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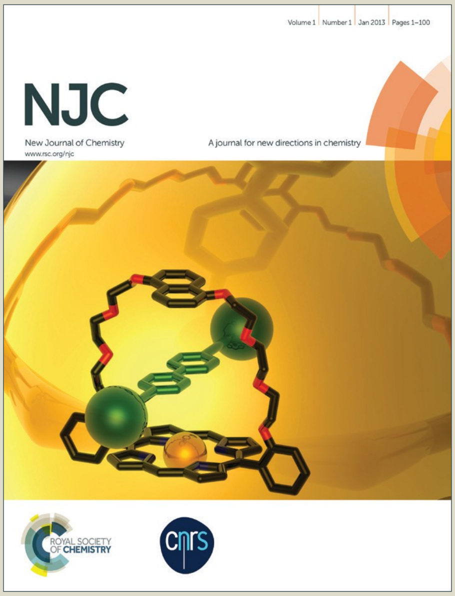

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Cycloaddition of CO_2 to epoxides using di-nuclear transition metal complexes as catalysts†

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Studies on the reaction and conversion of CO_2 to valuable products have made much progress in recent years, and the search for efficient catalysts is also expanding. Cycloaddition of CO_2 to epoxides was carried out selectively using di-nuclear Cu^{II}, Co^{II} and Ni^{II} complexes (**C1**, **C2** and **C3** respectively) as catalysts. The complexes were synthesized in good yield and characterized by various spectroscopic methods. In all complexes the ligand **L** acted as a bidentate NO donor favouring distorted octahedral, tetrahedral or square planar geometry for **C1**, **C2** and **C3** respectively. Complex **C2** in presence of n-Bu_4NI as cocatalyst showed the highest activity among the reported complexes in the cycloaddition reaction.

1. Introduction

The use of carbon dioxide as a safe and cheap C1 building block for the synthesis of organic chemicals can contribute to a more sustainable chemical industry.[1,2,3] CO_2 is a thermodynamically stable and chemically inert molecule due to the negative adiabatic electron affinity (EA) and large ionization potential (IP), thus making its conversion into useful products and chemicals difficult under normal conditions.[4] Methods to overcome the high energy barriers are based upon reduction, oxidative coupling with unsaturated compounds on low valent metal complexes and increasing the electrophilicity of the carbonyl carbon.[5] Several different catalysts ranging from heterogenous to homogenous to ionic liquids have been designed for the conversion of CO_2 to useful products.[1,2,3,4] Amongst these the catalytic cycloaddition of CO_2 to epoxides, leading to the synthesis of cyclic carbonates and polycarbonates has received much attention.[3,4] Cyclic carbonates are important class of compounds with several applications e.g., ethylene carbonate is an excellent solvent for many polymers and resins, they can be used as electrolytes in lithium ion batteries, as precursors for pharmaceutical intermediates, raw materials for plastics, and as environmentally friendly nonprotic solvents and degreaser.[6]

The cycloaddition between epoxides and carbon dioxide was usually carried out in conventional noxious organic solvents by various catalyst systems; [2,7] most catalysts for this process require the use of high reaction temperatures and/or high pressures of carbon dioxide. However, new excellent catalysts with high stability and reactivity have been designed which can work at room temperature and pressure under solvent free conditions.[8,9,10] Metal oxides were the first catalysts to be used for the cycloaddition reaction.[6] Research in this field has expanded in recent years and different heterogenous and homogenous catalysts, zeolites, and porphyrin based catalysts have been used for this cycloaddition.[2,11] Schiff base and salen complexes as homogeneous catalysts have been found to be efficient catalysts for the cycloaddition reaction of CO_2 to epoxides with high turnover number (TON) and high turnover frequency (TOF).[12] A variety of metal complexes, including Zn, Al, and Co, have also been reported as efficient catalysts for the cycloaddition of CO_2 to epoxides.[13] Use of bimetallic complexes is however scarce possibly due to emergence of studies showing no benefit of di-nuclearity in contrast to mono nuclearity.[13] Some recent studies have come which support the use of di-nuclear metal complexes for the cycloaddition of CO_2 and epoxides.[2,11,14,15] A study proves that the di-nuclear system maintains its activity even under highly diluted conditions at which the mononuclear system loses its efficiency.[14] Flexibly tethered di-nuclear cobalt salen and chromium salphen complexes have also exhibited a noticeably higher activity than their mononuclear analogues.[14] Salen type and porphyrin based catalysts have already been used, however no literature precedents were found describing the use of oxime based complexes as catalysts. Therefore the development of efficient non-precious metal catalysts for CO_2 conversion reactions is a challenging goal in both synthetic and industrial organic chemistry. Following our work on CO_2 capture and

