

## Palladium-catalysed *N,N'*-disubstituted urea synthesis by oxidative carbonylation of amines under CO and O<sub>2</sub> at atmospheric pressure

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### Abstract

*N,N'*-disubstituted ureas have been obtained in good yields by reaction of aromatic and aliphatic primary amines in alcohol solution with CO and O<sub>2</sub> under mild conditions (70–90°C, 1 atm) and in the presence of catalytic amounts of PdCl<sub>2</sub> or a palladium(II) complex. Under more drastic temperature and pressure conditions carbamate esters were obtained instead. In the aniline carbonylation, the catalysis involves the following reactions:



Reaction (1) occurs at room temperature but more drastic conditions (70–90°C) are necessary for reaction (2). The influence of onium salts, such as PhNH<sub>3</sub><sup>+</sup>X<sup>-</sup> (X = Cl, I) or CuCl<sub>2</sub>, on the catalytic activity has also been studied and the best results obtained with CuCl<sub>2</sub>. A side reaction involving carbon monoxide oxidation was almost suppressed when the reactions were carried out in alcohol, but enhanced when THF or dimethoxypropane was used as solvent.

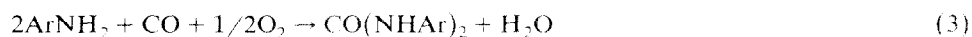
### Introduction

*N,N'*-substituted ureas are usually prepared by reactions of isocyanates or phosgene with amines or by direct carbonylation of amines or nitro compounds in the presence of a transition metal complex [1]. Ureas have also been obtained by oxidative carbonylation of amines by various oxidizing agents [2]. Recently the oxidative carbonylation of amines by CO and O<sub>2</sub> at 80 atm and 160–170°C in the presence of a catalyst system comprising a palladium group metal and either a alkali metal halide or an onium halide [3] has been described. We have found that

*N,N'*-disubstituted ureas can be prepared in good yields from amines and a (2/1) CO/O<sub>2</sub> mixture at atmospheric pressure at temperatures of 70–90 °C in the presence of a palladium(II) complex or PdCl<sub>2</sub>.

## Results and discussion

Treatment of aromatic primary amines with CO and O<sub>2</sub> under atmospheric pressure at temperatures of 70 to 90 °C in the presence of a palladium(II) complex of PdCl<sub>2</sub> was found to give the corresponding *N,N'*-disubstituted ureas in good yields; the reaction is represented by eq. 3.



(Ar = *p*-RC<sub>6</sub>H<sub>4</sub>; R = H, Cl, CH<sub>3</sub>)

Aliphatic primary amines RNH<sub>2</sub> (R = *n*-But or cyclohexyl) react in the same way, but give lower yields of 1,3-dialkylureas and variable amounts of CO<sub>2</sub> are formed in a side reaction. Aliphatic and aromatic secondary amines, such as diethylamine and *N*-methylaniline failed to yield the corresponding ureas; the main products were carbon dioxide and tertiary amines, and there were unidentified by-products. The tertiary amines were produced by a reaction between amine and alcohol. The yield of the urea depends on the solvent used. The most effective solvents were methanol and ethanol or aniline (in the case of its carbonylation) whilst use of other solvents, such as THF or dimethoxypropane (DMP), led to formation of large amounts of CO<sub>2</sub>. PdCl<sub>2</sub> or PdCl<sub>2</sub>L<sub>2</sub> (L = PPh<sub>3</sub>, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>) were found to be active catalysts for the reaction. Little change in the yield was observed when the ligand coordinated to the palladium was varied.

The results of the more significant experiments with various amines, catalysts and co-catalysts are shown in Table 1. The best results of the urea synthesis were obtained by use of CuCl<sub>2</sub> as co-catalyst. Most reactions were carried on for 6 h. Use of longer reaction times led to a decrease in the catalytic activity and a simultaneous increase in the production of carbon dioxide. This may be due to the formation of water as the catalysed reaction proceeds (see below).

