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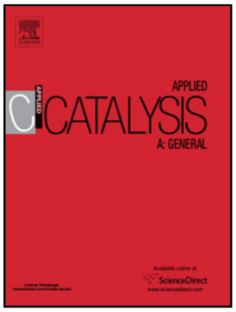

Triazole based cobalt catalyst for CO_2 insertion into epoxide at ambient pressure

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Triazole based cobalt catalyst for CO_2 insertion into epoxide at ambient pressure

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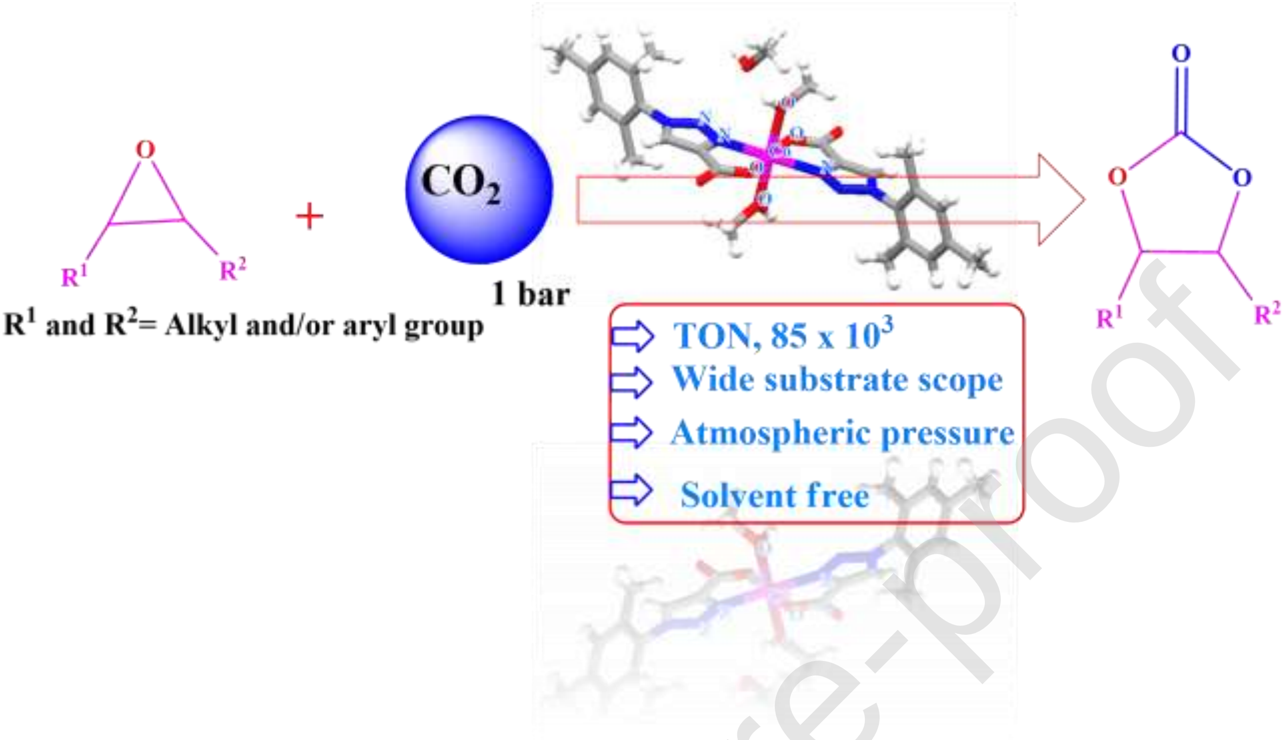
Graphical Abstract



Highlights

- Cyclic carbonates are produced using a triazole based Co-complex at ambient pressure.
- The catalyst is highly active under solvent free condition with TONs up to 85 × 10^3.
- The catalyst is used with the variety of substrate exhibiting good to excellent conversions.
- The catalyst is stable for at least five cycles with no significant loss in activity.

Abstract

Over the past decades, a lot of efforts have been made for the fixation of carbon dioxide (CO_2) into epoxide for the synthesis of industrially important cyclic carbonates. Here, a cobalt(II) complex based on triazole, namely Co(II)-1,2,3-1*H*-triazole-4-carboxylate, was synthesized, fully characterized by FTIR, NMR, mass spectrometry, and single crystal X-ray diffraction, and used as a catalyst for the cycloaddition of CO_2 to epoxides. The catalytic studies demonstrated that the catalyst is highly active for the CO_2 fixation, with high turnover number (TON, 85×10^3) even without the use of solvent and at ambient pressure (1 bar) to produce a variety of different cyclic carbonates depending on the epoxide. Remarkably, the catalyst was used continuously further by the addition of a fresh amount of the substrate within the same reaction mixture for at least five successive reaction cycles without any loss in the catalytic activity.

