd(OAc)_2$ (run 5 vs. 1), but the combination of $Pd(tfa)_2$ and Ag(tfa) caused a noteworthy increase of conversion and selectivity into phenylcarbamate (run 6). A less coordinating anion, such as trifluorocetate with respect to acetate and fluoride, allowed us to increase the catalytic activity, since it tends to compete to a minor extent than the substrate for the metal center.

Blank experiments carried out in the absence of palladium indicated that silver alone was completely inactive as catalyst.

The effect of Ag/Pd molar ratio has been reported in Table 2 ($Pd(OAc)_2$ and Ag(OAc) catalyzed experiments were studied). Keeping the palladium concentration constant, the best value of nitrobenzene conversion and selectivity into carbamate was found for an equimolar ratio between Ag and Pd. The silver synergic action on the catalytic system has been observed only when it was added to the usual palladium

Table 1
Effect of silver salts addition on the reductive carbonylation of nitrobenzene catalysed by $Pd(OAc)_2$ and $Pd(tfa)_2$

Run	Catalytic precursor	PhNO$_2$ conv. (% mol)	PhNHCOOMe selectivity (% mols)	PhNH$_2$ selectivity (% mol)	(PhNH)$_2$CO selectivity (% mol)	PhN=NPh selectivity (% mol)	PhN(O)=NPh selectivity (% mol)
1	Pd(OAc)$_2$	88	75	2.8	10	0.5	3.4
2	Pd(OAc)$_2$/AgOAc	94	78	2.3	9.1	0.3	1.9
3	Pd(OAc)$_2$/AgF	96	79	4.4	9	0.3	1.6
4	Pd(OAc)$_2$/Agtfa	86	81	1.5	11	0.1	2
5	Pd(tfa)$_2$	81	78	2	9.5	0.1	1.1
6	Pd(tfa)$_2$/Agtfa	95	83	1.8	8.5	0.3	1.4

Reaction conditions: [nitrobenzene] 1.34 M; [Pd] 6.68×10^{-4} M, [Ag] 6.68×10^{-4} M; [phen] 5.34×10^{-2} M, [PTS] 2.0×10^{-2} M, [nitrobenzene]:[Pd]:[Ag]:[phen]:[PTS] = 2000:1:1:70:30; $P(CO)$ = 60 bar; T = 135°C; t = 2 h; MeOH 100 ml, DMP 1 ml.
DMP = 2,2′-dimethoxypropane; OAc = acetate; tfa = trifluoroacetate; phen = 1,10-phenanthroline; PTS = p-toluenesulfonic acid.

Table 2

Effect of the variation of $Ag(OAc)/Pd(OAc)_2$ molar ratio in nitrobenzene reductive carbonylation at constant $Pd(OAc)_2$ concentration

Run	[Ag]/[Pd] molar ratio	PhNO$_2$ conv. (% mol)	PhNHCOOMe select. (yield) (% mol)
1	0	88	75 (66)
2	0.5	90	74 (67)
3	1	94	78 (73)
4	2	79	78 (62)

Reaction conditions: [nitrobenzene] = 1.34 M; [Pd] = 7×10^{-4} M; [phen] = 5.34×10^{-2} M; [PTS] = 2.0×10^{-2} M, $P(CO)$ = 60 bar; T = 135°C: t = 2 h; MeOH 100 ml; DMP 1 ml.
DMP = 2,2′-dimethoxypropane; OAc = acetate; phen = 1,10-phenanthroline; PTS = p-toluenesulfonic acid.

