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A novel and effective Ni complex catalyst system for the coupling reactions of carbon dioxide and epoxides

Fuwei Li, Chungu Xia,* Liwen Xu, Wei Sun and Gexin Chen
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 73000, P. R. China. E-mail: cgxia@ns.lzb.ac.cn; Fax: (+86) 931-827-7088

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The coupling of carbon dioxide and mono-substituted terminal epoxides or cyclohexene oxide to form cyclic carbonates under a Ni complex catalyst system without using additional organic solvents was achieved in excellent selectivity and TOF.

The search for environmentally benign and economic processes has been the impetus for much of the research involving epoxides and carbon dioxide coupling. During the last two decades, the chemical fixation of carbon dioxide has received much attention. This is in part due to the economic and environmental benefits of carbon dioxide to be used as a safe and cheap C_1 building block in organic synthesis.[1] One of the most promising methodologies in this area is the cycloaddition between epoxides and carbon dioxide to afford the five-membered cyclic carbonates, which are excellent aprotic polar solvents and are used extensively as intermediates in the production of pharmaceuticals and fine chemicals.[2] The cycloaddition between epoxides and carbon dioxide is usually carried out in conventional noxious organic solvents by various catalyst systems.[3] However, these catalyst systems all suffer from either low catalyst stability/reactivity, the need for a co-solvent, or the requirement for high pressure and/or high temperatures. Recently, Nguyen and Shi reported that Cr(III), Cu(II), Co(II) and Zn(II) salen-type metal complexes can efficiently catalyze the reaction of epoxide and carbon dioxide to synthesize cyclic carbonates in high TOF.[4] But these catalyst systems are all expensive and catalyst reactivities are not high enough.

De Pasquale disclosed a number of unsaturated nickel(0) complexes which exhibited excellent reactivity.[5] However, this catalyst system needs noxious benzene as a co-solvent and the reaction time is long; furthermore, the catalysts are very sensitive to air and are expensive. This result stimulated us to explore solvent-free, air-insensitive, cheap, shorter reaction time and simple separation catalyst systems. Herein, we report a very highly active, green Ni(II) catalyst system for the synthesis of cyclic carbonates from the cycloaddition between carbon dioxide and terminal epoxides or cyclehexene oxide under mild conditions. In this catalyst system, there is no co-solvent and the seperation of product from catalyst is extremely simple, therefore, it is an environmentally benign and green catalyst process.

During our investigation of the cycloaddition between propylene oxide **1a** and carbon dioxide catalyzed by a Ni(II) complex in the presence of quaternary salts and the reducing agent Zn powder (eqn. 1), we found that the propylene carbonate **2a** could be obtained in 99% yield and 3544 h^{-1} TOF without using any co-solvents (Table 1, entry 4). To the best of our knowledge, this is the best result in this reaction. When the reducing agent Zn powder was not used or there was only $n\text{-}Bu_4NBr$ in the catalyst system, the reaction activity was poor (Table 1, entries 1 and 2); the yield of the product was very low in the absence of the quaternary salt (Table 1, entry 3); however, increasing the quaternary salt from 1.0 equiv to 3.0 equiv of Ni complex catalyst, respectively, the yields and TOF increase markedly (Table 1, entries 5–7). We believe this may be due to the quaternary salt taking part in the catalysis cycle and only the Ni(0) complex generated *in situ* could not efficiently catalyze the reaction. These results ensured it was the cooperative effect between the Ni(0) complex generated *in situ* and the quaternary salt which led to the very efficient reaction. As shown in Table 1 (entries 4, 8–9), the catalyst system is quite sensitive to reaction temperature. When the temperature was decreased from 120 °C to 90 °C, the yields and TOF decreased. Hence, 120 °C is the optimum reaction temperature in this catalyst system. Besides these conditions, we also investigated the effect of the different quaternary salts on the reaction: among $n\text{-}Bu_4NBr$, $n\text{-}Et_4NBr$ and $n\text{-}Bu_4NCl$, $n\text{-}Bu_4NBr$ is the best quaternary salt under the same conditions (Table 1, entries 5, 10, 11). The best reaction conditions are as follows: propylene oxide (10.38 g, 0.179 mol), catalyst (0.028 mol%); $Ni(PPh_3)_2Cl_2/PPh_3/n\text{-}Bu_4NBr/Zn = 1:2:4:20$; time: 1 h; CO_2 initial pressure: 2.5 MPa; reaction temperature 120 °C.[10]

Table 1 Effect of reaction parameters on the coupling of carbon dioxide and propylene oxide[a]