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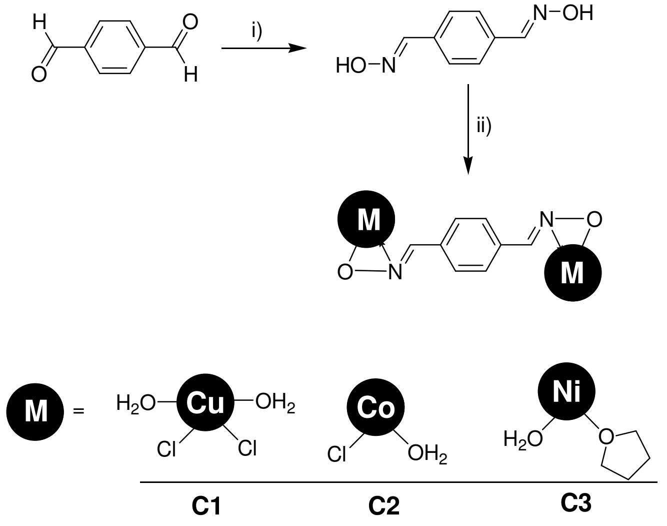
conversion[16-21] here we report the synthesis and catalytic behaviour of di-nuclear Cu^{II}, Co^{II} and Ni^{II} complexes of benzene-1,4-diylbis(N-hydroxy-methanimine) (**L**) towards the cycloaddition of CO_2 to epoxides.

2. Results and discussion

The ligand (**L**) was prepared by a Schiff base condensation reaction of benzene-1,4-dicarboxaldehyde (**1**) with hydroxylamine hydrochloride under basic conditions in water in 1:2 molar ratio as outlined in Scheme **1**. Complex **C1** was prepared by mixing 1:2 ratio of **L** and $CuCl_2.2H_2O$, in THF at room temperature. Similarly complexes **C2** and **C3** were prepared by adding a solution of $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ to half molar amounts of **L** in THF (Tetrahydrofuran) at room temperature, respectively. In case of complex **C3**, the metal salt was dissolved in a minimum quantity of ethanol and mixed slowly with the ligand dissolved in THF under magnetic stirring. Complexes were obtained in high yield (70–75%) and were purified by washing with *n*-hexane and recrystallized in ethanol/THF. They were remarkably stable in air in the solid state for a few days and soluble in DMF, DMSO, MeOH, EtOH and DCM but insoluble in water and have melting points higher than 250°C. The spectral data confirm that, for all three complexes studied, the metal-to-ligand stoichiometry is 2:1. The chemical structures of all the compounds were confirmed by electronic (UV-Vis), FTIR, ^1H NMR, ^{13}C NMR, MS (ESI^+) and TGA/DTG/DSC studies.



Scheme 1. Synthesis of ligand (**L**) and metal complexes **C1**-**C3**. Reaction Conditions: (i) $NH_2OH.HCl$, $NaHCO_3$, Water (ii) $CuCl_2.6H_2O$ (**C1**), $CoCl_2.6H_2O$ (**C2**), THF, reflux; $NiCl_2.6H_2O$ (**C3**), THF/ Ethanol reflux.

2.1. FTIR spectra

The infrared spectrum of the free ligand presents a broad band at 3200-3450 cm^{-1} corresponding to the -OH vibration. The changes in stretching frequencies concerned with ν(OH) could not be identified as that region is merged with ν(OH) of water and appear as a broad band in that region in the complexes. The strong band observed at 1620-1680 cm^{-1} in the spectrum of the free ligand is assigned to the C=N vibration. The weakening and negative shift of 20-30 cm^{-1} of υ (C=N) stretch in the complexes indicates the involvement of azomethine nitrogen in complexation. Stretching vibrations around 650-1000 cm^{-1} corresponding to THF molecules were also observed in the FTIR spectra of **C3** complex (Fig. **1**). For all of the metal complexes, two new bands appear at low frequencies, which are absent in the free ligand spectrum. These bands, in the 450-680 cm^{-1} range, are due to the M-O and M-N vibrations, an indication of coordination of the ligand to the metal centres probably through the deprotonated -OH and -C=N groups.