Table 4

Comparison between added Lewis acid redox-metal in $Pd(OAc)_2^-$ catalysed reductive carbonylation of nitrobenzene

Run	Cocatalyst	PhNO$_2$ conv. (% mols)	PhNHCOOMe select. (yield) (% mols)
1	none	88	75 (66)
2	Cu(OAc)$_2$	88	80 (71)
3	Ag(OAc)	94	78 (73)
4	Hg(OAc)$_2$	100	88 (88)

Reaction conditions: [nitrobenzene] = 1.34 M; [Pd] = 6.68×10^{-4} M, [Ag or Cu or Hg] = 6.68×10^{-4} M; [phen] = 5.34×10^{-2} M; [PTS] = 2.0×10^{-2} M; $P(CO)$ = 60 bar; T = 135°C; t = 2 h; MeOH 100 ml; DMP 1 ml.
DMP = 2,2′-dimethoxypropane; OAc = acetate; phen = 1,10-phenanthroline; PTS = p-toluenesulfonic acid.

amount. When a portion of palladium was substituited for the silver salt we observed a significant decrease both in conversion and in selectivity, as expected (Table 3).

Although at the moment the nature of the interplay between various palladium and silver salts is not clear, the beneficial effect on either selectivity or both selectivity and conversion of added silver salts is apparent. We tentatively propose some possibilities:

– The acidic nature of Ag (I) can contribute to avoid the azoxybenzene formation (Table 1, runs 2 and 3 vs. 1) increasing the selectivity towards phenylcarbamate. The acidity of Ag(I) was reported, e.g., in cubane isomerization to yield cuneane [24–26] and, more significantly, the strong acidity of Ag(I) in the presence of

CO was argued from ν(CO) higher than 2200 cm^{-1} in IR spectrum of $Ag(CO)_2B(OTeF_5)$ [27,28].

– The redox nature of Ag(I) [29] could contribute to avoid the formation of metallic palladium. The Lewis acidity combined with its redox nature makes Ag(I) an effective cocatalyst in palladium catalyzed reductive carbonylation. To verify this possibility, we compared mercury and copper acetates as cocatalysts and obtained results attribuitable both to Lewis acidity [30] and redox properties of the metal-cocatalyst (see Table 4). Indeed, the addition of mercuric acetate caused complete nitrobenzene conversion together with high selectivity (Table 4, run 4 vs. 3), while added cupric acetate increased only the selectivity (Table 4, run 2 vs. 3 and 1).

– Finally, Ag(I) forms very stable dinuclear complexes with azobenzene [31]. As a matter of fact, we found that added azobenzene [32] poisoned palladium catalysis, lowering both nitrobenzene conversion and selectivity into urethane (see Table 5, run 2 vs. 1). Ag(OAc), added when azobenzene was present, improved both selectivity and conversion (run 3 vs. 2). The higher activity observed in this case can be ascribed to the equilibrium, according to

Table 3

Effect of $AgF/Pd(OAc)_2$ molar ratio in nitrobenzene reductive carbonylation at a constant ([Ag]+[Pd]) concentration

Run	[Ag]/[Pd] molar ratio	PhNO$_2$ conv. (% mol)	PhNHCOOMe select. (yield) (% mol)
1	1	96	79 (76)
2	3	51	74 (37)
3	9	31	55 (17)

Reaction conditions: [nitrobenzene] = 1.34 M; [Pd]+[Ag] = 1.46 $\times 10^{-3}$ M; [PTS] = 2.0×10^{-2} M; [phen] = 5.34×10^{-2} M; $P(CO)$ = 60 bar; T = 135°C: t = 2 h; MeOH 100 ml; DMP 1 ml. DMP = 2,2′-dimethoxypropane; OAc = acetate; phen = 1,10-phenanthroline; PTS = p-toluenesulfonic acid.

$$2Ag(phen)_2^+ + 3Ar-N=N-Ar$$

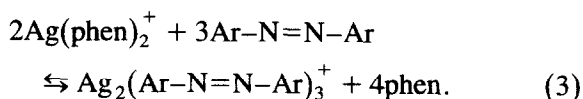$$\leftrightarrows Ag_2(Ar-N=N-Ar)_3^+ + 4phen. \qquad (3)$$

Table 5
Effect of azobenzene addition in the palladium catalyzed nitrobenzene reductive carbonylation in the presence and in the absence of silver cocatalyst

