Supplementary Material (ESI) for Chemical Communications

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*

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

Synthesis of complex 1:

1-Methyl-1-(3-N,N'-bis(2-pyridyl)propylamino) pyrrolidinium iodide (**L**) (2 mmol, 848 mg) in 2 ml of CH_2Cl_2 was refluxed with $Re(CO)_5Cl$ (2.2 mmol, 796 mg) in 10 ml of absolute ethanol overnight. After reaction, the solution was concentrated and n-hexane (10 ml) was added. The precipitate was collected and washed with hot n-hexane. The isolated $Re(CO)_3$(**L**)Cl complex was then treated with an excess amount of AgOTf (3 mol equivalents) in ethanol at room temperature to give a quantitative yield of **1** as a pure compound. ^{1}H NMR (400 MHz CD_3CN): δ2.05-2.21 (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. Calcd 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.

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General procedures for catalytic cycloaddition of epoxides with CO_2 in ionic liquid:

Epoxides (2.5mmol), ionic liquid **2** (520mg) and the catalyst (0.8 mol %) was well mixed in an autoclave. The compressed CO_2 was charged directly into the autoclave at room temperature and atmosphere. The mixture was reacted at 80 °C for 1 h at the autoclave with good stirring. After reaction, the autoclave was cooled by cold water and the pressure was released slowly. The reaction mixture was extracted with hot ethyl acetate (15 ml) and then the solution was decanted from the autoclave. The extraction process was repeated four times to ensure complete removal of products. The residue in the autoclave was recycled after removal of solvent under vacuum.

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S1. Crystallographic data for ligand **L**: 1-methyl-1-(3-N,N'-bis(2-pyridyl)propylamino) pyrrolidinium iodide

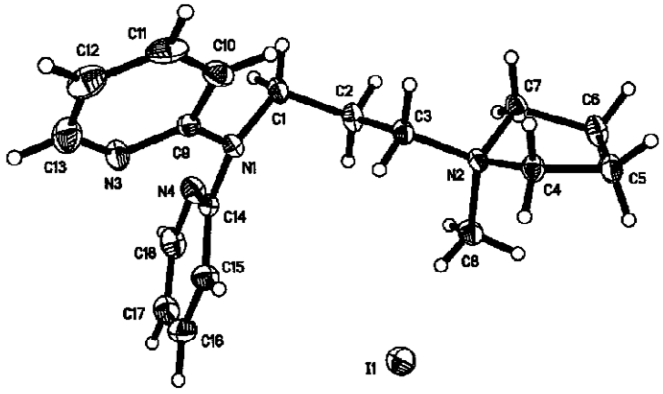

Figure S1.1 X-ray crystal structure of **L**: *ORTEP* representation (30% probability chosen for the ellipsoids).

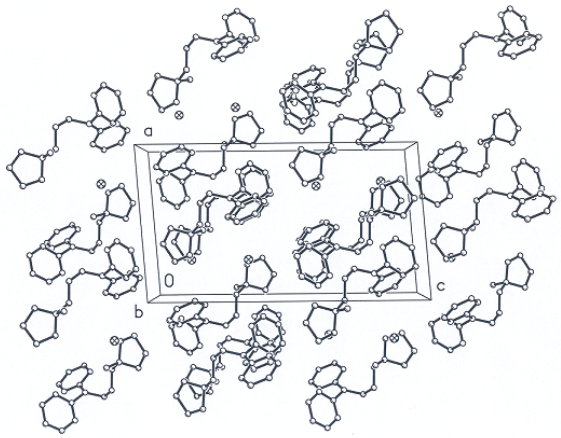

Figure S1.2 X-ray crystal structure of **L**: Molecular packing

Table S1.1 Crystal data and structure refinement for ligand **L**

Empirical formula	$(C_{18}H_{25}N_4)^+ I^-$	
Formula weight	424.32	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.756(2) Å	= 90°.
	b = 9.1086(19) Å	= 94.476(4)°.
	c = 19.236(4) Å	= 90°.
Volume	1878.9(7) $Å^3$	
Z	4	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	1.710 mm^{-1}	
F(000)	856	
Crystal size	0.50 x 0.32 x 0.26 mm^3	
Theta range for data collection	2.10 to 27.57°	
Index ranges	-13<=h<=13, -11<=k<=11, -24<=l<=25	
Reflections collected	17082	
Independent reflections	4337 [R(int) = 0.0379]	
Completeness to theta = 27.57°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.724	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4337 / 0 / 209	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0685	
R indices (all data)	R1 = 0.0425, wR2 = 0.0750	
Largest diff. peak and hole	0.483 and -0.406 $e.Å^{-3}$	