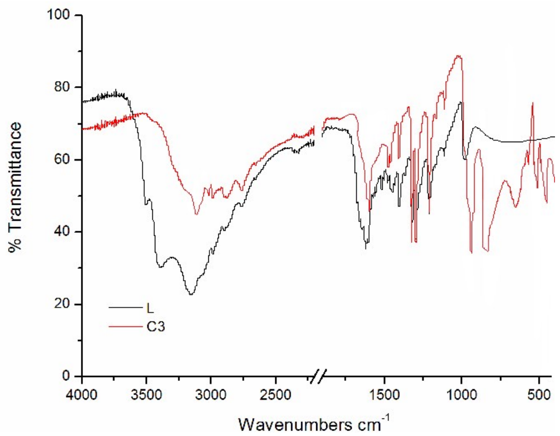


Fig. 1. FTIR spectra of ligand (L) and complex C3 showing weakening and shift of C=N stretching around 1620-1650 cm^{-1} and stretching vibrations around 650-1000 cm^{-1} corresponding to THF (ATR mode).

2.2. Electronic Spectra

The electronic spectrum of the ligand, shows two bands in the region 285-360 nm, corresponding to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition due to the (–C=N–OH) chromophore. These bands get red shifted by 5-10 nm and 10-40 nm respectively, in the electronic spectra of the complexes. In addition to ligand-originated bands, additional absorption bands due to metal-originated d-d transitions and charge transfer were observed in the spectra of the complexes, characteristic to their geometries.[22] In all cases, intense absorptions are observed below 400 nm, which are assigned to metal-to-ligand charge transfer transitions. The electronic spectrum of the Cu(II) complex (**C1**) display a band in the 690-790 nm region, assigned to $^2B_{1g}\rightarrow{}^2E_g$ transitions. Another intense band at 385 nm refers to charge transfer transition ($L\rightarrow Cu^{II}$ CT), indicating its tetragonally distorted octahedral geometry.[22] Co(II) complex (**C2**) showed two absorption bands in the visible region. First band at 525 nm is assigned to $^2A_1g\rightarrow{}^2E_g$ transitions and the second band at 680 nm is assigned to $^2A_1g\rightarrow{}^2B_{1g}$ transition, favouring a square planar geometry.[22] The electronic spectrum of Ni(II) complex (**C3**) display absorption bands in the regions 410, and 760 nm assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ transitions, respectively, indicating its tetrahedral geometry.[22] Thus, on the basis of these evidences, complexes **C1** shows octahedral geometry, **C2** follows square planar geometry and **C3** displays tetrahedral geometry as shown in scheme **1**. (See Fig. 2).

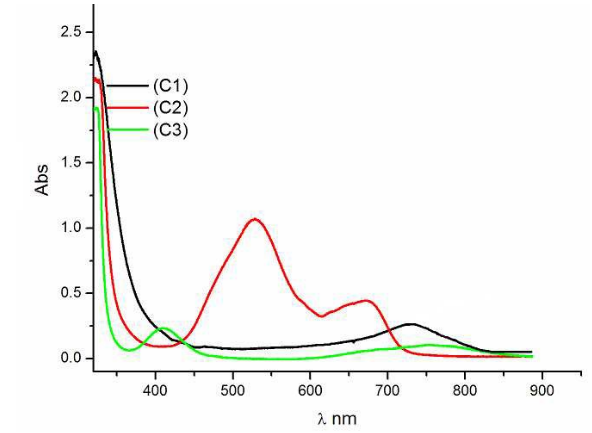


Fig. 2. UV-visible absorption spectra of the L, C1, C2 and C3 metal complexes (c = 9.4×10^{-3} M) in THF.

2.3. Nuclear magnetic resonance spectra

Further evidence for the formation of complexes was obtained from the ^{1}HNMR spectra. The complexes showed resonances at ca. 3.0-5.0 ppm, attributed to -OH proton resonance, so coordination of the deprotonated oxygen to the metal centre could not be ascertained. The aromatic ring protons were observed with the expected chemical shift and integral values in the same region as those of free ligand. The most interesting feature in the ^{1}HNMR spectra of Ni(II) complex (**C3**) is the existence of peaks corresponding to the THF molecules. Broad THF peaks at 4.68 and 2.11 ppm that are significantly shifted downfield from the signals for free THF indicates that the metal possesses direct and strong bonding with the THF molecule in the structure of the complex. Moreover, the ^{13}C NMR spectrum of the ligand taken in DMSO gave signals in good agreement with the probable structures. The ligand showed signals at 158.9 ppm assigned to azomethine (C=N) carbon. The signals from phenyl ring carbons were in the expected range. ^{13}C NMR spectra were also used for the elucidation of the coordination mode of the ligand in complexes. Assignments of the signals are based on the chemical shifts, intensity patterns and coordination induced shift (CIS), $\Delta\delta$ [$\Delta\delta = \delta$ (complex) - δ (free ligand)], of the signals for carbon atom in the vicinity of the coordinating functions. As a result of variation of electron density on coordination, azomethine carbon signal is shifted downfield by 5-10 ppm in their respective complexes, which indicates coordination of nitrogen lone pair to metal. Other phenyl ring carbons in these complexes resonate nearly at the same region as those of free ligand. In comparison to the free ligand, all signals in **C1**, **C2** and **C3** are shifted downfield, a consequence of complexation with the Lewis acidic metals.

