A tricarbonyl rhenium(I) complex with a pendant pyrrolidinium moiety as a robust and recyclable catalyst for chemical fixation of carbon dioxide in ionic liquid†

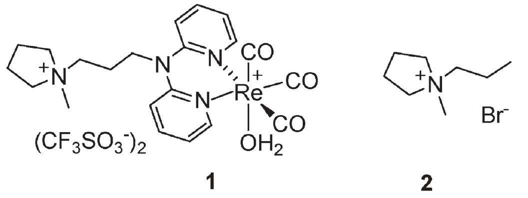
Wing-Leung Wong, Kwong-Chak Cheung, Pak-Ho Chan, Zhong-Yuan Zhou, Kam-Han Lee and Kwok-Yin Wong*

Received (in Cambridge, UK) 18th December 2006, Accepted 5th February 2007
First published as an Advance Article on the web 28th February 2007
DOI: 10.1039/b618423e

A novel Re(I) complex covalently anchored with a pyrrolidinium moiety was successfully synthesized and used as an efficient and recyclable catalyst in the cycloaddition of CO_2 with epoxides under mild reaction conditions to give excellent isolated yield and selectivity of cyclic carbonates in pyrrolidinium ionic liquid.

The development of efficient and recyclable catalytic systems to convert atmospheric carbon dioxide (CO_2) into useful chemicals and fuels is an important research topic in recent years[1] because the accumulation of CO_2 in the atmosphere causes serious environmental problems including the greenhouse effect and global warming. The use of electrochemical reduction and chemical fixation to transform this greenhouse gas into high-energy compounds and useful organic chemicals represents a promising strategy.[1a–c] These chemical processes are, however, usually performed in organic solvents and therefore the precious catalysts cannot be recycled easily. Room-temperature ionic liquids offer an alternative choice of medium for the transformation of CO_2 because of their high CO_2 solubility,[2] high conductivity, wide electrochemical window and non-volatility.[3] Moreover, the use of ionic liquids as reaction media allows the catalysts to be recycled efficiently. These advantageous properties, therefore, render ionic liquids an ideal reaction medium compared to traditional organic solvents for the transformation of CO_2.[4] In order to catalyze this reaction in ionic liquids, the catalyst must be preferentially soluble in these media. An effective way to achieve this purpose is to conjugate the catalyst with an ionic liquid moiety (Scheme 1).[5]

The activation of CO_2 using transition metal complexes as catalysts has been extensively studied.[1,6] In particular, tricarbonyl rhenium(I) bipyridine complexes have been found to be able to catalyze the electro- and photo-chemical reduction of CO_2 efficiently.[7] Surprisingly, their applications in the chemical fixation of CO_2 with epoxides remain rare.[8] As such, it is highly desirable to explore the potential of the rhenium complexes in catalyzing the activation and transformation of CO_2 into useful organic compounds such as cyclic carbonates, compounds that are widely used in a variety of areas including the manufacture of monomers, polar aprotic solvents, pharmaceutical, biomedical and fine chemical intermediates.[9]



Scheme 1 Structure of complex **1** and pyrrolidinium bromide **2**.

In this context, we report the use of a novel tricarbonyl rhenium(I) complex **1**, which is covalently associated with a pyrrolidinium ionic liquid moiety, as a robust and efficient catalyst for the chemical fixation of CO_2 with various epoxides under low pressure and temperature conditions. To the best of our knowledge, complex **1** is the first recyclable rhenium catalyst designed for the green synthesis of cyclic carbonates with CO_2 with pyrrolidinium bromide (**2**) as the reaction medium.

Complex **1** was first synthesized by refluxing $Re(CO)_5Cl$ with 1-methyl-1-(3-*N*,*N'*-bis(2-pyridyl)propylamino)pyrrolidinium iodide[10] (**L**) in ethanol to give $Re(CO)_3$(**L**)Cl. The complex was then treated with an excess amount of silver triflate in ethanol, giving a quantitative yield of **1** as the triflate salt, a non-coordinating anion. The complex was characterized by NMR, ESI-MS, and elemental analysis.‡ The crystal structure of **1** reveals that the pyrrolidinium ionic liquid moiety is covalently conjugated with the rhenium(I) complex (Fig. 1). The rhenium(I) ion is associated with the two pyridines of the ligand, an aquo molecule, and three CO groups in a facial orientation, forming an octahedral complex.[12] The bond lengths in **1** agree with those of the structurally similar *fac*-$Re^I(CO)_3$ bipyridine complexes.[7] The two Re–N bonds are very similar in length (2.18 Å), and the bond angles of the metal centre with the coordinated atoms of the ligands fall in the range of 80–96°, indicating that the complex adopts a slightly distorted octahedral geometry. This observation implies that the anchored pyrrolidinium ionic liquid moiety does not affect significantly the structure of the complex.