Keywords: Carbon dioxide; epoxide; cycloaddition; homogeneous catalysis; cyclic carbonates

Introduction

In the current era, extensive industrialization and urbanization have adversely affected our environment [1, 2]. The unwanted greenhouse gases are continuously emitted by various industrial plants and combustion of fossil fuels, affecting the ozone layer of the atmosphere, which may cause a devastating effect in the near future [3]. Reduction and recycling of carbon dioxide (CO_2) into value-added products can play a key role towards a clean environment, however, it is a challenging task due to thermodynamic and kinetic stability of CO_2 [4-6]. Due to its easy and harmless availability as well as being a renewable resource, CO_2 is a useful C1 source for the synthesis of industrially important products[7-10]. The anthropogenic emissions of CO_2 are continuously increasing day-by-day causing extreme environmental pollution and hence global warming [11, 12]. Therefore, any effort to use atmospheric CO_2 is highly appreciated. In the past, CO_2 utilization was restricted to only a few substrates such as aziridines and epoxides. However, in recent years, substrates have been extended to transform CO_2 elegantly due to synthetic design strategies. Consequently, a variety of synthetically important compounds have been prepared such as cyclic carbonates, 2-oxazolidinones, oxazolidinediones, benzoxazin-2-ones, 1,3,4-oxadiazole-2(3*H*)-ones, and maleic anhydrides [13]. In the last few decades, tremendous research efforts have been devoted to the application of carbon dioxide, particularly the catalytic cycloaddition of CO_2 to epoxides for synthesizing fine chemicals *e.g.* cyclic carbonates [14]. Cyclic carbonates are the industrial commodities offering a viable non-redox carbon dioxide fixation way which are formed by the coupling reaction of epoxide and CO_2. It has diverse applications like polar aprotic solvents, electrolytes in lithium batteries, synthetic intermediates of polycarbonates, fuel additive, *etc* [15, 16].

So far, various homogeneous (metal-organic complexes, coordination compounds) and heterogeneous catalysts have been designed for the cycloaddition of CO_2 to epoxide including ionic liquids [17, 18], complexes [19-23], metal oxide [24], alkali metal halides and carbonates,[25-27] phosphonium salts/quaternary ammonium [28, 29], functional polymer [30, 31], MOFs [32-34], COFs [26, 35] and core-shell of organic-inorganic hybrid microspheres [36].The majority of heterogeneous catalysts usually requires a high temperature and pressure [37]. Among the major limitations regarding ionic liquids are the toxicity and combustible effect, hence careful handling in performing the reactions is required [38]. Therefore, there is still a need for highly active and stable catalysts, which should be less toxic or non-toxic, less volatile and can be safely used.

Recently, many transition metal catalysts have been reported, nonetheless, their limitations are long reaction time [39, 40], high CO_2 pressure [39-41], low conversions [39] and TONs [39, 41] and thus not fulfilling the industrial demands. Plenty of research work has been reported on cobalt-based complexes for the insertion of carbon dioxide into epoxides to produce the desirable cyclic carbonates[42-46]. Still, there is a high demand to design catalysts and work out the reaction conditions that would involve a relatively lower pressure of CO_2 (preferably ambient pressure), efficient conversions having higher TONs and more importantly to be used for a variety of substrates.

From a green and sustainable chemistry point of view, the perspective of clean production, organic solvent free processes would exhibit remarkable potential applications in the industry owing to their relatively simplified workup and recycling of the catalyst. The reported literature demonstrated that nitrogen-rich bases (triazoles and N-heterocyclic carbenes) are highly active for the coupling of CO_2 into epoxide[47, 48]. Recently, our group reported the *in-situ* synthesis of a Co(II)-TCA complex and used it as a molecular catalyst for the efficient photo and electrochemical water oxidation[49]. Herein, we report a similar triazole cobalt-based catalyst, which demonstrates a high TON (85 x 10^3) towards CO_2 coupling with epoxides at an ambient gas pressure of CO_2 (1 bar). This cobalt(II) triazole-based complex catalyzes efficiently the cycloaddition of CO_2 to various epoxides under solvent-free conditions at atmospheric pressure of CO_2. The experimental results revealed that the catalyst is highly active, and selective towards cyclic carbonates products. The synthesis of the catalyst is straightforward and low in cost in comparisons to the other metal complexes. The complex was continuously used for five times by consecutively adding the substrate in the same reaction mixture without any activity loss, demonstrating the excellent stability and continued usability of the catalyst.

Experimental Section

Synthesis and Characterization of Ligand and Complex

Synthesis of (1): 2-azido-1,3,5-trimethylbenzene

The compound (**1**) was synthesized according to the reported procedure[50]. Typically, mesityl amine (7 mL) and H_2O (60 mL) were charged in a round bottom flask containing a Teflon coated magnetic bar stirrer. Then, concentrated HCl (8.7 mL, 0.1 mol) was added dropwise to the reaction mixture and stirred for 20-30 min, at 0 °C. Freshly prepared cold $NaNO_2$ (3.25 g, 0.05 mol) in 30 mL water was added dropwise under vigorous stirring and cooling using an ice bath. In the next step NaN_3 (3.25 g, 0.05 mol in 30 mL water) was added to the reaction mixture. The reaction mixture was stirred for 4 hours at room temperature followed by extraction using ethyl acetate. The obtained organic fractions were combined and dried with anhydrous Na_2SO_4 and then filtered. A yellow liquid was obtained after drying under vacuum at 30-40 °C. Yield: 60%. Compound (**1**) was characterized by NMR: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 2H), 2.33 (s, 6H), 2.26 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 135.3, 134.3, 131.8, 129.5, 20.7, 18.0.