2.4. TGA/DTG/DSC studies

Thermal behaviour of the complexes (**C1**, **C2** and **C3**) was studied in the temperature range 25-1200°C and the analysis indicates that the decomposition of the obtained complexes proceeds in several stages. The TG-DSC thermogram of **C2** exhibits an exothermic event at around 280°C (553.15 K) accompanied by a mass loss of 30.50% (Calc. 30.48%), assignable for the removal of coordinated water molecules and chloride ions or THF molecules in **C3**. The pyrolysis of **C2** showed that the complex is stable up to 280°C and then continuous mass loss occurs in the range 280-950°C. Additional highly exothermic peaks at 425°C and 465°C are attributed to the decomposition of 1.15 moles of ligand (Found 35.90%; Calc. 35.82%), which continues up to 930°C, forming 1.5 moles of CoO as final solid products (Found 20.35%; Calc. 20.25%) Fig. **3**. The thermal decomposition of complexes **C1** and **C3** is similar to that of the decomposition of **C2**. Although decomposed fragments of the ligand could not be approximated due to continuous weight loss, the total % weight loss of the complexes corresponds to the loss of the ligand after considering the transfer of one oxygen atom to the metal ion and residue corresponds to the metal oxide. In all complexes, the experimental mass loss values agree well with the calculated values.

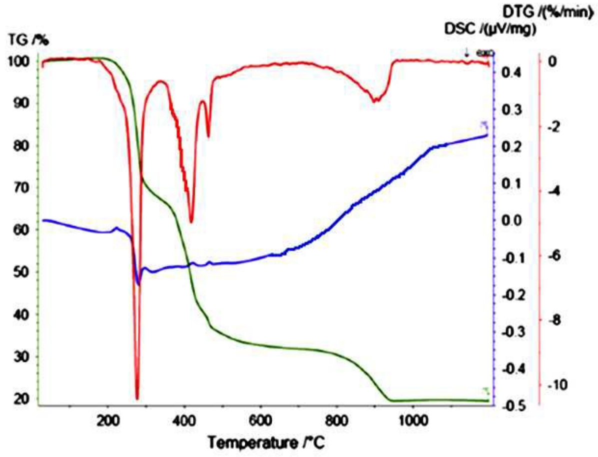


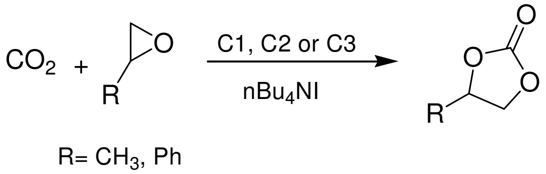
Fig. 3. TGA-DTG-DSC curve of **C2**

2.5. ESI-MS studies

The positive ion ESI mass spectrum of the ligand (**L**) and complexes (**C1**, **C2** and **C3**) showed a number of informative fragment ions of different intensities confirming their molecular weights. The result presented here is interpreted in terms of simple bond cleavages. The molecular ion peak was observed as 164.1 $[M+H]^+$ for ligand and the major fragmentation pathway involved the cleavage of N-OH bonds and subsequent -C=N bond cleavage giving fragment at m/z 150.1, 140.1, 115.1 and 88.5, corresponding to phenyl ring fragment. The mass spectrum of the metal complexes (**C1**, **C2** and **C3**) obeyed a similar pattern of fragmentation with the molecular ion peaks observed as $[M+Na^++H]^+$, $[M+Na^+]$ (Metal adduct ions) and $[M+H]^+$.

2.6. Cycloaddition Studies

The metal complexes (**C1**, **C2** & **C3**) were used as catalysts for the cycloaddition reaction between carbon dioxide and epoxides to afford the five membered cyclic carbonate (Scheme **2**).



Scheme 2. Synthesis of cyclic carbonate from CO_2 and epoxides.