In all the experiments, only trace amounts of alkylcarbamates were found; this is a different result from that reported by Halper and Hartstock [5], who obtained carbamate esters in nearly quantitative yields with a PdCl<sub>2</sub>/CuCl<sub>2</sub>/HCl catalyst. Even the addition of CuCl<sub>2</sub> to our system did not change the composition of the reaction product, but there was an increase in the rate of reaction (3). The PdCl<sub>2</sub>L<sub>2</sub>/CuCl<sub>2</sub> system thus proved to be the most effective for the urea synthesis, but an increase in the production of carbamate esters can be brought about by carrying out the reaction under CO/O<sub>2</sub> mixture at 30 atm pressure and temperatures of 110 to 150 °C. Control experiments showed that in the same temperature range *N,N'*-diphenylurea reacts with methanol to give methyl-*N*-phenylcarbamate, in the equilibrium process depicted in 4.



Thus it is very likely that the carbamates are not formed by direct interaction of aniline, CO, and alcohol, but rather by alcoholysis of the urea. This view is consistent with the conditions found to be necessary with systems capable of converting the diphenylurea into carbamate esters [5]. In this context, the results

Table 1. Catalysed *N,N'*-disubstituted urea synthesis <sup>a</sup>.

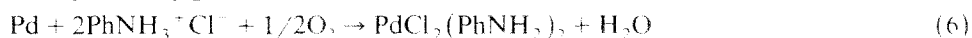
Run	Catalyst	Co-catalyst	Amine <sup>b</sup>	Solvent <sup>c</sup>	Time (h)	<i>N,N'</i> -urea <sup>d</sup> (mmol)	CO/O <sub>2</sub> <sup>e</sup> (absorbed)	CO <sub>2</sub> (mmol)
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	-	PhNH <sub>2</sub>	PhNH <sub>2</sub>	6	7.07(91.6) /	260(173)	trace
2	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	-	PhNH <sub>2</sub>	PhNH <sub>2</sub>	6	7.04(92.6) /	259(172.7)	trace
3	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub>	PhNH <sub>2</sub>	6	7.02(91.3) /	258(172.2)	trace
4	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	-	PhNH <sub>2</sub> (22.0)	MeOH	6	3.54(84.3)	141(94.0)	trace
5	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PyH <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	6	3.55(84.1)	142(94.5)	trace
6	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	CuCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PhNH <sub>2</sub> (22.0)	MeOH	6	5.19(86.5)	197(131)	trace
7	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	6	3.51(83.4)	142(94.5)	trace
8	PdCl <sub>2</sub>	-	PhNH <sub>2</sub> (22.0)	EtOH	6	3.52(84.2)	140(93.3)	trace
9	PdCl(PPh <sub>3</sub> ) <sub>2</sub> COOCH <sub>3</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	6	3.48(78.9)	149(99.0)	trace
10	PdCl <sub>2</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub>	-	<i>p</i> -Cl-aniline (15.7)	MeOH	6	2.07(74.7)	98(65.3)	trace
11	PdCl <sub>2</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	<i>p</i> -Cl-aniline (15.7)	MeOH	6	6.02(90)	234(156)	trace
12	PdCl <sub>2</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub>	-	<i>p</i> -toluidine (18.7)	MeOH	6	1.45(61.7)	79(52.6)	trace
13	PdCl <sub>2</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	<i>p</i> -toluidine (18.7)	MeOH	6	5.20(85.2)	205(136.6)	trace
14	PdCl <sub>2</sub>	-	<i>n</i> -butNH <sub>2</sub> (20.3)	MeOH	6	1.95(62)	115(77.2)	0.8
15	PdCl <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	<i>n</i> -butNH <sub>2</sub> (20.3)	MeOH	6	3.94(61.6)	179(119.5)	0.7
16	PdCl <sub>2</sub>	-	Cyclohexyl-NH <sub>2</sub> (17.8)	MeOH	6	1.82(64.3)	91(60.9)	trace
17	PdCl <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	Cyclohexyl-NH <sub>2</sub> (17.8)	MeOH	6	5.95(88.3)	232(154.8)	trace
18	Pd <sub>3</sub> (CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>4</sub>	-	PhNH <sub>2</sub> (22.0)	MeOH	12	-	-	trace
19	Pd <sub>3</sub> (CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>4</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	6	3.48(83.2)	144(95.8)	trace
20	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	10	0.91(56.8)	105(70.2)	1.5
21	PdI <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	PhNH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	10	0.88(55.6)	107(71.2)	1.6
22	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	NEt <sub>3</sub> CH <sub>3</sub> <sup>+</sup> I <sup>-</sup>	PhNH <sub>2</sub> (22.0)	MeOH	10	0.90(55.7)	109(72.6)	1.6
23	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	-	PhNH <sub>2</sub> (22.0)	DMP/MeOH (1/1)	12	0.62(47.1)	61(40.7)	0.5
24	PdCl <sub>2</sub> (PhNH <sub>2</sub> ) <sub>2</sub>	-	PhNH <sub>2</sub> (22.0)	THF	12	1.20(63.1)	87.4(58.2)	0.7
25	PdCl <sub>2</sub>	-	PhNHCH <sub>3</sub> (18.5)	MeOH	12	-	38	3.13
26	PdCl <sub>2</sub>	CuCl <sub>2</sub> ·H <sub>2</sub> O	PhNHC <sub>2</sub> H <sub>5</sub> (15.9)	MeOH	12	-	28	2.13
27	PdCl <sub>2</sub>	-	NHEt <sub>2</sub>	MeOH	12	-	30	2.28