S2. Crystallographic data for complex **1**:

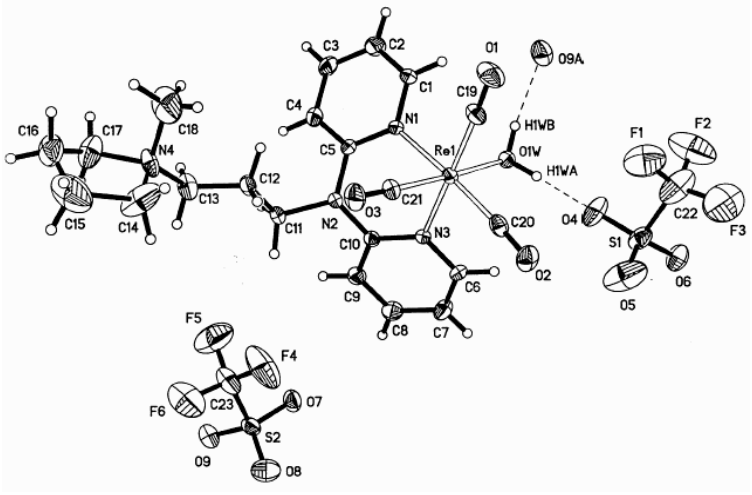

Figure S2.1 X-ray crystal structure of complex **1**: *ORTEP* representation (30% probability chosen for the ellipsoids).

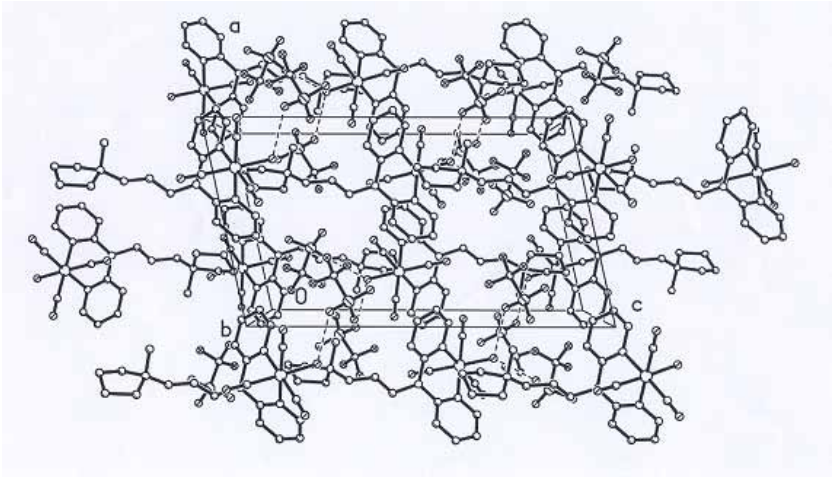

Figure S2.2 X-ray crystal structure of complex **1**: Molecular packing

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Table S2.1 Crystal data and structure refinement for complex **1**

Empirical formula	$Re(H_2O)(CO)_3(C_{18}H_{25}N_4)\ .2(CF_3SO_3)$	
Formula weight	883.81	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.800(2) Å	= 90°.
	b = 16.235(3) Å	= 102.601(3)°.
	c = 18.666(4) Å	= 90°.
Volume	3193.9(10) $Å^3$	
Z	4	
Density (calculated)	1.838 Mg/m^3	
Absorption coefficient	4.027 mm^{-1}	
F(000)	1736	
Crystal size	0.38 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.68 to 27.53°	
Index ranges	-13<=h<=14, -20<=k<=21, -24<=l<=24	
Reflections collected	29441	
Independent reflections	7313 [R(int) = 0.0502]	
Completeness to theta = 27.53°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.724	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7313 / 5 / 404	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1008	
R indices (all data)	R1 = 0.0637, wR2 = 0.1143	
Largest diff. peak and hole	1.091 and -0.710 $e.Å^{-3}$	

Table S2.2 Selected X-ray crystal data for complex **1**

Bond lengths /Å		Bond angles /º			
Re−N1	2.185(3)	N1−Re−N3	80.65(10)	N3−Re−C21	96.39(13)
Re−N3	2.184(3)	N1−Re−C19	95.47(15)	N3−Re−O1W	81.11(9)
Re−C19	1.907(4)	N1−Re−C21	93.22(14)	C19−Re−C20	89.40(18)
Re−C20	1.919(4)	N1−Re−O1W	82.14(9)	C19−Re−C21	87.75(16)
Re−C21	1.901(4)	N3−Re−C20	94.41(14)	C19−Re−O1W	94.47(13)
Re−O1W	2.201(2)				