

# First gold(I) complex-catalyzed oxidative carbonylation of amines for the syntheses of carbamates

Feng Shi and Youquan Deng\*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, and Laboratory of Environmental and Applied Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.

E-mail: ydeng@ns.lzb.ac.cn; Fax: +86-931-8277088

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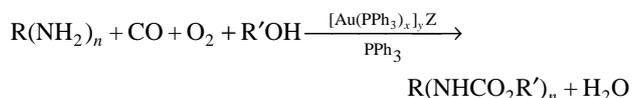
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At 200 °C and 5 MPa of initial total pressure, the oxidative carbonylation of amines for the synthesis of the corresponding carbamates by Au(I) complexes as catalysts was conducted with excellent conversion and selectivity.

Gold catalysts have been receiving growing attention and many reactions catalyzed over Au catalysts,<sup>1</sup> such as CO oxidation,<sup>2</sup> selective oxidation,<sup>3</sup> water-gas shift reactions,<sup>4</sup> asymmetric aldol reactions,<sup>5</sup> carbonylation of olefins<sup>6</sup> and dehydrogenative dimerization of trialkylstannane,<sup>7</sup> have been reported to be high performance. These reactions indicate that using gold complexes as catalysts for those synthetic reactions traditionally catalyzed with Pd, Rh *etc.* complexes should be not only possible but also practical and even highly efficient.

Produced either by oxidative carbonylation of amines or by reductive carbonylation of nitro compounds in the presence of an alcohol, carbamates as intermediates for the synthesis of isocyanates by non-phosgene routes have been extensively studied over the past two decades.<sup>8</sup> Pd, Ru and Rh complexes and other transition metals were employed as the catalysts,<sup>9</sup> and complexes of Pd coordinated with N-containing compounds were among the most effective of these catalyst systems.<sup>10</sup> Although reductive carbonylation of nitro compounds should be the more attractive route for indirect production of isocyanates, the occurrence of catalyst deactivation due to the reduction of noble metal ions, *e.g.* Pd<sup>2+</sup> to Pd<sup>0</sup>, under the strong reductive conditions may be difficult to be overcome,<sup>11</sup> and the catalyst systems were generally more complicated than those for oxidative carbonylation. Furthermore, no studies concerning the oxidative carbonylation of amines or reductive carbonylation of nitro compounds for carbamate formation by Au complexes have been reported yet.

Herein, the first example of the oxidative carbonylation of amines for the synthesis of the corresponding carbamates by Au complexes, *i.e.* HAuCl<sub>4</sub> **1**, Au(PPh<sub>3</sub>)Cl **2**, Au(PPh<sub>3</sub>)<sub>2</sub>Cl **3**, Au(PPh<sub>3</sub>)NO<sub>3</sub> **4** and [Au(PPh<sub>3</sub>)<sub>2</sub>S] **5** as the catalysts with excellent performance, is reported:



R = Ph, Alkyl; R' = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>; n = 1 or 2;

x, y = 1 or 2; Z = Cl, NO<sub>3</sub>, S.

The oxidative carbonylation of a series of aromatic and aliphatic amines over the above mentioned Au(I) complexes was examined (Table 1). When aniline as substrate was subjected to carbonylation, different catalytic performances were observed over catalysts **1**–**5**. The highest selectivity was 70% over **2**, and the highest conversion 62.2% over **3**. The catalyst **5** was even less effective than catalyst **1**. The main by-product resulting from catalyst **1** was azobenzene, while *N*-methylaniline and quinazoline were detected over the catalysts **2**–**5**. Other by-products such as azoxybenzene over catalyst **1** and quinazoline over catalyst **2** were also identified. When

catalyst **1** was employed, decomposition of the catalyst, *i.e.* reduction of Au<sup>3+</sup> to Au<sup>0</sup>, occurred. A very thin film, light-yellow in color, was observed to have been deposited on the wall of the glass tube inside the reactor after the reaction; no such phenomenon was observed with catalysts **2**–**4**.

The conversion and selectivity for the desired products were greatly enhanced if extra PPh<sub>3</sub> (0.1 g) was further added into the reaction, entries 6–9. It is noteworthy that 97.2% conversion and 89% selectivity were achieved over catalyst **2** + PPh<sub>3</sub>. The TOF reached 36, which is comparable to the result of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (**6**) + PPh<sub>3</sub> used as the catalyst, where 98.5% conversion and 86% selectivity was obtained, entry 8. Such enhancement in catalytic activity may partially be attributed to the stabilization of organic Au(I) complexes by the additional PPh<sub>3</sub> which may replace the oxidized ligand, since it is possible that small amounts of PPh<sub>3</sub> could be oxidized under oxidative conditions during the reaction. The same main by-product, quinazoline, was found over catalysts **2** + PPh<sub>3</sub> and **6** + PPh<sub>3</sub>, indicating that a similar reaction mechanism occurred over catalysts **2** and **6**.