The ability of **1** to catalyze the chemical fixation of CO_2 with 1,2-epoxy-3-phenoxypropane in the ionic liquid of pyrrolidinium bromide[11] was studied. With 0.8 mol% of **1** (relative to the epoxide), this complex was found to be able to convert the epoxide into 3-phenoxy-1,2-propylene carbonate in the presence of CO_2 (1.0 MPa) with 66% conversion and over 99% selectivity for cyclic carbonate within 0.5 h at 80 °C (Table 1). When increasing the reaction time to 1 h under the same conditions, the conversion was

---

Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China. E-mail: bckywong@polyu.edu.hk; Fax: +852 2364 9932; Tel: +852 3400 8686

† Electronic supplementary information (ESI) available: Synthesis and X-ray crystal data for complex **1** and ligand **L**. See DOI: 10.1039/b618423e

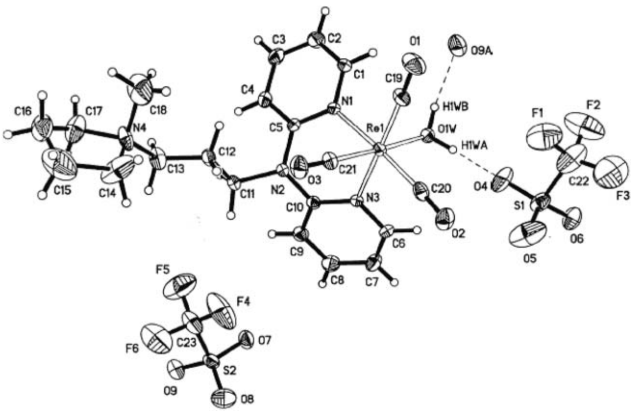


Fig. 1 X-Ray crystal structure of **1** (30% probability chosen for the ellipsoids, O9A atom is at equivalent position ($x - 1$, ½ − y, $z - 1/2$) of O9 atom).

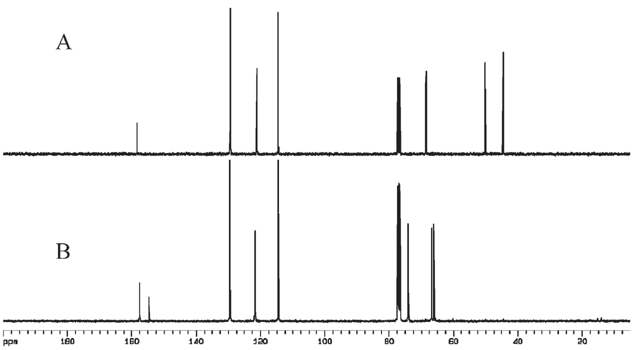
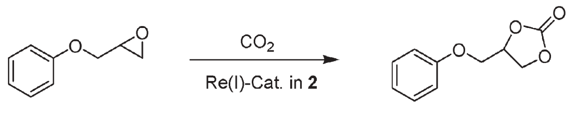


Fig. 2 ^{13}C NMR spectra of (A) the reactant and (B) the crude product collected in the 10th experiment.

remarkably increased to 95%. When the CO_2 pressure was reduced to 0.5 MPa, the conversion dropped to 82% (entry 3). Nevertheless, the reaction was found to be completed within 1 h at 80 °C when the pressure of CO_2 was increased to 1.5 MPa (Table 1, entry 5). These results indicate that complex **1** is a very efficient catalyst for the synthesis of cyclic carbonates in ionic liquids under mild reaction conditions.