Run	Catalyst	Azobenzene (% mol)	PhNO$_2$ conv. (% mol)	PhNHCOOMe select. (yield) (% mol)
1	Pd(OAc)$_2$	0	88	75 (66)
2	Pd(OAc)$_2$	10	62	78 (48)
3	Pd(OAc)$_2$/Ag(OAc)	10	100	88 (88)

Reaction conditions: [nitrobenzene] = 1.34 M; [Pd] = 6.68 × 10^{-4} M; [Ag] = 6.68 × 10^{-4} M; [phen] = 5.34 × 10^{-2} M; [PTS] = 2.0 × 10^{-2} M; P(CO) = 60 bar; T = 135°C; t = 2 h; MeOH 100 ml; DMP 1 ml.
DMP = 2,2'-dimethoxypropane; OAc = acetate; phen = 1,10-phenanthroline; PTS = p-toluenesulfonic acid.

Indeed, shift to the right of the equilibrium of Eq. (3) was observed when we carried out the reaction between Ag(phen)$_2$(OSO$_2$CF$_3$) [33] and an excess of azobenzene (see Section 3). The azoderivative-Ag complex could be more effective to detach the palladium coordinated azobenzene in respect to the more stable Ag(phen)$_2^+$ complex [34]. Further experiments are underway to clarify this point.

In conclusion, the addition of Ag, Hg or Cu salts to the palladium catalyst results in improvements in conversion and selectivity, which may be relevant performing industrial catalytical cycles.

3. Experimental

3.1. Chemicals and instrumentation

Methanol (C. Erba), nitrobenzene (Aldrich), azobenzene (Aldrich), 2,2'-dimethoxypropane (Fluka), 1,10-phenanthroline monohydrate (Aldrich), p-toluenesulfonic acid monohydrate (Fluka), palladium, cupric, mercuric and silver acetates (Aldrich), palladium and silver trifluoroacetates (Fluka), AgF (Strem) and carbon monoxide (Rivoira) were used as received.

Ag(phen)$_2$(OSO$_2$CF$_3$) was synthesized according to the literature [33].

All reactions were carried out in triplicate and the products were analyzed by HPLC, using an HPLC Hewlett-Packard G mod. 1090, furnished of a Lichrosphere 100 RP 18 column (Merks), to determine the yield of the products.

3.2. Procedure

All reactions were carried out in a Hastelloy C autoclave (500 ml), equipped with a mechanical stirrer, a manometer and heating mantle. A teflon-coated thermocouple allowed the internal temperature to be measured.

In a typical reaction run the reactants were charged into the autoclave that, subsequently, was purged three times with CO, filled with CO to the desired pressure and heated at the required temperature.

At the end of the reaction, the reactor was degased and the homogeneuos solution was diluted with methanol to the required volume and analyzed by HPLC.

3.3. Reaction of Ag(phen)$_2$(OSO$_2$CF$_3$) with azobenzene

To 0.29 g of Ag(phen)$_2$(OSO$_2$CF$_3$) (0.48 mmols) in 40 ml of anhydrous methanol were added 0.90 g of azobenzene (4.8 mmol). The solution was stirred under argon at 60°C for 24 h and, finally, analyzed for the content of phenanthroline and azobenzene. The results indicated a complete exchange of phenanthroline for azobenzene, on the silver complex.

References

[1] S. Cenini, C. Crotti, in: A.F. Noels, M. Graziani, H.J. Hubert (Eds.), Metal Promoted Selectivity in Organic Synthesis, Kluwer Academic Publishers, Dordrecht, 1991, p. 311.
[2] A. Bontempi, E. Alessio, G. Mestroni, G. Chanos, J. Mol. Catal. 42 (1987) 67.

[3] C.W. Lee, J.S. Lee, S.M. Lee, K.D. Kim, J.S. Oh, S.N. Cho, J. Mol. Catal. 81 (1993) 17.

[4] P. Wehman, G.C. Dol, E.R. Moorman, P.J. Kamer, P.W.N.M. Van Leeuwen, J. Fraanje, K. Goubitz, Organometallics 13 (1994) 4856.