<sup>a</sup> All reactions were carried out at 80 °C under atmospheric pressure of a 2/1 CO/O<sub>2</sub> mixture; 0.28 mmol Pd-catalyst and 0.40 mmol of co-catalyst were used. <sup>b</sup> Mol in parentheses. <sup>c</sup> 20 ml of solvent were used. <sup>d</sup> Unless otherwise stated, the yields in parentheses are based on the amount urea isolated and reacted amine; the urea solubility was not taken into account. <sup>e</sup> The volume (ml) absorbed was measured at room temperature; the calculated volume of the reacted CO is given in parentheses based on the initial mixture composition. <sup>f</sup> The yields are based on reacted CO.

obtained by Halper and Hartstock [4] are surprising, and we assume that a different mechanism operates in their system.

### Catalytic cycle

Independent of the catalyst used, in the catalysed reactions some metallic palladium, which formed a black suspension, appeared in the reaction solutions. The amount of metal was increased when the proportion of CO in the gas above the solution was increased, and decreased when the proportion of oxygen was increased. Addition of onium salts, such as  $\text{PhNH}_3^+ \text{X}^-$  ( $\text{X} = \text{Cl}, \text{I}$ ) or  $\text{PyH}^+ \text{Cl}^-$  also lowered the amount of the metal formed. The question arises of whether the reaction involves heterogeneous catalysis by metallic palladium or homogeneous catalysis by a soluble palladium complex. Both types have been reported [8,4]. We found that, at least in aniline carbonylation and in the absence of  $\text{CuCl}_2$ , the catalysed process involves the following reactions:

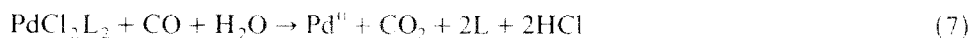


Reaction (5) occurs at room temperature when the palladium(II) complex is allowed to react with carbon monoxide in an alcohol aniline solution. The resulting metallic palladium can be recovered by filtration, and the *N,N'*-diphenylurea can be isolated by cooling the mother liquor. Finally, the soluble anilinium salt may be isolated by evaporating the residual mother liquor. Attempts to isolate the postulated carbamoyl complex intermediates in reaction (5) failed. Depending on the initial palladium compound, the amine, and the temperature, either palladium metal or a  $\text{Pd}^{\text{II}}$  or  $\text{Pd}^0$  complex were obtained. *N,N'*-diphenylurea and the known carbonyl cluster  $\text{Pd}_3(\text{CO})_2(\text{PPh}_3)_4$  [9] were isolated when  $\text{PdCl}_2(\text{PPh}_3)_2$  was used as catalyst with aniline as substrate and the reaction was carried out at 20–60°C. The alkoxycarbonyl  $\text{PdCl}(\text{PPh}_3)_2\text{COOCH}_3$  [9] was formed instead at these temperatures when *p*-chloroaniline or *p*-toluidine was used as the amine. No intermediate species were isolated from the other  $\text{PdCl}_2\text{L}_2$  ( $\text{L} = \text{ArNH}_2$ ;  $\text{Ar} = p\text{-ClC}_6\text{H}_4$ ,  $p\text{-CH}_3\text{C}_6\text{H}_6$ ) complexes, but metallic palladium was formed at all the temperatures used.

The reaction shown in equation (6) was brought about either by treating the mixture obtained from reaction (5) directly with  $\text{O}_2$ , or by filtering off the metallic palladium and treating it under oxygen with a solution containing aniline and anilinium chloride ( $\text{Pd}/\text{PhNH}_2/\text{PhNH}_3^+ \text{Cl}^- = 1/4/3$ ). The resulting  $\text{PdCl}_2(\text{PhNH}_2)_2$  was identified from its elemental analysis and IR spectrum. The reoxidation of palladium is slow at room temperature, and so must be carried out at higher temperatures  $\theta$  ( $> 60^\circ\text{C}$ ). Thus, this reaction is the rate-determining step in the catalysed process.

In order to increase the rate of oxidation of the palladium, onium salts such as  $\text{C}_6\text{H}_5\text{NH}_3^+ \text{X}^-$  ( $\text{X} = \text{Cl}, \text{I}$ ) or  $\text{CuCl}_2$  were added to the catalyst systems. The best results were obtained when  $\text{CuCl}_2(\text{PhNH}_2)_2$  was used (Table 1).

Finally, the oxidation of CO to  $\text{CO}_2$ , the main side reaction, must be considered. This process has been observed with palladium [6] and nickel [7] compounds, and a mechanism based on a nucleophilic attack of a water molecule on the CO coordinated to metal has also been reported [7] (eq. 7).



In our system it is probable that the  $\text{CO}_2$  is formed in a similar way, and support for this is provided by the observed increase in the amount of  $\text{CO}_2$  formed during prolonged reactions. Further support comes from the observation that the initial catalytic activity can be regenerated when the metallic palladium recovered from reaction (3) is added to a fresh alcoholic solution containing aniline and anilinium chloride.

## Experimental

All solvents were reagent-grade and were used without further purification. Aliphatic primary and secondary amines were distilled and stored over molecular sieves, while the anilines  $p\text{-RC}_6\text{H}_4\text{NH}_2$ , were used as purchased (Carlo Erba). Published methods were employed for the preparation of  $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4$  [9],  $\text{PdCl}(\text{PPh}_3)_2\text{COOCH}_3$  [9]. The  $\text{PdCl}_2\text{L}_2$  complexes ( $\text{L} = \text{PhNH}_2$ ,  $p\text{-ClC}_6\text{H}_4\text{NH}_2$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$ ,  $\text{PPh}_3$ ,  $\text{CH}_3\text{CN}$ ) were obtained by stirring  $\text{PdCl}_2$  with the ligand in methanol. Chromatographic analysis of gases were carried out with Porapak Q 3.5 m column in a Carlo Erba Fractovap C gas chromatograph fitted with a thermal conductivity detector connected to a Hewlett Packard 3380 A integrator. GLC analyses were carried out with a GP 20% SP 2100 0.1% Carbowax 1.8 m column in a Varian Vista 6000 gas chromatograph connected to a Varian 4270 integrator, toluene being used as internal standard. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer.

