ChemComm

The first syntheses of diformamides by carbonylation of aliphatic diamines with Au(I) complex catalysts

Feng Shi, Youquan Deng,* Hongzhou Yang and Tianlong SiMa

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: +86-931-8417088

Received (in Cambridge, UK) 17th November 2000, Accepted 12th January 2001
First published as an Advance Article on the web 7th February 2001

Organic Au(I) complexes could be highly effective catalysts for the synthesis of diformamides by carbonylation of aliphatic diamines, with selectivity significantly enhanced in the presence of the appropriate amount of oxygen.

Gold as a catalytic material has recently been receiving growing attention. Many reactions catalysed over Au catalyst such as CO oxidation,[1,2] selective oxidation,[3,4] removal of NO_X,[5] selective hydrogenation,[6] methane combustion,[7,8] carbonylation of olefins,[9] dehydrogenation dimerization of trialkylstannane,[10] asymmetric aldol reactions[11] and C–C bond making reactions,[12–14] have been reported to have excellent performances. These results indicate that the potential of gold as a catalyst may be tremendous and is worthy of further investigation, since gold has been little explored in comparison with precious metals such as Pd, Pt, Rh *etc*.

In this communication, we show that organic Au(I) complexes can be highly effective catalysts for the synthesis of diformamides, which are useful as intermediate compounds to pharmaceutical substances,[15] by carbonylation of aliphatic diamines in the presence of appropriate amounts of oxygen [eqn. (1)].

$$H_2N(CH_2)_mNH_2 + CO \xrightarrow[O_2]{[Au(PPh_3)_a]_bX} OHCHN(CH_2)_mNHCHO \qquad (1)$$

m = 6 or 8; a = 1 or 2; b = 1 or 2; X = Cl, NO_3, or S

$Au(PPh_3)Cl$, $Au(PPh_3)_2Cl$, $Au(PPh_3)NO_3$ and $[Au(PPh_3)]_2S$, synthesized according to the literature,[16–18] were used as the catalysts. $HAuCl_4$ and $Pd(PPh_3)_2Cl_2$ were also employed for the purpose of comparison. All reactions were performed in a 90 cm^3 stainless steel autoclave equipped with a magnetic stirrer. Typically, for each reaction we employed catalyst 0.75–1.6 mol% (relative to the substrate), solvent 20 ml, substrate 0.5 ml or 0.5 g (3–6.5 mmol). These were successively charged into the reactor, and then CO 4–5 MPa and O_2 0–1 MPa were successively introduced with an initial pressure 5.0 MPa at room temperature. The reaction was allowed to proceed with stirring at 150–200 °C for 3 h. The resulting liquid mixture was analyzed with a Hewlett-Packard 6890/5793 GC/MS equipped with a HP 5MS column. The concentrations of reactant and product were given directly by the GC/MS chemstation from the area of each chromatograph peak.

The results of carbonylation of aliphatic amines are shown in Table 1. Although the oxygen was not involved directly in the carbonylation reaction according to eqn. (1), it was found that oxygen had a remarkable impact on the selectivity. For example, when 1,6-hexanediamine was used as the substrate in the presence of $Au(PPh_3)Cl$ as catalyst, entry 1, only 47.2% of the selectivity for desired diformamide could be obtained in the absences of oxygen although the conversion was almost 100%. The main by-product was monoformamide (52.5%), and a very small amount of *N*,*N*,*N*′,*N*′-tetramethyl 1,6-hexanediamine was also detected, which probably resulted from the reaction of 1,6-hexanediamine with methanol. The selectivity, however, was significantly enhanced when a small amount of O_2 was introduced, and it can also be seen that high selectivities could not be achieved if the addition of O_2 was deficient or excessive (entries 2–4), *i.e.* there existed an optimum $P(CO):P(O_2)$ ratio for high selectivities of *ca.* 4.5:0.5, under which only monoformamide (8%) was detected. Hexanolactam (1%), an over oxidized by-product, could be found if the ratio of $P(CO):P(O_2)$ reached 4.0:1.0. Since O_2 was not directly incorporated into the products it was conjectured that O_2 plays a role in maintaining the Au species in an appropriately active state during the reaction.