Synthesis of (2): 1-mesityl-1*H*-1,2,3-triazole-4-carboxylic acid

The compound (**2**) was produced according to a published method[51], with some modifications. 10 mL $CuSO_4 \cdot 5H_2O$ (40 mg, 0.16 mmol), sodium ascorbate (64 mg, 0.32 mmol) were dissolved in H_2O (1.0 mL) under Ar atmosphere (the click catalyst). Thereafter, compound (1) (525 mg, 1.0 equiv., 3.26 mmol) and propiolic acid (254 μL, 1.2 equiv., 3.92 mmol) were dissolved individually in 0.5 mL *ter*-BuOH and injected to the previously prepared click catalyst solution. The reaction mixture was stirred for 24 h at room temperature under inert atmosphere. 15 mL saturated $NaHCO_3$ was used to quench the reaction and a yellow precipitate was observed. The yellow precipitate was filtered and washed twice with ether (40×2 mL). Then, 0.5 M aqueous solution of H_2SO_4 (100 mL) was added to the yellow product and extracted with ethyl acetate. The organic fractions were then combined and dried using anhydrous Na_2SO_4. Filtration followed by evaporation of ethyl acetate under reduced pressure gave a white solid. Yield: 72.5%. FTIR (neat): ν_{max}=3147, 2958, 2921, 2646, 2569, 1687, 1539, 1496, 1411, 1353, 1292, 1190, 1033, 935, 850, 771, 582, 547 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.04 (s, 2H), 2.39 (s, 3H), 2.00 (s, 6H); ^{13}C-NMR ((126 MHz, $CDCl_3$) δ 163.74, 140.81, 139.35, 134.82, 132.60, 130.24, 129.33, 21.15, 17.31.

The synthesis of (3): Co-TCA

0.865 mmol (200 mg) of compound 2 was added in 10 mL MeOH in addition of 0.1 mL of triethylamine. Stirring at room temperature for 10 minutes, anhydrous cobalt nitrate (0.45 mmol, 83.5 mg) was added resulting in a clear solution. After 12 h, a pink precipitate was obtained and after one-week crystals were observed which were suitable for single crystal X-ray analysis.

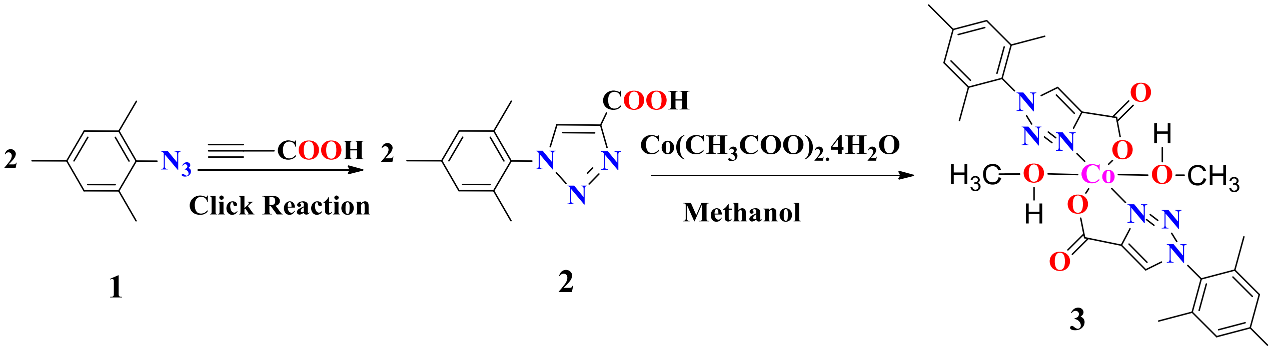
Yield: 71%. FTIR (neat): 3151, 2945, 1595, 1556, 1494, 1315, 1261, 1205, 1078, 1035, 862, 717, and 478 cm^{-1}; MS m/z calcd. for $C_{26}H_{30}CoN_6O_6$ 581.15, found 581.14.

General Experimental setup of CO_2 cycloaddition into epoxide

Five-membered cyclic carbonates were synthesized from carbon dioxide and the corresponding substrates (10 mmol) in the appropriate molar ratios by using 5.83 mg (0.01 mmol) of Co(II)-1-mesityl-1,2,3-1*H*-triazole-4-carboxylate (Co-TCA) as a catalyst in combination with a co-catalyst (tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), DMAP (4-(dimethylamino)pyridine) and TBAI (tetrabutylammonium iodide)) which were transferred into the reactor. The reactor was charged with the reaction mixture (catalyst, cocatalyst, and substrate) and was purged with CO_2 for 3 times at room temperature. The reactor was heated to 120 °C in the oil bath and then pressurized to 1 bar of CO_2. After completion, the reactor was slowly cooled to room temperature. The catalyst (Co-TCA) was directly used for the consecutive reaction cycles to identify the further usability and stability of the catalyst. In addition, column chromatography was executed to isolate the product from the reaction mixture using petroleum ether/ethyl acetate mixture (3:1) as eluent. After performing the column chromatography, the solvent was evaporated to obtain the target-isolated product and the yield. Then, the sample was analyzed by ^1H, ^{13}C-NMR and FTIR (Figure S3, S5, S7, S9, S11, S13, S15, S17, S19, S21, S23, S25, S27) analysis.