The reaction conditions were standardized by observing the effect of temperature, pressure and catalyst loading on the yield and percentage conversion of epoxides (propylene oxide and styrene oxide) into cyclic carbonates. Cycloaddition of CO_2 was carried out in absence of a solvent, by charging the respective epoxides and catalyst into a stainless steel Parr reactor, which was then sealed. The activity of the synthesized catalysts with and without nBu_4NI as cocatalyst was checked at different temperatures for the synthesis of cyclic carbonates. The presence of catalysts alone did not give encouraging results and we finally decided to use a cocatalyst. nBu$_4$NI was chosen as a cocatalyst because of the previously reported reactions showing its higher efficiency.[23] The results revealed that the catalyst (**C2**) in presence of an equimolar ratio of the cocatalyst and 1000 equivalent of propylene oxide or styrene oxide results in highest TOF for the reaction which indicates the necessary synergistic effects between the catalyst and cocatalyst in the acceleration of the reaction. Figure **4** shows the turnover number (TON) of propylene carbonate production at various temperatures. The TON increases with an increase in temperature and at 75°C at a reaction time of 6h, propylene oxide was found to have completely converted to the product. An increase of temperature beyond this point does not have any appreciable effect on the activity of the catalysts or the reaction conditions. On increasing the temperature beyond 75 °C the rate of reaction does not increase. The reaction of styrene oxide also followed a similar trend, which reveals that there is no effect of substituents on the activation and further reaction of epoxides with CO_2. However this observation warrants studies with other structurally diverse epoxides to establish the point. To further validate that the activity was due to the complexes, we used the metal salts alone, which did not give us any appreciable results possibly due to the saturated coordination geometry of the salts. Coordination geometry and the oxidation state of the metal are important factors which decide the fate of the metal based catalysts.

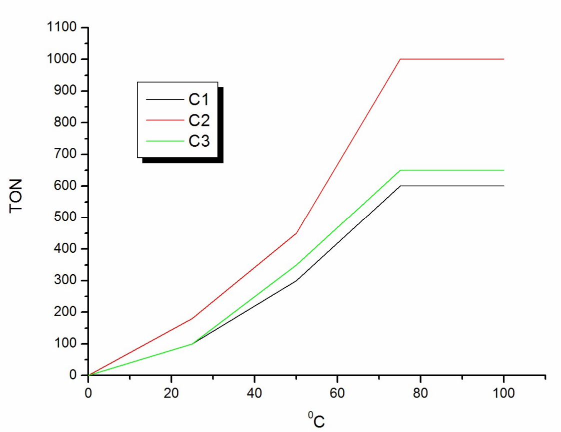


Fig. 4. TON for catalyst (C1), (C2), (C3)/ nBu$_4$NI system as a function of temperature (°C). Reactions conditions: catalysts, 5.66 mg for C2 (9.8× 10^{-6} mol); n-Bu$_4$NI, 3.69 mg (9.8× 10^{-6} mol, 1 equiv); propylene oxide, 0.7 mL (9.8 mmol, 1000 equiv); CO_2, 10 barr; 6 h.

In order to understand the effect of pressure on activity, we also have tested the activity of the catalyst with varying CO_2 pressure. Figure **5** shows the effect of CO_2 pressure on the TON of propylene carbonate production. With increasing CO_2 pressure, the TON increases and reaches a maximum at a CO_2 pressure of 10 bar (145.03 psig). A TON of ~1000 at 10 bar indicates that the catalyst retains sizable activity even at lower pressures. Further increase of the CO_2 pressure did not lead to an increase in the yield. The reason for this phenomenon was ascribed to the phase behaviour involving CO_2-rich gas phase and epoxide-rich liquid phase in the system.[3b]

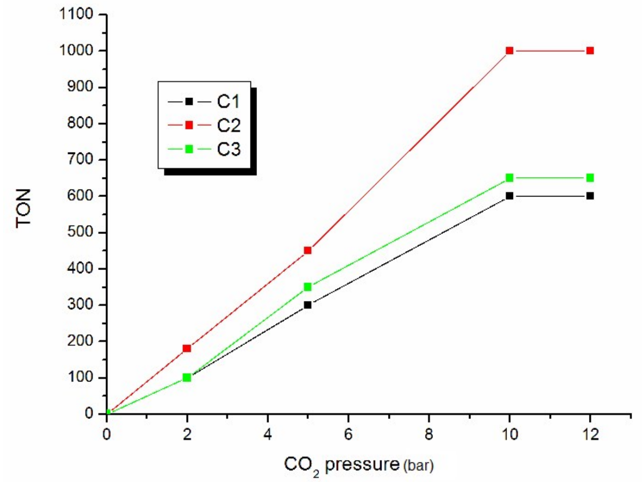


Fig. 5. TON for (C1/C2/C3)/nBu$_4$NI system as a function of CO_2 pressure. Reaction conditions: 75 °C; (C1) (C2) (C3), 5.66 mg C2 (9.8× 10^{-6} mol); 3.69 mg (9.8× 10^{-6} mol, 1 equiv); propylene oxide, 0.7 mL (9.8 mmol, 1000 equiv); 6 h.