Entry	Catalyst	Quaternary salt[b]	T/°C	Yield[c] (%)	Selectivity (%)	TOF[d]/h^{-1}
1	$Ni(PPh_3)_2Cl_2/PPh_3$	$n\text{-}Bu_4NBr$	120	12	98	430
2	—	$n\text{-}Bu_4NBr$	120	5	98	179
3	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	—	120	2	97	72
4	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$	120	99	100	3544
5	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$[e]	120	10	100	358
6	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$[f]	120	62	100	2220
7	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$[g]	120	85	100	3043
8	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$	110	83	100	2971
9	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NBr$	90	28	100	1002
10	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Et_4NBr$	120	10	100	358
11	$Ni(PPh_3)_2Cl_2/PPh_3/Zn$	$n\text{-}Bu_4NCl$	120	66	100	2363

[a] Reaction conditions: propylene oxide (12.5 ml, 10.38 g, 0.179 mol), catalyst (32.7 mg, 0.028 mol%), $Ni(PPh_3)_2Cl_2/PPh_3/n\text{-}Bu_4NBr/Zn = 1:2:4:20$, time: 1 h, CO_2 initial pressure: 2.5 MPa. [b] Used 4.0 equiv of Ni catalyst. [c] Isolated yields. [d] Moles of propylene carbonate produced per mole of catalyst per hour. [e] Used 1.0 equiv of Ni complex catalyst. [f] Used 2.0 equiv of Ni complex catalyst. [g] Used 3.0 equiv of Ni complex catalyst.

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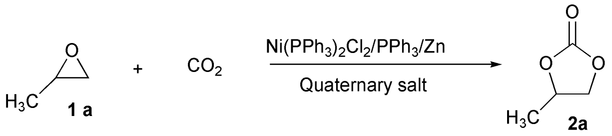
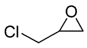
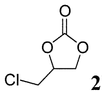
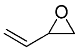
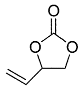
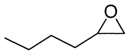
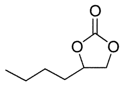
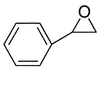
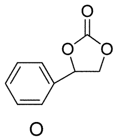
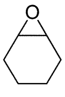
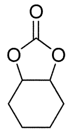


(1)

Under optimized reaction conditions, we next examined the cycloaddition reaction of the other mono-substituted terminal epoxides **1b–1e** and cyclohexene oxide **1f** with carbon dioxide. The results are summarized in Table 2. From Table 2, we can see that this catalyst system is very effective and almost all of the mono-substituted terminal epoxides can be completely transformed to the corresponding five-membered cyclic carbonates **2b–2e** in very high yields, selectivity and TOF. Cyclohexene oxide was used to synthesis the corresponding cyclic carbonate in 68% yield and 1519 h^{-1} TOF, this is due to the effect of high steric hindrace of cyclohexene epoxide. To the best of our knowledge, this is the first report of the synthesis of cyclic cyclohexylcarbonate **2f** directely from cyclohexene oxide and carbon dioxide in such a high selectivity. Judged by GC and NMR, the purities of the produced cyclic carbonates are $>99\%$.

From the results above mentioned, we deduced a plausible mechanism for this reaction. The Ni(II) complex was reduced to a Ni(0) complex by the reducing agent Zn powder,[6,7] and the Ni(0) complex $Ni(PPh_3)_3$ could efficiently activate the inert carbon dioxide to afford a three-membered Ni(0) active intermediate.[5] In another catalytic cycle, the quaternary salts open the ring of the epoxide by means of nucleophilic attack, which leads to an oxyanion species,[8] which attacks the three-membered Ni(0) intermediate to afford another oxyanion species which eventually yields the cyclic carbonate product. This mechanism can explain why there is almost no reaction in the absence of quaternary salts (Table 1, entry 3), while the reaction is very efficient in the presence of quaternary salts (Table 1, entry 4). Based on the above result, we think the Ni(0) complex can activate carbon dioxide[5,9] but its ability to open the ring of the epoxides is low; it is the cooperative effect between the Ni(0) complex and quaternary salts which leads to the very efficient reaction.

Table 2 Cycloaddition between CO_2 and various epoxides catalyzed by the Ni(II) complex in the presence of Zn powder and n-Bu_4NBr^a

Entry	Epoxide	Product	Yield^b (%)	TOF^c/h^{-1}
1	 **1b**	 **2b**	98	3234
2	 **1c**	 **2c**	94	3122
3	 **1d**	 **2d**	96	2000
4	 **1e**	 **2e**	94	2066
5^d	 **1f**	 **2f**	68	1519

^{a} Reaction conditions: all the catalyst components are 1/3 equiv of the optimum reaction conditions, epoxides 4.2 ml, the others are the same as in Table 1, the product selectivities are all $>98\%$. ^{b} Isolated yields. ^{c} Moles of carbonate produced per mole of catalyst per hour. ^{d} 4.0 equiv PPh_3 and 8.0 equiv n-Bu_4NBr of Ni complex catalyst were used.