Results and Discussion

Molecular catalysts for the CO_2 activation process can serve to understand the catalytic cycle which can finally be involved in the catalyst design optimization. Lewis basicity of the ligand and Lewis acidity of the metal center are crucial for the catalyst's activity. The straightforward construction of a triazole ring along with its high basicity and capability to adsorb CO_2 are very attractive features for using a substituted triazole ring as a bidentate ligand for constructing a cobalt complex for CO_2 cycloaddition to epoxide [52, 53]. The bidentate ligand, 1-aryl-1*H*-1,2,3-triazole-4-carboxylic acid, was readily prepared *via* copper catalyzed azide-alkyne cycloaddition "click reaction" of aryl azide and propiolic acid (Scheme 1).



Scheme 1. Synthesis of $[Co(TCA)_2.2MeOH]_3$

The catalyst **3** was simply prepared by reacting the ligand with cobalt acetate salt (with 2:1 ligand and cobalt ratio). The catalyst structure was established based on elemental analysis, FTIR, ESI-MS, and also confirmed in the solid state from X-ray single crystal analysis. The ESI-MS of the complex exposed a molecular ion peak at m/z = 581.14 corresponding to $[Co(TCA)_2(OCH_3)_2]$ (M^+). (Figure S29 in SI)

The complex crystallized in space group P-1 of the centro-symmetric triclinic. $Co(TCA)_2(CH_3OH)_2$ complex included an asymmetric unit and an inversion center, organized with a methanol molecule. The cobalt complex and methanol molecule are connected by a hydrogen bond via a coordinated methanol molecule Co-TCA(O-(H)---O space of 2.704(3) Å. The Co-complex exhibit an octahedral coordination geometry, in which two TCA ligands are coordinated in a bidentate manner via the carboxylate-oxygen and triazole-nitrogen atom, and two methanol molecules are positioned axially to the octahedral equatorial plane, Figure 1. The two Co-O bond distances are different from each other, namely 2.1181 Å (15) and 2.0716 Å (16) while the two Co-N distances are identical (2.123(2) Å). Aromatic triazole and mesityl ring π-π stacking interactions and mesityl ring mutually interactions are observed i.e., the distances ranges are 5.5854 (13) Å - 4.9105 (14) Å. The Co-complex organized in 100 directions is given in Figure 1.

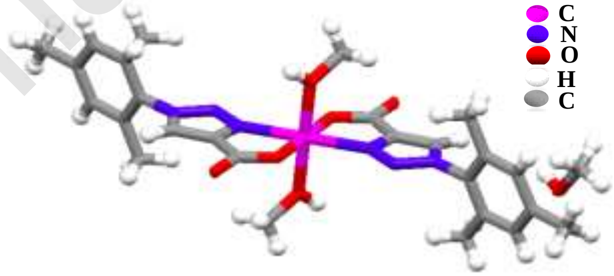
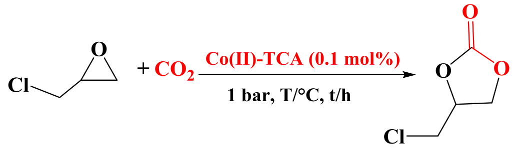


Figure 1. Crystal structure of complex, **3**.

The effect of different parameters is extremely important to distinguish the catalyst's efficiency (Table 1). Therefore, the reaction conditions for the cycloaddition of CO_2 to epoxides were optimized. The reaction temperature, catalyst loading, reaction time and use of the co-catalyst are studied in the presence of epichlorohydrin (ECH). Table 1 displays the obtained conversions to carbonate products under various catalytic reaction conditions. As shown in Table 1 (entries 1-5), the catalyst activity is very sensitive to the variations in the reaction temperature. At lower temperature i.e., 25 and 50 °C, no conversions were observed (Table 1, entries 1-2). Whereas, at 75 °C and higher temperature, the catalyst is active indicating the influence of temperature. When the temperature was raised to 75, 100, and 120 °C, the respective conversions increased to 7, 78, and 100% (entries 3-6). Increasing the reaction temperature accelerates the conversion, where the complete conversion was achieved at 120 °C. The reaction time is also a key factor, the conversion increased from 81 to 100% when the reaction time increased from 12 to 15 hours (Table 1, entries 5 and 6). The effect of catalyst loading was investigated also (entries 6-9) and revealed that the catalyst to substrate ratio is very crucial for the catalytic performance. Under the optimized conditions of temperature (120 °C) and time (15 h) the catalyst to substrate ratio of 1:1,000 afforded the complete conversion (Table 1, entry 6). Whereas at 120 °C, the catalyst

Table 1. The optimization reaction conditions of cycloaddition of CO_2 and epichlorohydrin as a model substrate.

