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Chemical fixation of carbon dioxide catalyzed via cobalt (III) ONO pincer ligated complexes

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Chemical insertion of carbon dioxide into epoxides under ambient conditions has become one of the most important methods for the construction of cyclic organic carbonates. Various active salen, salophen, and phenolate ligand based complexes have been reported for the synthesis of cyclic organic carbonates. Here we demonstrate a series of ONO pincer type cobalt (III) complexes as efficient catalysts for the cycloaddition of carbon dioxide to epoxides in neat conditions at atmospheric pressure with and without co-catalyst. A turnover number of up to 200,000 under atmospheric pressure is achieved. Moreover, the in situ generated complex shows high activity and the catalyst can be reused for at least 11 cycles without any decline in catalytic performance.

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The upcoming generation's viable development mainly relies on more sensible resource management. The current level of sustainability still needs a huge improvement as it is far from an acceptable level. To date, crude oil, natural gas, and coal are the main carbon resources. Therefore, along with biomass, carbon dioxide can be another suitable option for the renewable carbon economy. After the industrial revolution, a considerable amount of CO₂ has been released into the biosphere due to the combustion of fossil fuels in order to fulfill the global energy requirement. Carbon dioxide is a primary component of greenhouse gases, resulting in global warming and disastrous climatic change¹.

Chemical fixation of CO₂ to construct industrially vital chemicals and products under mild conditions encounters great challenges because of two main reasons: (i) the high ionization potential (IP), and (ii) the negative adiabatic electron affinity (EA) of carbon dioxide. Therefore, most of the reported studies use highly reactive substrates and/or harsh reaction conditions to overcome the high thermodynamic stability and chemical inertness of carbon dioxide². Hence, designing excellent catalytic systems for the conversion of CO₂ into economically valuable products is expected to be of great interest for chemists over the course of this century³. Moreover, the synthesis of cyclic carbonates (five-membered compounds), having numerous applications as aprotic solvents, electrolytes for lithium-ion batteries, fuel additives, synthetic intermediates, and materials for engineering plastics, is an atom economical way to utilize CO₂ via cycloaddition to epoxides^{4–8}. For the synthesis of cyclic carbonates from epoxides, CO₂ serves as an abundant, cheap, and non-toxic renewable C1 resource.

Various kinds of catalysts, such as metal oxides⁹, molecular sieves¹⁰, metal-organic frameworks^{11–13}, ion-exchange resins¹⁴, nanoparticles^{3,15}, ionic liquids¹⁶, functionalized polymers¹⁷, biopolymer-supported catalysts¹⁸, and metal complexes including aluminum,^{19–21} zinc^{22,23} chromium^{24,25}, iron^{26,27}, tin²⁸ and vanadium, etc.^{29–31}, have been investigated for this reaction.

On the other hand, cobalt complexes are an ideal choice for the CO₂/epoxide coupling due to its abundant and environment-friendly nature. Cobalt complexes have been extensively studied for this reaction and recently reviewed by Lu and Darenbourg³². Among them, salen^{33,34}, chiral Co^{35–37}, bis(phenoxyiminato)³⁸, amine-bis(phenolato)³⁹, porphyrin⁴⁰ ligand based cobalt complexes are more frequently studied. Moreover, Wani et al. investigated some di-nuclear transition metal complexes/nBu₄N⁺ as catalyst/co-catalysts for the cycloaddition of CO₂ to epoxides exhibiting a low turnover frequency of 167 h⁻¹ at high pressure of 10 bar⁴¹.

Previous literature reveals that highly active and stable catalytic systems based on a new class of ligands are urgently needed. Most, if not all, reported active catalytic systems towards CO₂/epoxide coupling exist for salen, salophen, and porphyrin ligated complexes of Al, Cr, Zn, Co, and other metal complexes, which have been studied for years^{40,42,43}. Furthermore, high catalyst loading and high pressure of CO₂ have been needed in most of these catalytic systems, and specifically in those based on cobalt complexes.