Although 150 °C was high enough for almost complete conversion of the substrate (entry 5), the highest selectivity for

Table 1 The results of catalytic carbonylation of aliphatic amines with different Au(I) complexes

Ent.	Sub.	Cat.	Sol.	$P(CO)$: $P(O_2)$	T/°C	Con. (%)	Sel. (%)	TOF[a]	TOFP[b]
1	HDA[c]	$Au(PPh_3)Cl$	MeOH	5.0/0	175	100	47.2	30	14.2
2	HDA	$Au(PPh_3)Cl$	MeOH	4.8/0.2	175	100	59.5	30	17.9
3	HDA	$Au(PPh_3)Cl$	MeOH	4.5/0.5	175	100	92	30	27.6
4	HDA	$Au(PPh_3)Cl$	MeOH	4.0/1.0	175	100	87	30	26.1
5	HDA	$Au(PPh_3)Cl$	MeOH	4.5/0.5	150	100	63	30	18.9
6	HDA	$Au(PPh_3)Cl$	MeOH	4.5/0.5	200	100	99	30	29.7
7	HDA	$Au(PPh_3)Cl$	CH_3CN	4.5/0.5	175	100	90	30	27
8	HDA	$Au(PPh_3)Cl$	C_6H_6	4.5/0.5	175	100	95	30	28.5
9	HDA	$Au(PPh_3)_2Cl$	C_6H_6	4.5/0.5	175	100	94	30	28.2
10	HDA	$Au(PPh_3)NO_3$	C_6H_6	4.5/0.5	175	100	93	30	27.9
11	HDA	$[Au(PPh_3)]_2S$	C_6H_6	4.5/0.5	175	100	96	30	28.8
12	HDA	$HAuCl_4$	C_6H_6	4.5/0.5	175	100	10	30	3.0
13	DDA[d]	$Au(PPh_3)Cl$	MeOH	4.5/0.5	200	100	98	20	19.6
14	n-HA[e]	$Au(PPh_3)Cl$	MeOH	4.5/0.5	200	95	51.8	26	13.5
15	c-HA[f]	$Au(PPh_3)Cl$	MeOH	4.5/0.5	200	68	70	38	26.6
16	HDA	$Pd(PPh_3)_2Cl_2$	MeOH	4.5/0.5	150	100	39.5	30	11.9
17	HDA	$Pd(PPh_3)_2Cl_2$	MeOH	4.5/0.5	175	100	79.7	30	23.9

[a] Mole substrate per mole Au per h. [b] Turnover frequency for product. [c] 1,6-Hexanediamine. [d] Decanediamine. [e] n-Hexylamine. [f] Cyclohexylamine.

DOI: 10.1039/b009257f

the desired product was achieved at *ca.* 175 °C, and by-products, such as hexanolactam (0.1%) were detected if the temperature was further increased to 200 °C (entry 6). From entries 3, 7 and 8 it can be seen that the best results were obtained when benzene was employed as solvent, with 95% selectivity achieved; 92% and 90% selectivities were obtained if methanol or acetonitrile were used as solvents, respectively.

$Au(PPh_3)_2Cl$, $Au(PPh_3)NO_3$ and $[Au(PPh_3)]_2S$ were also tested for catalytic activity (entries 9–11). The best catalytic performance was achieved with $[Au(PPh_3)]_2S$ although the differences in selectivities for the desired product were not large with these Au complexes, while the selectivity, when using $HAuCl_4$ as catalyst, was significantly inferior to that with the Au(I) complexes, indicating that the chemical state of Au and the organic ligands played an important role in the selectivity.