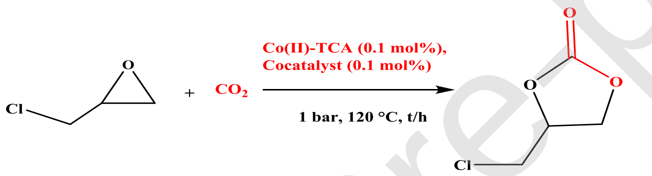


Entry	Temp (°C)	Catalyst / substrate ^{a}	Time (h)	Conv. (%)^{b}	TON	TOF (1/h)
1	25	1: 1,000	12	0	0	0
2	50	1: 1,000	12	0	0	0
3	75	1: 1,000	12	7	70	5
4	100	1: 1,000	12	78	780	65
5	120	1: 1,000	12	81	810	67
6	120	1: 1,000	15	100	1,000	66
7	120	1: 100	7	100	100	14
8	120	1: 10,000	6	3	300	50
9	120	1: 10,000	24	50	5,000	208

All reactions were conducted without any solvent. ^{a} 5.83 mg (0.01 mmol) of the Co(II)-TCA catalyst is used. ^{b} Conversion is based on ^{1}H-NMR.

loading of 1: 10,000 did not proceed well in the range of 6 to 24 h of reaction time (Table 1, entries 8 and 9) and might need a longer reaction time. To deal with this issue we employed different co-catalysts. According to the previously reported literature, it was demonstrated that the use of co-catalysts increased catalytic performance. In this study without the use of co-catalyst, the reaction time is relatively long to reach the complete conversion. In order to find out the best combination of catalyst and co-catalyst, the catalytic performance was tested in the presence of different co-catalysts (tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), 4-(dimethylamino) pyridine (DMAP) and tetrabutylammonium iodide (TBAI) as shown in Table 2, entries 1-8. In the literature, the most commonly used co-catalyst is TBAB for the title reaction.

Table 2. Reaction condition of cycloaddition of CO_2 and epichlorohydrin in the presence of co-catalysts.



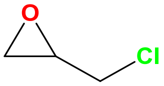
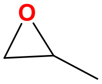
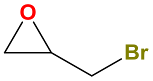
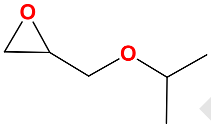
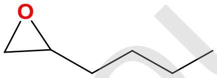
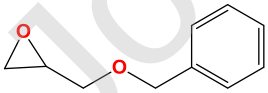
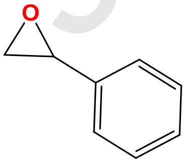
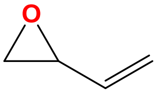
Entry	**Cocatalyst**	**Cat./Cocat./ Substrate** [a]	**Time (h)**	**Conv. (%)**	**TON**	**TOF (1/h)**
1	TBAB	1:1:1,000	1	41	410	410
2	TBAC	1:1:1,000	1	48	480	480
3	DMAP	1:1:1,000	1	47	470	470
4	TBAI	1:1:1,000	1	37	370	370
5	DMAP	1:1:1,000	4	95	950	237
6	**TBAC**	**1:1:1,000**	**4**	**95**	**950**	**237**
7	TBAB	1:1:1,000	4	91	910	227
8	TBAI	1:1:1,000	4	87	870	217
9	TBAC	1:1:10,000	9	75	7,500	833
10	TBAC	1:1:50,000	18	75	37,500	2083
11	**TBAC**	**1:1:100,000**	**48**	**85**	**85,000**	**1770**
12	TBAC	0:1:1,000	3	39	390	130
13	TBAB	0:1:1,000	3	39	390	130
14	TBAI	0:1:1,000	3	18	180	60
15	DMAP	0:1:1,000	3	37	370	123
16	*Co-salt	0:1:1,000	3	11	110	36
17	Ligand	1:0:1,000	3	16	160	53
18	Co-TCA	1:0:1,000	3	47	470	156

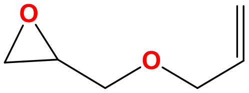
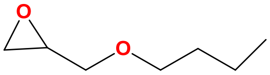
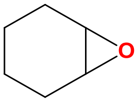
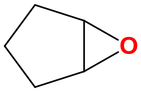
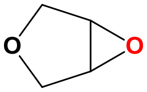
All reactions were carried out in bulk and conversion was determined by ^{1}H-NMR. a 5.83 mg (0.01 mmol) of the Co(II)-TCA catalyst is used. TBAB, TBAC, DMAP and TBAI are abbreviations for tetrabutylammonium bromide, tetrabutylammonium chloride, 4-(dimethylamino)pyridine and tetrabutylammonium iodide. *****cobalt acetate salt is used.