[5] P. Wehman, V.E. Kaasjager, W.G.J. De Lange, F. Hartl, P.J. Kamer, P.W.N.M. Van Leeuwen, J. Fraanje, K. Goubitz, Organometallics 14 (1995) 3751.

[6] S. Cenini, F. Ragaini, F. Demartin, Organometallics 13 (1994) 1178.

[7] C.V. Rode, S.P. Gupte, R.V. Chaudhari, C.D. Pirozhkov, A. Lapidus, J. Mol. Catal. 91 (1994) 195.

[8] S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni, E. Alessio, J. Mol. Catal. 64 (1991) 179.

[9] S. Cenini, C. Crotti, M. Pizzotti, F. Porta, J. Org. Chem. 53 (1988) 1243.

[10] J.D. Gargulak, A.J. Berry, M.D. Noirot, W.J. Gladfelter, J. Am. Chem. Soc. 114 (1992) 8933.

[11] S. Cenini, F. Ragaini, S. Tollari, J. Mol. Catal. 85 (1993) L1.

[12] W.J. Glafelter, J.D. Gargulak, A.C.S. Symp. 557 (1995) 47.

[13] E. Drent, P.V.N.M. Van Leeween, E.P. Patent 82481 (1983).

[14] S. Cenini, F. Ragaini, La Chimica e l'Industria 78 (1996) 401.

[15] S.P. Gupte, R.V. Chaudhari, J. Mol. Catal. 24 (1984) 197.

[16] S.B. Halligudi, R.V. Chaudhari, W.L.K. Dorais, Ind. Eng. Chem. Process Res. Dev. 23 (1984) 794.

[17] K. Schwetlick, K. Unverferth, H. Tietz, M. Pfeifer, German (East) Patent 146043; Chem. Abstract 95 (1981) 115023r.

[18] K. Schwetlick, K. Unverferth, H. Tietz, Z. Chem. 20 (1980) 295.

[19] K. Schwetlick, K. Unverferth, R. Hontsch, J. Prat. Chem. 321 (1979) 86.

[20] K. Schwetlick, K. Unverferth, R. Hontsch, J. Prat. Chem. 321 (1979) 928.

[21] N.D. Zelinskii, Netherland Patent 79,01,656; Chem. Abstract 94 (1981) 208523w.

[22] J.S. Oh, S.M. Lee, J.K. Yeo, C.W. Lee, J.S. Lee, Ind. Eng. Chem. Res. 30 (1991) 1456.

[23] E. Alessio, G. Mestroni, G. Clauti, J. Mol. Catal. 29 (1985) 77.

[24] L. Cassar, P.E. Eaton, J. Halpern, J. Am. Chem. Soc. 92 (1970) 6866.

[25] W.G. Dauben, M.G. Buzzolini, C.H. Schallhorn, D.L. Whalen, Tetrahedron Lett. (1970) 787.

[26] L.A. Paquette, J.C. Stowell, J. Am. Chem. Soc. 92 (1970) 2584.

[27] P.K. Hulburt, J.J. Rack, S.F. Dec, O.P. Anderson, S.H. Strauss, Inorg. Chem. 32 (1993) 373.

[28] P.K. Hulburt, O.P. Anderson, S.H. Strauss, J. Am. Chem. Soc. 113 (1991) 6277.

[29] J. Sebin, B. Schamburger, J. Inorg. Nucl. Chem. 24 (1962) 1153.

[30] R.D. Hancock, B.D. Nakani, F. Marsicano, Inorg. Chem. 22 (1983) 2531.

[31] R. Huttel, A. Konietzny, Chem. Ber. 106 (1973) 2098.

[32] R. Santi, A.M. Romano, F. Panella, unpublished results.

[33] R.H. Nutall, E.R. Roberts, D.W.A. Sharp, J. Chem. Soc. (1962) 2854.

[34] W.J. Peard, R.T. Pflaum, J. Am. Chem. Soc. 80 (1958) 1593.