### *General procedure for the preparation of $N,N'$ -disubstituted ureas*

The reactions were carried out in a glass vessel (from 120 to 150 ml) which was placed in an electric oven. The reactor was charged with the indicated amounts of the palladium catalyst, co-catalyst, amine and solvent, and the magnetically stirred mixture was kept for 6 h at the specified temperature under an atmosphere of  $\text{CO}/\text{O}_2$  in 2/1 ratio. Every 2 h the reactor was cooled to room temperature, the volume of gas absorbed was recorded, and samples of the reaction mixture (solution and gas) were withdrawn and analyzed by gas chromatography. The reactor was then refilled with  $\text{CO}$  and  $\text{O}_2$  and the reaction continued.

### *Preparation of $N,N'$ -diarylureas*

#### *$N,N'$ -diphenylurea*

(a) *In aniline.* A mixture of  $\text{PdCl}_2(\text{PhNH}_2)_2$  (0.28 mmol) and aniline (20 ml) in a glass reactor (130 ml) was kept for 6 h at  $80^\circ\text{C}$  under one atmosphere pressure of a 2/1  $\text{CO}/\text{O}_2$  mixture. During this period, 260 ml of the gas mixture, corresponding to 173 ml of carbon monoxide, were absorbed. The resulting brown solution was filtered while warm, and the metallic palladium (0.021 g) was separated. The filtrate was cooled to room temperature and the crystalline  $N,N'$ -diphenylurea which separated was filtered off and dried in vacuo. The yield (1.56 g) was 91.6% based on the carbon monoxide taken up. The product was identified from its IR and NMR spectra;  $\delta$  (in  $\text{Me}_2\text{SO}-d_6$ ) 8.72(s) and 7.77–6.86(m) ppm.

(b) *In methanol.*  $\text{PdCl}_2(\text{PhNH}_2)_2$  (0.28 mmol),  $\text{PhNH}_2$  (22.0 mmol),  $\text{CuCl}_2(\text{PhNH}_2)_2$  (0.40 mmol) and  $\text{MeOH}$  (20 ml) were placed into a glass reactor (120 ml) and reaction with  $\text{CO}$  and  $\text{O}_2$  was carried out as described above for 6 h; 197 ml of the gas mixture were absorbed and 0.019 g of metallic palladium was

obtained by filtration. Analysis of the filtrate by gas chromatography revealed the presence of  $\text{PhNH}_2$  (16.0 mmol) and trace amounts of methylcarbamate. The diphenylurea (1.10 g, 86.5% of the reacted aniline) was identified from its IR spectrum.

*N,N'-di-p-chlorophenylurea*

A mixture of  $\text{PdCl}_2(p\text{-ClC}_6\text{H}_4\text{NH}_2)_2$  (0.28 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.40 mmol), *p*-chloroaniline (15.70 mmol) and MeOH (20 ml) was subjected to the usual procedure at 80 °C. The reaction solution (which contained some unchanged *p*-chloroaniline (9.01 mmol)) was cooled to give *N,N'*-di-*p*-chloro-phenylurea (1.69 g, 90% of the reacted amine), which was identified from its IR and NMR spectra:  $\delta$  ( $\text{Me}_2\text{SO}-d_6$ ) 8.93(s), 7.74(d) and 7.46(d).

*N,N'-di-p-tolylurea*

A mixture of  $\text{PdCl}_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)_2$  (0.28 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.40 mmol), *p*-toluidine (18.70 mmol) and MeOH (20 ml) was subjected to the usual procedure. The solution obtained (which contained unchanged *p*-toluidine (12.20 ml)) was cooled to give *N,N'*-di-*p*-tolylurea (1.33 g, 85% of the reacted amine), which was identified from its IR spectrum.

*N,N'-dicyclohexylurea*

A mixture of  $\text{PdCl}_2$  (0.28 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.40 mmol), cyclohexylamine (17.84 mmol) and MeOH (20 ml) was subjected to the usual procedure. The solution obtained (which contained unreacted cyclohexylamine (11.10 mmol)) was cooled to yield *N,N'*-dicyclohexylurea (1.33 g, 88.3% of the reacted amine), which was identified from its IR spectrum.