We also measured the TON and TOF of propylene carbonate production at different time intervals at a particular temperature (Figure **6**). The reaction is complete in 6h at 75°C. Therefore, we established our optimum reaction time and temperature of 6h at 75°C respectively at 10 bar CO_2 pressure based on the above-mentioned findings. An equimolar ratio of catalyst/cocatalyst (1:1) under the above optimized conditions resulted in highest TON for **C2.** Although, the maximum TOF was obtained at 3h, the complete conversion took place in 6h. At the optimized conditions (10 bar (145.03 psig) CO_2, 75°C, 6h, and 1:1 catalyst/ nBu$_4$NI) reaction of epoxides affords significant yield of cyclic carbonates using **C1**, **C2** and **C3** as catalysts with highest TON for **C2** and >99% selectivity (Figure **6**; Also see supporting information Fig. S1-S5). Blank reaction under similar conditions in the absence of the catalyst and cocatalyst showed little product formed. This indicates the need for both catalyst and cocatalyst for an optimum activity.

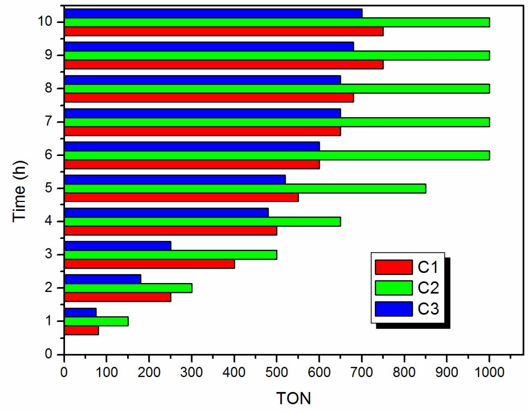


Fig. 6. TON for (C1) (C2) (C3)/nBu$_4$NI system as a function of time (h). Reaction conditions: 75 °C; CO_2 10 bar; 5.66 mg for C2 (9.8× 10^{-6} mol); 3.69 mg (9.8× 10^{-6} mol, 1 equiv); propylene oxide, 0.7 mL (9.8 mmol, 1000 equiv).

Since it was observed that complex **C2** shows better activity compared to the complexes **C1** and **C3**, it appears that cobalt is a superior metal, where epoxide coordinates and ring opening occurs. Copper and Nickel are less efficient in coordinating with the epoxides, which probably results in their less activity; this could be due to their different Lewis acidic nature and different coordination geometry of these complexes. The optimized conditions of temperature, pressure and catalyst loading also demonstrate that at 75°C, the catalyst-cocatalyst system achieves maximum homogeneity in the reaction mixture, thereby furnishing more effective collisions of substrates with the active catalysts. An increase of pressure beyond 10 bar also did not improve the yield. Changing the catalyst/co-catalyst ratio and loading from the optimized parameters did not produce any significant increase in the product yield (Table. **1**), probably because of the mass transfer resistances between the active site and reagent caused by the low dispersity of the excess catalysts in the reaction mixture.[3b] At a fixed molar ratio of cat./co-cat. of 1:1, we obtained 99% yield of CC in 6h, which suggested that the thermodynamic factors had a more significant impact than dynamic factors. Therefore, C2/*n*Bu$_4$NI catalyst system displayed promising application prospect.

Table **1**. Effect of Reaction Conditions on the Cycloaddition of PO and CO$_2$ using C2/*n*Bu$_4$NI catalyst system[#]

Entry	Molar ratio Cat./co-cat	Temp (°C)	Time (h)	Yield[a] (%)	TOF[b]
01	1:0	75	6	10	25
02	1:0.25	75	6	65	88
03	1:0.5	75	6	75	110
04	**1:1**	**75**	**6**	99	167
05	1:1.5	75	6	99	167
06	1:1	25	6	45	33.3
07[c]	1:1	75	3	65	167
08	1:1	100	6	99	167
09	1:2	75	6	99	167
10	1:2	100	9	95	167

[#]Reaction conditions: P(CO$_2$) = 10 bar (145.03 psig); [b]On the basis of ^{1}HNMR; [b]Turnover frequency (TOF) = (mol of PO consumed)/((mol of catalyst) h); [c]High TOF obtained but not complete conversion.