The obtained results reveal that TBAC and DMAP gave good conversions (95%) (Table 2, entries 2-3 and 5-6) than TBAB and TBAI (Table 2, entries 1, 4, 7-8) when these co-catalysts were used together with the Co(II)-complex catalyst. Due to the corrosive nature and more importantly toxicity of DMAP[54], we preferred TBAC for further analysis. The stand-alone activity of the co-catalysts such as TBAC, TBAB, TBAI, and DMAP was also investigated under the optimized set of reaction conditions (catalyst to substrate ratio of 1:1,000, 3 h, 120 ºC, 1 bar and epichlorohydrin). The experimental studies reveal that these co-catalysts alone have some activity (Table 2, entries 12-15), but less active than the catalyst when we examined the catalytic performance of Co-TCA without using any co-catalyst (Table 2, entry 18). Literature studies also suggest that the sole use of these co-catalysts required high pressure to achieve a satisfactory yield[55-58]. The catalytic performance of the precursors that are used for the synthesis of Co-TCA complex was also tested (Table 2, entries 16-17). The results demonstrated that the complex is much more active than its precursors, *i.e.* TCA ligand and cobalt salt. After optimization of co-catalyst and reaction time (4 h) then the reaction was performed using different catalyst loading ratios (keeping the co-catalyst amount constant) varying from 1: 1,000 to 1: 100,000 (Table 2, entries 6, 9-11). At 120 °C and a pressure of 1 bar of CO_2 different reaction times (1-48 h), ratios of catalyst, co-catalyst, and substrates (1:1:1,000-1:1:100,000) were examined. By increasing the substrate ratio, relatively longer reaction times are required for the conversion of CO_2 and epichlorohydrin into the product. The catalyst exhibits a good activity with a maximum turnover number (TON) of 85,000 (Table 2, entry 11).

With the help of these results, the overall optimal reaction conditions were 0.01 mmol of catalyst (5.83 mg Co-TCA) in the presence of 0.01 mmol of TBAC co- catalyst, 10 mmol of epoxide, 1 bar CO_2 pressure at 120 °C in 5-8 h. Using the above-mentioned optimized set of reaction conditions, various epoxides having a variety of substituents were tested as substrates. The experimental results of different substrates conversions are summarized in Table 3. The presence of different substituents attached in the substrate shows a considerably remarkable effect on the progress of the reaction. Therefore, it is worth noting that substrates bearing electronwithdrawing groups display excellent catalytic efficiencies in 5 h (Table 3, entries 1, 3, 4, 6, 9 and 10). On the contrary, substrates having electron-donating groups (alkyl groups) are less efficiently converted (Table 3, entries 2, 5, 7 and 8). Significantly, in the current catalytic system good to excellent isolated yields were achieved for all epoxides, more importantly, the catalyst was highly selective (>99%) to the formation of the cyclic carbonate, and no side products were observed. Additionally, in the case of cyclohexene oxide, the product showed a higher selectivity toward the cis product [46] as in Table 3. Although many complexes can ring-open terminal epoxides, only some are active under mild conditions towards ring-opening of terminal epoxides. Thus, with the high activity of our catalytic system in mind, we have used it against internal epoxides, as this is still a problem in this research area and this data can be used to really highlight the activity of a catalyst.

Table 3. Reaction conditions for the cycloaddition of CO_2 and different epoxide in the presence of cocatalysts.

Entry	Epoxides	Conv. (%)	Time(h)	TON	TOF/h	Yield (%)^C	Product Spectrum in S.I.
1		100	5	1,000	200	97	Figure S2
2		100	8	1,000	125	80	Figure S4
3		100	5	1,000	200	96	Figure S6
4		99	5	990	200	89	Figure S8
5		100	8	1,000	125	91	Figure S10
6		100	5	1,000	200	93	Figure S12
7		100	8	1,000	125	90	Figure S14
8		100	8	1,000	125	88	Figure S16

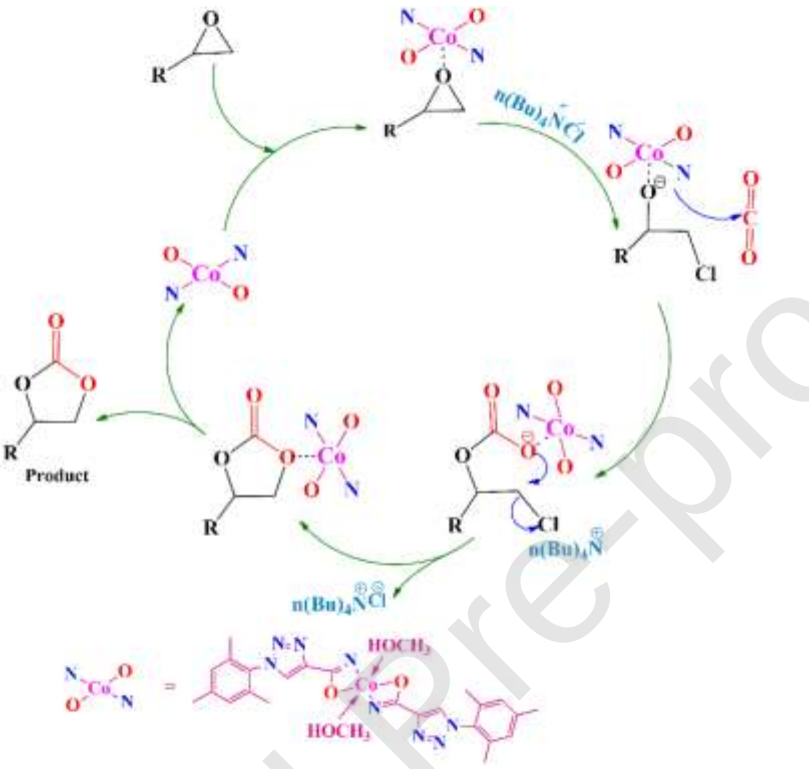
9		100	5	1,000	200	82	Figure S18
10		100	5	1,000	200	95	Figure S20
11		48	28	480	17	32	Figure S22
12		100	28	1,000	35	80	Figure S24
13		100	28	1,000	35	78	Figure S26