*N,N'-di-n-butylurea*

A mixture of  $\text{PdCl}_2$  (0.28 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.40 mmol), *n*-butylamine (20.30 mmol) and methanol (20 ml) was subjected to the usual procedure: 180 ml of gas were absorbed. The gas mixture at the end of the reaction was found to contain  $\text{CO}_2$  (0.70 mmol, about 13% of reacted CO). The deep-brown reaction solution was filtered to remove the metallic palladium (0.021 g) and analyzed by GLC, which revealed the presence of *n*-butylamine (13.90 mmol) and two unidentified products. The solution was then evaporated in vacuo and the residue dissolved in ether. The ether solution was cooled to -30 °C to give a white precipitate (0.68 g, 61.6% based on the amine used up), which was identified as *N,N'*-di-*n*-butylurea (IR).

*Reaction of PdCl<sub>2</sub>(PhNH<sub>2</sub>)<sub>2</sub> with CO and aniline*

A suspension of  $\text{PdCl}_2(\text{PhNH}_2)_2$  (1.00 mmol) in MeOH (5 ml) and aniline (11.00 mmol) was stirred under one atmosphere pressure of carbon monoxide at 80 °C. The yellow suspended solid became black and the solution became pale-yellow (1 h). The hot reaction mixture was filtered to remove the black metallic palladium (0.095 g) and then cooled to 0 °C, to give crystalline *N,N'*-diphenylurea (0.19 g) which was filtered off. The mother liquor was evaporated in vacuo and the residue was washed with diethyl ether then collected and dried. The IR spectrum of the pale-yellow solid obtained (0.23 g) showed IR bands from both  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$  and diphenylurea.

*Reaction of metallic palladium with  $C_6H_5NH_3Cl$  and  $O_2$*

A mixture of metallic palladium (0.095 g),  $C_6H_5NH_3Cl$  (0.39 g) and aniline (4.00 mmol) in MeOH (10 ml) was stirred under one atmosphere pressure of dioxygen at 70 °C. The black suspension yielded a yellow precipitate which was filtered off, washed with methanol, and dried in vacuo to give 0.28 g of a solid with an IR spectrum identical with that of an authentic sample of  $PdCl_2(PhNH_2)_2$ .

Elemental analysis: Found (%)  $C_{12}H_{14}Cl_2N_2Pd$  calc: C, 39.7 (39.62); H, 3.7 (3.85); N, 7.6 (7.71); Cl, 19.1 (19.54).

*Carbamate ester synthesis*

$PdCl_2(PhNH_2)_2$  (0.28 mmol),  $PhNH_2$  (22.00 mmol) and 10 ml of a 2/1 mixture of methanol/dimethoxypropane were placed in a stainless steel autoclave (55.6 ml). The autoclave was charged to 10 atm with  $O_2$  then to a total pressure of 30 atm with CO and then kept in an electric oven at 110 °C for 6 h then cooled. *N,N'*-diphenylurea (4.60 mmol) was filtered off, and the filtrate was analysed by gas chromatography, which revealed the presence of methyl-*N*-phenylcarbamate (1.32 mmol), *N*-methylaniline (0.31 mmol), and aniline. The gas phase contained a large amount of  $CO_2$ .

When the reaction was carried out at 150 °C, the product mixture contained *N,N'*-diphenylurea (2.12 mmol), methyl-*N*-phenylcarbamate (4.72 mmol), *N*-methylaniline (0.78 mmol), and aniline.

*Catalysis in the presence of alkyl and aryl secondary amines*

$PdCl_2$  (0.28 mmol), *N*-methylaniline (2 ml), methanol (20 ml), were placed in a glass reactor (130 ml) and allowed to react under one atmosphere pressure of a 2/1  $CO/O_2$  mixture. After 12 h the reactor was cooled to room temperature and the volume of the gas absorbed was measured (38 ml). Gas chromatographic analysis of the reaction mixture (gas and solution) showed the presence of  $CO_2$  (3.13 mmol, 80.9% of the CO in the starting mixture), *N*-dimethylaniline (0.46 mmol), *N*-methylaniline, and two unidentified products.

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