The mechanism of action of these complexes although not studied could be thought to be similar to those of reported di-nuclear metal complexes reported earlier.[12b,14,15,24] The epoxides could be activated by the Lewis acidic sites of the catalyst and CO$_2$ in turn by *n*Bu$_4$NI co-catalyst by forming a zwitterionic adduct between the base and CO$_2$.[3b] A tentative mechanism may involve the coordination of the epoxide oxygen with the metal centers and simultaneous nucleophilic attack of the iodide anion of *n*Bu$_4$NI on the less sterically hindered β-carbon atom of the epoxide, causing the ring opening of the epoxide. The activated CO$_2$ as zwitterionic adduct undergoes a nucleophilic attack by the activated epoxide to produce the new alkyl carbonate compound. By subsequent intramolecular ring closure, the cyclic carbonate product could be formed and the catalysts regenerated simultaneously. The synergetic catalytic roles played by C2 and *n*Bu$_4$NI made the reaction proceed smoothly. However further studies need to be done to establish the mechanism of the reaction.

3. Conclusions

In conclusion, cycloaddition of CO$_2$ with epoxides was performed without solvent using the metal complexes **C1–C3** as catalysts in the presence of *n*Bu$_4$NI as cocatalyst. After optimizing the reaction conditions we found that the reaction at 75 °C under the conditions of a fixed [**C1** or **C2** or **C3**]/[cocatalyst] ratio at 10 bar results in the highest TON (~1000) and TOF value (TOF = 167 h^{-1}) for complex **C2** as catalyst. Propylene oxide and styrene oxide were easily converted into the cyclic carbonate with high selectivity (>99%) without any polymerized products. The structure of the catalyst is being further optimized to reduce the use of a cocatalyst.

4. Experimental

4.1. General Considerations: All manipulations were carried out under a dinitrogen atmosphere using standard techniques. All chemicals were purchased from Aldrich and used as supplied unless otherwise indicated. Melting points (mp) were performed using a Mel-temp instrument, and the results are uncorrected. Reactions were monitored using thin-layer chromatography (TLC) using commercially available precoated plates (Merck Kieselgel 60 F254 silica). Visualization was achieved with UV light at 254 nm or I$_2$ vapor staining.

4.2. Measurements: ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AVANCE 400 NMR spectrometer using standard parameters. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet. All chemical shifts are reported in δ units with reference to the residual peaks of CDCl$_3$ (δ 7.24, ^{1}H NMR; δ 77.0, ^{13}C NMR) or DMSO-*d*$_6$ (δ 2.50, ^{1}H NMR; δ 39.52, ^{13}C NMR). FT-IR spectra were recorded using a Thermo Nicolet 380 instrument equipped with a Smart Orbit ATR attachment. The absorption spectra were recorded using an OCEAN OPTICS USB 4000 UV spectrometer. The ESI MS of all the compounds were recorded on a JEOL SX 102/DA-6000 Mass Spectrometer/Data System. Thermogravimetric analysis (TGA) of the complexes was performed on a TG 51 thermogravimetric analyzer under nitrogen atmosphere with the heating rate of 10 ºC min^{-1}. Cycloaddition reactions of CO$_2$ were done in Parr high pressure reactor (Series 5500 HPCL Reactor, Parr Instrument Company).

4.3. Synthetic procedures

4.3.1. Synthesis of Ligand (L)

Benzene-1,4-diylbis(N-hydroxymethanimine).

To a solution of benzene-1,4-dicarboxaldehyde (1 eq) and hydroxylamine hydrochloride (2 eq) in water (10 mL), a solution of sodium bicarbonate (2.25 eq) in water (10 mL) was added gradually with stirring, and the mixture was stirred for further 5 h with the formation of a solid white precipitate, which was filtered, dried and recrystallized from methanol.

Yield 89 %; m.p 132.5 ; IR ν_{max} cm^{-1}: 3250 (O-H), 2864 (C-H), 1632 (C=N), 936 (N-O stretch); ^{1}HNMR (DMSO-*d*$_6$) δ(ppm): 4.93 (broad s, 2H, N-OH), 7.98 (s, 2H, CH=N-OH), 7.10 (s, 4H, Ar); ^{13}C NMR (DMSO-d$_6$) δ(ppm): 158.9 (C=N), 140.2, 135.2; ESI-MS m/z: [M$^+$+H] 164.1.