All reactions were conducted without any solvent and conversion was determined by ^{1}H and ^{13}C-NMR. Selectivity is > 99 % for all substrates. ^{C} isolated yield. Reaction conditions: CO_2 pressure 1 bar; Temperature: 120 °C; catalyst: Co-TCA (0.01 mmol); cocatalyst: TBAC (0.01 mmol); Catalyst: Cocatalyst: substrate: 1:1: 1,000.

It is worth mentioning that the catalyst is also active for internal epoxides (cyclohexene oxide, *cis:trans* (87:13), 3,6-dioxabicyclo [3,1.0] hexane, *cis:trans* (99:1) and cyclopentene oxide, *cis:trans* (99:1)), Table 3, entries 11-13.

Catalytic mechanism insight into CO_2 cycloaddition to epoxides

The mechanistic study is explained for the catalytic cycloaddition of CO_2 with epoxides (epichlorohydrin) [20] for the investigated cobalt complex with TBAC as a co-catalyst. In the first step, an interaction between the Co-complex and the substrate results in the activation of the epoxy ring through the less hindered side resulting in an intermediate, as supported by MALDI-TOF MS (Figure 2 (iii)) and ^{1}H-NMR (Figure 2 (iv)) of the reaction mixture followed by the nucleophilic attack of a Lewis base i.e., co-catalyst [59, 60], leading to the ring opening. Afterwards, the generated metal bound alkoxide ion acts as a nucleophile and in turn activates CO_2, followed by the ring formation. The cooperative effect of the Co-TCA complex and TBAC results in attacking the epoxy ring and the consecutive addition of CO_2 to generate the corresponding cyclic carbonate. Almost similar to the mechanism proposed by Nguyen [61]. In an attempt to detect the first suggested intermediate in the proposed mechanism, the Co-TCA catalyst and epichlorohydrin substrate were mixed in a molar ratio of 1:50, and stirred under an argon atmosphere at 65 ºC for an hour. After 1 hour, a sample of the reaction mixture could be characterized using MALDI-TOF MS and ^{1}H-NMR (Figure 2 (iii) and (iv)). Both analyses displayed the formation of a coordination product between the substrate and the catalyst. Therefore, a proposed mechanism is partially drawn based on the experimental evidences from ^{1}H-NMR and MALDI-TOF for Scheme 2.



Scheme 2. Proposed catalytic mechanism for cyclic carbonate synthesis catalyzed by 3.

Stability and usability

Since the catalytic process is homogenous, therefore, to find out the stability and effectiveness of the catalytic system, further usability of the catalyst was carried out by adding another prescribed amount (catalyst: substrate, 1: 100, see Table 1, entry 7) of fresh substrate (ECH) and this mixture was exposed to the reaction conditions i.e., 1 bar CO_2 pressure at 120 °C for 7h [20]. This process is repeated till five reaction cycles with the single loading of the catalyst without using co-catalyst during catalyst reusability. The formation of the cyclic carbonate was calculated from the integration of the proton NMR spectra ($CDCl_3$ as solvent) [43, 62, 63]. The separation of the Co(II)-TCA complex from the reaction mixture after five cycles is performed by using column chromatography to isolate the product (isolated cyclic carbonates and complex from the reaction mixture) using a petroleum ether/ethyl acetate mixture (3:1) as eluent. Once the cyclic carbonate product is separated then the complex (Co-TCA) was recovered from the column by using methanol and characterized by FTIR and PXRD. The characterized recovered catalyst has no significant change with the fresh one (Figure S28). This revealed the potential stability of the catalyst to be used for the successive reaction cycles. As noted (Figure S28), complete conversion of the substrate into the product is obtained without any loss of the catalyst's activity (100% conversions). These results signposted that the catalyst has remarkable stability and reusability, thus these two factors have potential importance for an industrial application.