We then investigated the possibility of recycling complex **1** in the synthetic process. The complex was used to catalyze the cycloaddition of 1,2-epoxy-3-phenoxypropane with CO_2 for 10 cycles, and the extent of conversion of the epoxide was examined. Surprisingly, both the extents of conversion of the epoxide in the 1st and 10th experiments were found to be very similar (95%, Table 1: entry 6), indicating that there was no significant loss of catalysts in the product extraction processes. The crude product was characterized by both GC-MS and NMR to examine the selectivity of the reaction and the purity of the product in each experiment. As shown in the NMR spectrum (Fig. 2(B)), a new carbon signal given by the carbonate product appears at 154.7 ppm. This signal, however, does not appear in the NMR spectrum of the reactant. For comparison, a control experiment was also performed in which the 2,2′-dipyridylamine tricarbonyl rhenium(I) complex was used as the catalyst. Under similar conditions, this complex was found to be able to catalyze the cycloaddition but the recyclability was much poorer (conversion reduced to 88% at the 4th cycle) compared to complex **1** due to the leaching of catalysts in the product extraction processes. These observations, therefore, suggest that the anchored pyrrolidinium moiety in complex **1** can effectively minimize the loss of the catalyst compared to the pyrrolidinium-free complex.

Table 1 Cycloaddition of 1,2-epoxy-3-phenoxypropane with CO_2 catalyzed by **1** at different pressures using **2** as the reaction medium[a]



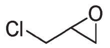
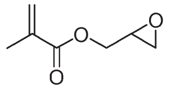
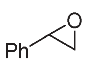
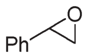
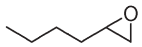
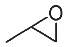
Entry	Catalyst (mol%)	Pressure[b]/MPa	Time/h	Conv.[c]/%
1	0.8	1.0	0.5	66
2	0.8	1.0	1	95
3	0.8	0.5	1	82
4	—	1.0	1	36
5	0.8	1.5	1	98
6[d]	0.8	1.5	1	95 (10th cycle)

[a] *Reaction conditions*: epoxide (2.5 mmol, 340 μL), ionic liquid **2** (2.5 mmol, 520 mg), temperature: 80 °C. [b] CO_2 was charged directly into an autoclave at room temperature and atmosphere. [c] Determined by GC-MS. The selectivity for cyclic carbonates were over 99% in all cases. [d] Conversion of the 10th experiment in the recycling studies.

As expected, complex **1** can also catalyze the cycloaddition of other terminal epoxides with CO_2 under mild reaction conditions in the ionic liquid. Epoxides that are highly polar (*e.g.* epichlorohydrin and glycidyl methacrylate) give excellent conversion efficiencies (100%) and isolated yields (99%) within 1 h (Table 2, entries 1 and 2). Styrene oxide was found to be less reactive, presumably due to the steric hindrance of the phenyl group; only 86% conversion was obtained in the first hour (Table 2: entry 3). When this reaction was allowed to proceed for another 2 h, the conversion was increased to 95% with high selectivity for cyclic carbonate (>99%). For the aliphatic terminal epoxide 1,2-epoxyhexane, this molecule, which is relatively non-polar, shows only moderate reactivity (Table 2: entry 5). For the low boiling epoxide such as propylene oxide, only 13% of propylene carbonate was obtained after 1 h under the same reaction conditions. This is because at 1.5 MPa and 80 °C propylene oxide exists as a gas and most of which probably stays in the headspace region of the reaction vessel. The cycloaddition of cyclic epoxides such as cyclohexene oxide was much less efficient compared to the others; the conversion was found to be less than 30% even though the reaction was allowed to proceed for 2 h. The mechanism of the cycloaddition of epoxides with CO_2 catalyzed by complex **1** probably follows that proposed for $Re(CO)_5Br$,[8] in which oxidative addition of epoxide to the Re-catalyst to give a cyclic oxorhenium intermediate was followed by insertion of CO_2 into the Re–O bond, and finally reductive elimination to produce cyclic carbonate. As shown in Table 1 (entry 4), the ionic liquid itself can catalyze the reaction through a Lewis-acid mechanism[4c] with the assistance of Br^- as the nucleophile, though the conversion is much lower. Whether the formation of cyclic carbonates in this study occurs *via* the catalysis of Re-catalyst only or a combination of both catalytic pathways cannot be differentiated at this stage.