In conclusion, $Ni(PPh_3)_2Cl_2/PPh_3/Zn$ with n-Bu_4NBr[10] is a highly efficient catalyst system in the cycloaddition of carbon dioxide to epoxides under mild reaction conditions. It is an air stable, easily synthesized, cheap, extremely robust and environmentally benign catalyst system, which is free of co-solvent and can tolerate multiple substrates. These characteristics make it an ideal catalyst system in terms of potential industrial application in chemical carbon dioxide fixation. In addition, a reaction mechanism has been proposed which plausibly explains the reaction result.

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Notes and references

1 (*a*) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063; (*b*) W. Leitner, *Coord. Chem. Rev.*, 1996, **155**, 257; (*c*) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27; (*d*) A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH Publishers, New York, 1988; (*e*) *Carbon Dioxide Fixation and Reduction in Biological and Model Systems*, ed. C.-I. Brauden and G. Schneider, Oxford University Press: Oxford, UK, 1994.

2 K. Biggadike, R. M. Angell, C. M. Burgess, R. M. Farrekk, A. P. Hancick, A. J. Harker, A. J. Irving, W. R. Irving, C. Ioannou, P. A. Procopiou, R. E. Shaw, Y. E. Solanke, O. M. P. Singh, M. A. Snowden, R. Stubbs, S. Walton and H. E. Weston, *J. Med. Chem.*, 2000, **43**, 19–21.

3 (*a*) N. Kihara, N. Hara and T. Endo, *J. Org. Chem.*, 1993, **58**, 6198; (*b*) H. Kisch, R. Millini and I. J. Wang, *Chem. Ber.*, 1986, **119**, 1090; (*c*) M. Ratzenhofer and H. Kish, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 317; (*d*) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang and S. O. Kang, *Angew. Chem., Int. Ed.*, 2000, **39**, 4096; (*e*) T. Aida and S. Inooue, *J. Am. Chem. Soc.*, 1983, **105**, 1304; (*f*) K. Yamaguchi, K. Ebitani, T. Yoshida, H. Ishiguro and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526; (*g*) H. Kawanami, A. Sasaki, K. Matsui and Y. Ikushima, *Chem. Commun.*, 2003, 896; (*h*) J. J. Peng and Y. Q. Deng, *New J. Chem.*, 2001, **25**, 639; (*i*) H. S. Kim, J. J. Kim, H. N. Kwon, M. J. Chung, B. G. Lee and H. G. Jang, *J. Catal.*, 2002, **205**, 226; (*j*) H. Yasuda, L. N. Hen and T. Sakakura, *J. Catal.*, 2002, **209**, 547; (*k*) W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725.

4 (*a*) R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **121**, 11498; (*b*) Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559.

5 (*a*) R. J. De Pasquale, *J. Chem. Soc., Chem. Commun.*, 1973, 157–158; (*b*) R. J. De Pasquale, *US Patent* 3,748,345, 1973; M. Aresta and C. F. Nobile, *J. Chem. Soc., Chem. Commun.*, 1975, 636; (*c*) C. A. Wright, M. Thorn, J. W. Mcgill, A. Sutterer, S. M. Hinze, R. B. Prince and J. K. Gong, *J. Am. Chem. Soc.*, 1996, **118**, 10305.

6 V. Percec, J. Y. Bae, M. Y. Zhao and D. H. Hill, *Macromolecules.*, 1995, **28**, 6726.

7 V. Percec, J. Y. Bae and D. H. Hill, *J. Org. Chem.*, 1995, **60**, 6895.

8 V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561.

9 (*a*) L. M. Venanzi, *J. Chem. Soc.*, 1958, 719; (*b*) F. A. Cotton, O. D. Faut and D. M. Goodgame, *J. Am. Chem. Soc.*, 1961, **93**, 344.

10 Representative procedure for the reaction of epoxide with carbon dioxide: All cycloaddition reactions were performed in a 70 ml stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, $Ni(PPh_3)_2Cl_2$ (32.7 mg, 0.05 mmol), PPh_3 (26.2 mg, 0.1 mmol), n-Bu_4NBr (64 mg, 0.2 mmol), Zn powder (65 mg, 1 mmol) and 12.5 ml propylene oxide **1a** (10.4 g, 0.18 mol) were successively charged into the reactor without using any additional solvent. The reactor vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate and then heated to 120 °C for 1 h. After cooling to ambient temperature, the result mixture was transferred to a 50 ml round bottom flask. Firstly, Unreacted propylene oxide was removed *in vacuo*, then the product propylene carbonate **2a** was obtained as a colorless liquid. All the cyclic carbonates were identified by GC/MS (HP6890/5973) and 400 MHz NMR.