4.3.2. Synthesis of complexes C1, C2 and C3

We prepared the complexes with $CuCl_2.2H_2O$, $CoCl_2.6H_2O$ and $NiCl_2$ salts. The THF solution of metallic ion salt (2 mmol/5 mL THF in C1 and C2; 5 mL ethanol in C3) was mixed with a half molar THF solution of the ligand (L1) (1 mmol/10 mL THF). For complex C3, the nickel salt was dissolved in a small quantity of ethanol and slowly mixed with stirring solution of the ligand (L) in THF. After stirring the solution for 3-4 h, Na_2CO_3 or CH_3COONa was added until the pH reached 8–8.5 and after keeping the contents at 4^oC, colored complex separated out in each case. It was filtered, washed successively with water, THF, cold ethanol and diethylether and finally dried under vacuum.

C1: Yield: 70%; UV/Vis: λ(nm) (THF) 375, 690-790; IR: υ_{max} (cm^{-1}) 2860 (C-H), 1611 (C=N), 748 (C-Cl), 498, 450 (Cu-O, Cu-N); ^{1}HNMR (DMSO-d_6) δ(ppm): 8.10 (s, 2H, CH=N), 7.39 (s, 4H, Ar); ^{13}C NMR (DMSO-d_6) δ(ppm): 154.5 (C=N), 139.8, 132.2; ESI MS: m/z: 527.82 $[M+ Na^+]^+$, 504.86 $[M+ H]^+$.

C2: Yield: 72%; (DMSO); UV/Vis: λ(nm) 525, 680; IR: υ_{max} (cm^{-1}) 2862 (C-H), 1602 (C=N), 743 (C-Cl), 478, 428 (Co-O, Co-N); ^{1}HNMR (DMSO-d_6) δ(ppm): 8.02 (s, 2H, CH=N), 7.35 (s, 4H, Ar), 4.65, 2.10 (4H, bs, THF); ^{13}C NMR (DMSO-d_6) δ(ppm): 149.5 (C=N), 139.5, 132.6, 26.2. 11.6; ESI MS: m/z: 412.15 $[M+ Na^++H]^+$, 388.85 $[M+ H]^+$.

C3: Yield: 75%; (DMSO); UV/Vis: λ(nm) 410, 760; IR: υ_{max} (cm^{-1}) 2860 (C-H), 1617 (C=N), 738 (C-Cl), 487, 450 (Ni-O, Ni-N); ^{1}HNMR (DMSO-d_6) δ(ppm): 8.12 (s, 2H, CH=N), 7.38 (s, 4H, Ar), 4.62, 2.11 (4H, bs, THF); ^{13}C NMR (DMSO-d_6) δ(ppm): 152.8 (C=N), 138.8, 132.4, 26.0. 11.2; ESI MS: m/z: 485.02 $[M+ Na^+]^+$; 462.10 $[M+ H]^+$.

4.4. Cycloaddition Tests of CO_2 to Propylene Oxide.

Cycloaddition of CO_2 was carried out by charging propylene oxide and metal catalysts (C1, C2 & C3 respectively) into a 20 mL stainless steel Parr reactor which was then sealed. The reactor was pressurized to 10 bar of CO_2 and was heated to the reaction temperature (75 °C). After the contents were stirred for 6 h, the reactor was cooled and vented, and a small sample of the mixture was taken for ^{1}H NMR analysis. Turnover frequency (TOF) was calculated as the moles of propylene carbonate produced per mole of catalyst and TOF in turn as TON per hour.

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Cycloaddition of CO_2 to epoxides using di-nuclear transition metal complexes as catalysts

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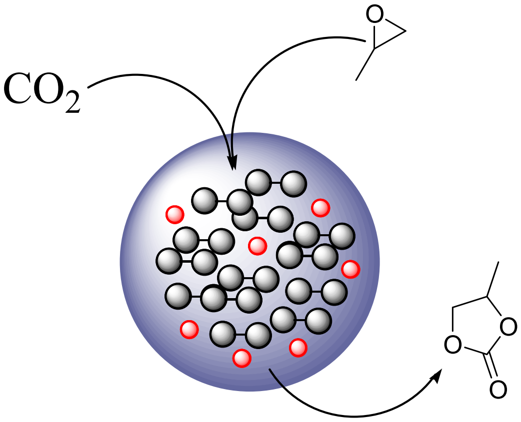

Cycloaddition of CO_2 to propylene oxide was carried out selectively using di-nuclear Cu^{II}, Co^{II} and Ni^{II} complexes (**C1**, **C2** and **C3** respectively) as catalysts.