In conclusion, we have successfully prepared a new tricarbonyl rhenium(I) complex covalently associated with a pyrrolidinium ionic liquid moiety. This complex can serve as an efficient and

Table 2 Catalytic cycloaddition of CO_2 (1.5 MPa) with different terminal epoxides at 80 °C[a]

Entry	Epoxide	Time/h	Conversion[b] (%)	Yield[c] (%)
1		1	100	99
2		1	100	99
3		1	86	86
4		2	95	94
5		2	80	79
6		1	—	13

[a] *Reaction conditions*: epoxide (2.5 mmol, 340 μL), catalyst **1** (0.8 mol%), ionic liquid **2** (2.5 mmol, 520 mg). CO_2 (1.5 MPa) was charged directly into an autoclave at room temperature and atmosphere. [b] Determined by GC-MS. [c] Isolated yield based on 2.5 mmol of epoxides.

recyclable catalyst for the green synthesis of cyclic carbonates with CO_2 in pyrrolidinium ionic liquids under low temperature and pressure conditions. Moreover, the metal complex can be recycled efficiently in the synthetic process.

We acknowledge the support from The Hong Kong Polytechnic University and the Research Grants Council (Grant no. PolyU 5015/05P). W. L. W. acknowledges the award of a postdoctoral fellowship administered by the Research Committee of The Hong Kong Polytechnic University.

Notes and references

‡ Selected characterization for complex **1**: ^1H NMR (400 MHz CD_3CN): δ 2.05–2.21 (m, 6H), 2.93 (s, 3H), 3.37–3.52 (m, 6H), 4.15 (t, 2H, J = 8 Hz), 7.41 (t, 2H, J = 6 Hz), 7.67 (d, 2H, J = 8 Hz), 8.17 (t, 2H, J = 8 Hz), 8.75 (d, 2H, J = 6 Hz); ESI-MS m/z: 716.9 ($M^+ - CF_3SO_3^-$). Anal. Calc. for $Re(H_2O)(CO_3)(C_{18}H_{25}N_4)(CF_3SO_3)_2$: C, 31.26; H, 3.09; N, 6.34. Found: C, 31.21; H, 3.12; N, 6.61%.

Crystal data for **1** (CCDC 631247): $Re(H_2O)(CO)_3(C_{18}H_{25}N_4)\cdot 2(CF_3SO_3)$, M = 883.81; monoclinic, $P2_1/c$; a = 10.800(2), b = 16.235(3), c = 18.666(4) Å, β = 102.601(3)°; V = 3193.9(10) Å^3; T = 294(2) K; Z = 4; μ = 4.027 mm^{-1}; reflections collected = 29441; independent reflections = 7313 (R_{int} = 0.0502); final R values [$I > 2\sigma(I)$]: $R1$ = 0.0415, $wR2$ = 0.1008; R values (all data): $R1$ = 0.0637, $wR2$ = 0.1143.

Crystal data for ligand **L** (CCDC 632736): $(C_{18}H_{25}N_4)^+I^-$, M = 424.32; monoclinic, $P2_1/n$; a = 10.756(2), b = 9.1086(19), c = 19.236(4) Å, β = 94.476(4)°; V = 1878.9(7) Å^3; T = 294(2) K; Z = 4; μ = 1.710 mm^{-1}; reflections collected = 17082; independent reflections = 4337 (R_{int} = 0.0379); final R values [$I > 2\sigma(I)$]: $R1$ = 0.0283, $wR2$ = 0.0685; R values (all data): $R1$ = 0.0425, $wR2$ = 0.0750.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618423e

1 (*a*) *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, ed. B. P. Sullivan, K. Krist and H. E. Guard, Elsevier, Amsterdam, 1993; (*b*) *Chemical Fixation of Carbon Dioxide: Methods for Recycling CO_2 into Useful Products*, ed. M. M. Hallman, CRC Press, Boca Raton, FL, 1993; (*c*) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*, ed. P. T. Anastas and T. C. Williamson, Oxford University Press, New York, 1998; (*d*) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063; (*e*) H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. Dubois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953; (*f*) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475.

2 (*a*) L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28; (*b*) J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2002, **106**, 7315; (*c*) C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.*, 2004, **126**, 5300.