Using alcohol as one of the reaction substrates and solvent had a strong impact on the reaction. Much higher selectivity could be achieved when methanol was used, entry 6, although slightly higher conversion was obtained with ethanol under the same reaction conditions, entry 7. This may be due to the easier formation of quinoline in the simultaneous presence of aniline and ethanol. Treatment of 2,4-diaminotoluene and 4,4'-diaminodiphenylmethane with carbon monoxide and methanol in the presence of catalyst **2** + PPh<sub>3</sub> afforded excellent conversion and selectivity, entries 11 and 12. The main by-product from 2,4-diaminotoluene was the mono-carbonylated product, while the main by-product from 4,4'-diaminodiphenylmethane was 4,4'-diaminobenzophenone.

An attempt was also made to test the oxidative carbonylation of aliphatic amines using catalyst **2** + PPh<sub>3</sub>, the best catalyst system found for the carbonylation of aromatic amines. Although the conversion of the corresponding amines was almost complete for *n*-hexylamine (entry 13) and cyclohexylamine (entry 14), poor selectivities for the desired product were obtained, but relatively high selectivities for the corresponding alkylureas were achieved. For 1,6-hexanediamine (entry 15) almost no desired product could be observed, but it is noteworthy that 63% selectivity for *N,N'*-hexylmethylenediformamide could be achieved. This may imply that the Au(I) complexes could be a promising catalyst for the synthesis of other N-containing compounds from aliphatic amines under suitable reaction conditions.

In summary, the experimental results suggest that organic Au(I) complexes show an excellent performance towards the oxidative carbonylation of aromatic amines to form corresponding carbamates, and also exhibit a promising catalytic performance towards the carbonylation of aliphatic amines to produce either alkylureas or formamides. To the best of our knowledge this is the first reported study of Au(I) complexes for this kind of reaction.

**Table 1** The catalytic performances of Au(I) complexes towards oxidative carbonylation of amines

Entry	Sub.	Cat.	Con. (%)	Sel. (%)	TOF <sup>a</sup>	Products	By-products	Others <sup>b</sup>
1	aniline	HAuCl <sub>4</sub>	33.7	37	11			9 34(20)
2	aniline	Au(PPh <sub>3</sub> )Cl	38.8	70	14			10 18(2)
3	aniline	Au(PPh <sub>3</sub> ) <sub>2</sub> Cl	62.2	60	23			15 23(2)
4	aniline	Au(PPh <sub>3</sub> )NO <sub>3</sub>	42.1	43	16			13 41(3)
5	aniline	[Au(PPh <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> S	32.2	30	11			30 39(1)
6	aniline	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	97.2	89	36			7 3(1)
7 <sup>c</sup>	aniline	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	98.8	60	36.5			21 19
8	aniline	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> + PPh <sub>3</sub>	98.5	86	36			11 2(1)
9	aniline	Au(PPh <sub>3</sub> )NO <sub>3</sub> + PPh <sub>3</sub>	96	83	36			13 41(3)
10	aniline	[Au(PPh <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> S + PPh <sub>3</sub>	48	69	17			5 23(3)
11	TDA <sup>d</sup>	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	98	93	28			5 (2)
12	MDA <sup>e</sup>	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	89	88	17		DBP <sup>f</sup>	2 (10)
13	n-hexyl-amine	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	99	35	30	C <sub>6</sub> H <sub>15</sub> NHCO <sub>2</sub> Me	(CH <sub>3</sub> C <sub>6</sub> H <sub>10</sub> NH) <sub>2</sub> CO	40 24(1)
14	cyclohexyl-amine	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	100	58	30			22 18(2)
15	1,6-hexane-diamine	Au(PPh <sub>3</sub> )Cl + PPh <sub>3</sub>	99	–	30	(CH <sub>2</sub> ) <sub>6</sub> (NHCO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	(OHCHN) <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub>	63 37

<sup>a</sup>Mol substrate converted per mol Au per hour. <sup>b</sup>Unidentified in brackets. <sup>c</sup>Ethanol as solvent. <sup>d</sup>2,4-Diaminotoluene. <sup>e</sup>4,4'-Diaminodiphenylmethane. <sup>f</sup>4,4'-Diaminobenzophenone.

The following experimental procedure was used: the syntheses of the Au(I) complexes were as reported in previous papers.<sup>12</sup> Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (**6**) was also employed for the purpose of comparison. The reactions were performed in glass tubes with magnetic stirring within an autoclave. For each reaction, 0.05 mmol Au(I) complex or the mixture of 0.05 mmol Au(I) complex and 0.1 g PPh<sub>3</sub> was added to the solution of amine (0.5 g or 0.5 ml) and alcohol (20 ml, MeOH or EtOH) at rt. Then O<sub>2</sub> (99.99% purity 1 MPa) and CO (99.99% purity, 4 MPa) were respectively introduced into the reactor to 5 MPa total pressure. The reaction was allowed to proceed at 200 °C for 3 h and the resulting liquid mixture was then directly analyzed with a HP 6890/5973 GC-MS.

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