The carbonylation of other substrates using $Au(PPh_3)Cl$ as catalyst was further examined under the same reaction conditions (entries 13–15). For decanediamine, almost 100% of conversion and 98% of selectivity were achieved. But $Au(PPh_3)Cl$ as catalyst was less effective when n-hexylamine and cyclohexylamine were used as substrates. The selectivities for the desired products were only 51.8% and 70% respectively, and the main by-products were the corresponding dialkylureas. These results suggested that the organic Au(I) complex catalysts used here were especially effective for the carbonylation of aliphatic diamines to form the corresponding alkyldiformamide.

$Pd(PPh_3)_2Cl_2$ as catalyst was also employed for this reaction, and only 79.7% selectivity was obtained at 175 °C (entry 16) although the conversion could be almost 100%. The main by-products were hexanolactam (5.7%) and monoformamide (14.6%). The catalytic performance of $Pd(PPh_3)_2Cl_2$ was even poorer at 150 °C. This indicates that Au(I) complexes as catalysts for such specific carbonylation are better than the corresponding Pd(II) complexes, although it was well known that Pd complexes are the most effective catalysts for many other carbonylation processes.

It is worth noting that the TOFs listed in Table 1 do not distinguish clearly the differences in performance among these catalysts. For example, the TOFs for entries 1–4 are the same. So, in this work, TOFP (turnover frequency for product), *i.e.* mole product per mole catalyst per hour has been used to characterize the performance of a catalyst. The differences in the catalytic performances are clearly shown with TOFP, for example, at 175 °C the best catalyst is $[Au(PPh_3)]_2S$.

In summary, the organic Au(I) complexes mentioned above can effectively catalyse the carbonylation of aliphatic diamines to produce the corresponding diformamides in the presence of an appropriate amount of oxygen. To our knowledge, this is the first reported study of organic Au(I) complexes as homogeneous catalysts for the synthesis of diformamides by carbonylation of aliphatic diamines. Further optimization towards the gold catalyst system for the carbonylation reaction is now ongoing.

Notes and references

1 A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Hakkinen, R. N. Barnett and Uzi Landman, *J. Phys. Chem. A.*, 1999, **103**, 9573.
2 J. Jansson, *J. Catal.*, 2000, **194**, 55.
3 L. Prati and M. Rossi, *J.Catal.*, 1998, **176**, 552.
4 T. Hayashi, K. Tanaka and M. Haruta, *J.Catal.*, 1998, **178**, 566.
5 T. M. Salama, R. Ohnishi and M. Ichikawa, *Chem. Commun.*, 1997, 105.
6 J. E. Bailie and G. J. Hutching, *Chem. Commun.*, 1999, 2151.
7 R. J. H. Grisel, P. J. Kooyman and B. E. Nieuwenhuys, *J. Catal.*, 2000, **191**, 430.
8 R. D. Waters, J. J. Weimer and J. E. Smith, *Catal. Lett.*, 1995, **30**, 181.
9 Q. Xu, Y. Imamura, M. Fujiwara and Y. Souma, *J. Org. Chem.*, 1997, **62**, 1594.
10 H. Ito, T. Yajima, J.-i Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 1999, **40**, 7807.
11 V. A. Soloshonok and A. D. Kacharov, *Tetrahedron.*, 1996, **52**, 245H.
12 A. S. K. Hashmi, L. Schwarz, J.-H. Choi and T. M. Frost, *Angew. Chem., Int. Ed*, 2000, **39**, 2285.
13 T. Hayashi, M. Sawamura and Y. Ito, *Tetrahedron.*, 1992, **48**, 1999.
14 Y. Ito, M. Sawamura and T. Hayashi, *J. Am. Chem. Soc.*, 1986, **108**, 6405.
15 J. W. Mitchell and T. A. Johnson, US Patent 5919979.
16 *Inorganic Syntheses*, ed. R. N. Grimes, Wiley, New York, 1992, **29**, 280.
17 C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton. Trans.*, 1979, **1**, 1730.
18 F. Canales, C. Gimeno, A. Laguna and M. D. Villacampa, *Inorg. Chim. Acta*, 1996, **244**, 95.