3 (*a*) *Ionic Liquids as Green Solvents: Progress and Prospects*, ed. R. D. Rogers and K. R. Seddon, ACS Symposium Series 856, American Chemical Society, Washington DC, 2003; (*b*) *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, 2003; (*c*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*d*) C. M. Gordon, *Appl. Catal., A*, 2001, **222**, 101; (*e*) H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A: Chem.*, 2002, **182**, 419; (*f*) J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667.

4 Some recent examples of activation and transformation of CO_2 in ionic liquids: (*a*) R. Sheldon, *Chem. Commun.*, 2001, 2399; (*b*) J. J. Peng and Y. Q. Deng, *New J. Chem.*, 2001, **25**, 639; (*c*) V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561; (*d*) H. Kawanami, A. Sasaki, K. Matsui and Y. Ikushima, *Chem. Commun.*, 2003, 896; (*e*) M. Alvaro, C. Baleizao, D. Das, E. Carbonell and H. García, *J. Catal.*, 2004, **228**, 254; (*f*) Y. L. Gu, F. Shi and Y. Q. Deng, *J. Org. Chem.*, 2004, **69**, 391; (*g*) J. M. Sun, S. Fujita, F. Y. Zhao and M. Arai, *Green Chem.*, 2004, **6**, 613; (*h*) J. Palgunadi, O. S. Kwon, H. Lee, J. Y. Bae, B. S. Ahn, N. Y. Min and H. S. Kim, *Catal. Today*, 2004, **98**, 511; (*i*) F. W. Li, L. F. Xiao, C. G. Xia and B. Hu, *Tetrahedron Lett.*, 2004, **45**, 8307; (*j*) H. B. Xie, H. F. Duan, S. H. Li and S. B. Zhang, *New J. Chem.*, 2005, **29**, 1199; (*k*) J. M. Sun, S. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490.

5 Numerous examples of immobilization of catalysts with ionic liquids were reported in literatures but only few of them were designed through covalent linking: (*a*) N. Audic, H. Clavier, M. Mauduit and J. C. Guillemin, *J. Am. Chem. Soc.*, 2003, **125**, 9248; (*b*) Q. W. Yao and Y. L. Zhang, *Angew. Chem., Int. Ed.*, 2003, **42**, 3395; (*c*) C. Baleizão, B. Gigante, H. Garcia and A. Corma, *Tetrahedron Lett.*, 2003, **44**, 6813; (*d*) S.-G. Lee, Y. J. Zhang, J. Y. Piao, H. Yoon, C. E. Song, J. H. Choi and J. Hong, *Chem. Commun.*, 2003, 2624.

6 (*a*) A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951; (*b*) M. Yoshida and M. Ihara, *Chem. Eur. J.*, 2004, **10**, 2886; (*c*) G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618; (*d*) J. Sun, S.-I. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490.

7 (*a*) J. Hawecker, J. M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536; (*b*) B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1414; (*c*) S. Cosnier, A. Deronzier and J. C. Moutet, *New J. Chem.*, 1990, **14**, 831; (*d*) P. Christensen, A. Hamnett, A. V. G. Muir and J. A. Timney, *J. Chem. Soc., Dalton Trans.*, 1992, **9**, 1455; (*e*) T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1993, 631; (*f*) G. Ruiz, E. Wolcan, A. L. Capparelli and M. R. Feliz, *J. Photochem. Photobiol., A*, 1995, **89**, 61; (*g*) H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani and T. Ibusuki, *J. Photochem. Photobiol., A*, 1996, **96**, 171; (*h*) K.-Y. Wong, W.-H. Chung and C.-P. Lau, *J. Electroanal. Chem.*, 1998, **453**, 161.

8 Only one report on using $Re(CO)_5Br$ as the catalyst: J. L. Jiang, F. X. Gao, R. M. Hua and X. Q. Qiu, *J. Org. Chem.*, 2005, **70**, 381.

9 (*a*) W. J. Peppel, *Ind. Eng. Chem.*, 1958, **50**, 767; (*b*) A. Behr, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 661; (*c*) A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951; (*d*) J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663.

10 For the X-ray structural characterization of **L**, see ESI†.

11 1-Methyl-1-*N*-propylpyrrolidinium bromide (**2**) was prepared according to the literature: D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164.

12 For the X-ray structural characterization of complex **1**, see ESI†.