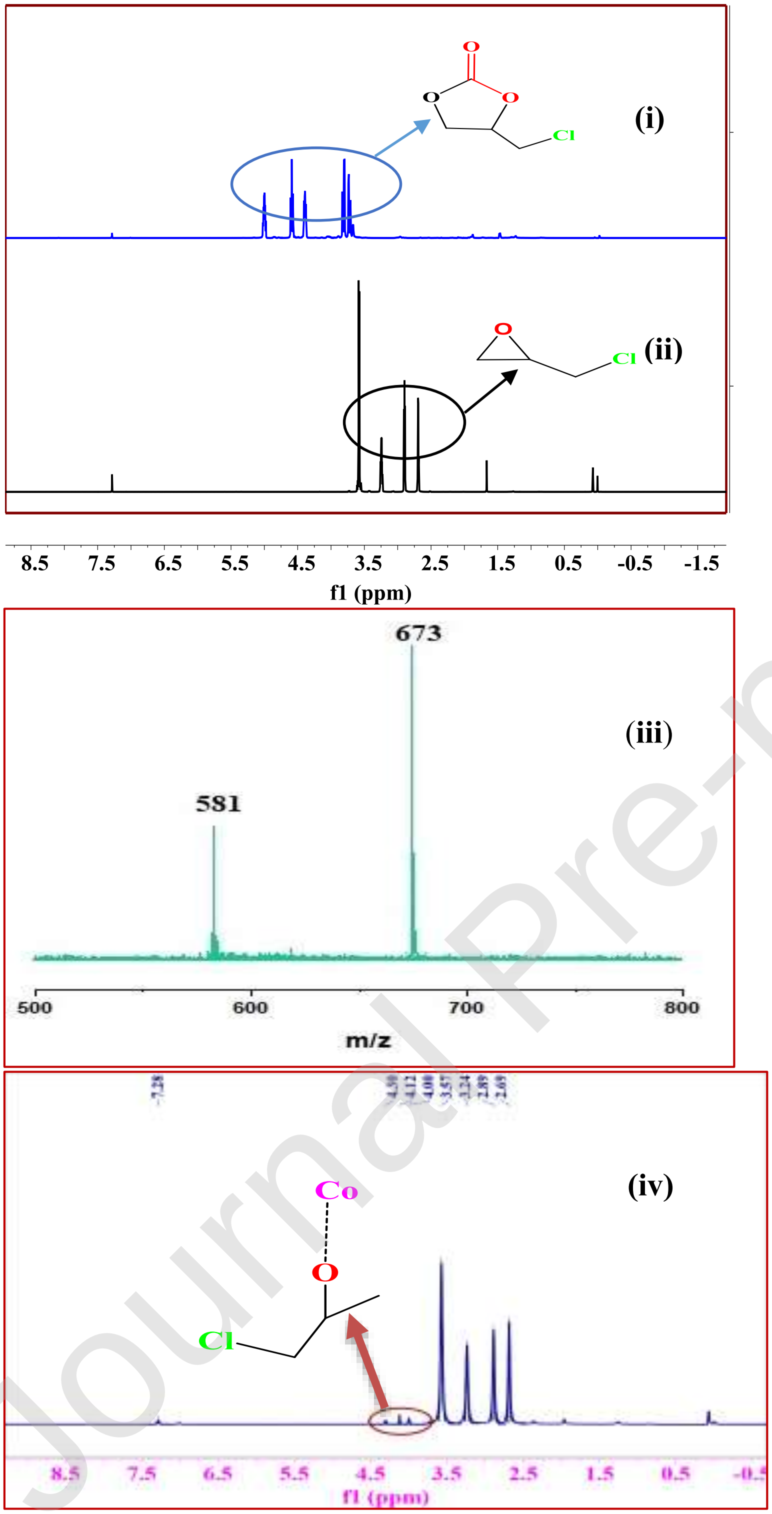


Figure 2. Mechanistic investigation of Co-TCA complex catalysing CO_2 insertion into epoxides. (i) ^{1}H-NMR of 4-(chloromethyl)-1,3-dioxolan-2-one in $CDCl_3$ (ii) ^{1}H-NMR of epichlorohydrin in $CDCl_3$ (iii) MALDI-TOF MS spectrum catalyst/substrate molar ratio (1:50) shows mass of complex product and intermediate. (iv) ^{1}H-NMR of intermediate.

Conclusions

In summary, a cobalt complex based on the carboxylic ligand having triazole ring was studied as an active homogeneous catalyst for the cycloaddition of carbon dioxide to epoxide substrate. The catalyst proficiently catalysed various epoxides to industrially important cyclic carbonates at ambient pressure (1 bar) under solvent-free conditions. A low catalyst loading can be used (Catalyst: co-catalyst: substrate ratios (1:1:100,000)). Significantly, we achieved the higher TON values (85000), amongst cobalt-based catalyst under atmospheric pressure and solvent free condition. Furthermore, good to excellent isolated yield is achieved for each product and the continuous use of the catalyst for five successive reaction runs resulted in the same activity revealing the remarkable stability of this Co-TCA system. Therefore, fixation of CO_2 has a remarkably high potential for making desirable cyclic carbonates with industrial importance.

Suleman Suleman, Francis Verpoort**:** Conceptualization, Methodology. Suleman Suleman, Hussein A. Younus, Nazir Ahmad, Zafar A. K. Khattak: investigation, Writing- Original draft preparation. Habib Ullah, Jihae Park, Baoyi Yu: NMR, FTIR and single crystal analysis. Taejun Han, Francis Verpoort*:* Supervision. **Francis Verpoort:** Writing- Reviewing and Editing

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