Here, keeping these concerns in mind, we design tridentate hydrazone linked ONO pincer type ligands and their hexacoordinated cobalt (III) complexes, which exhibit excellent catalytic activities towards the CO₂/epoxide coupling reaction at ambient pressure with and without co-catalyst in the absence of a solvent. Owing to the wide-range flexibility in the choice and design of components, the hydrazone scaffold possesses numerous advantages over other types of ligands. These include a one-step synthesis by a condensation reaction between aldehyde and hydrazide, air stability, and tunability of the side chain.

Furthermore, these hydrazone ligated cobalt complexes can serve as efficient and recyclable catalytic systems for the chemical fixation of CO₂ to epoxides, exhibiting turnover numbers of up to 200,000 at ambient pressure.

Results

Synthesis of ligands and complexes. Novel hydrazone based ligands **1a–c** and their respective cobalt complexes **2a–c** were synthesized according to a reported procedure⁴⁴ by reacting the respective hydrazide with 3,5-di-tert-butyl-2-hydroxybenzaldehyde (Supplementary Fig. 1). The final products were further characterized by infrared spectroscopy, NMR, mass spectrometry, elemental analysis, and single crystal XRD analysis.

All ligands and complexes were characterized via 1D and 2D ¹H-NMR spectroscopy in DMSO-d₆ (Supplementary Figs. 2–16). The absence of the phenolic OH proton in the corresponding complexes, the slight shifting of the hydrazine NH proton, and the downfield shifting of the azomethine proton in the NMR spectra confirm the successful complexation of the cobalt ion to the ligand. In addition, the disappearance of phenolate hydroxyl bands, the shifting of azomethine C=N stretch vibration towards a lower wave number, and the appearance of new bands for C–O in FTIR spectra of the complexes indicate the formation of complexes. (Supplementary Figs. 17–19). High-resolution mass spectrometry (HRMS) of the synthesized ligands and complexes exactly match with the theoretically calculated masses. (Supplementary Figs. 20–23). Finally, the structure of ligands **1a**, **1b**, and complex **2a** (Supplementary Tables 1–18) were confirmed by X-ray single crystal analysis.

According to the single crystal analysis, the asymmetric unit of complex **2a** contains the complex molecule along with one ethanol and water molecule per complex molecule (Fig. 1a). In order to sustain the electro-neutrality of the complex molecule, the Co(III) is octahedrally bonded via two ONO tridentate ligands of different protonation state⁴⁵. Four oxygen atoms occupy the equatorial plane while imino nitrogen atoms are axially positioned in the octahedron with bond distances of 1.874(3) Å and 1.864(3) Å for Co1–N1 and Co1–N3, respectively. The bond distances of Co–O (phenolate) bonds for Co1–O3 and Co1–O6 are 1.858(2) and 1.868(2) Å, respectively, while the Co–O cobalt to (hydrazonato) oxygen atoms distances values of Co1–O1 and Co1–O4 correspond to 1.914(2) Å and 1.930(2) Å, respectively. One ligand behaves as a hydrazonato HL⁻, while the other is a hydrazidato L²⁻. One ligand is singly-deprotonated, which is evidenced from the longer bond distance of Co1–O1 1.914(2) Å compared with Co1–O3 1.858(2) Å. Comparing bond distances within the coordination sphere, the O1 atom of the doubly deprotonated ligand (Co1–O1 bond distance of 1.914(2) Å within the five-membered chelate ring fragment) is found to be more strongly bound to the Co(III) ion than the O4 atom of the singly deprotonated ligand (Co1–O4 1.930(2) Å).

An analogous phenomenon can be seen for Co1–N1 1.874(3) Å and Co1–N3 1.864(3) Å bonds showing stronger bond with the nitrogen atom of the doubly deprotonated hydrazonato ligand due to a larger delocalization. The coexistence of both forms within the complex can be witnessed by the bond distance values in the region of the five-membered chelate. Hence the bond distance of keto C21–O4 1.297(3) Å is contrary to the bond distance value of C1 to O1 1.309(3) Å. (Supplementary Tables 13–18).

Catalytic cycloaddition of carbon dioxide to epoxides. The synthesized hydrazone linked ONO pincer type cobalt (III) complexes were subsequently screened for the cycloaddition of CO₂ to epoxides under solvent-free conditions. All reaction

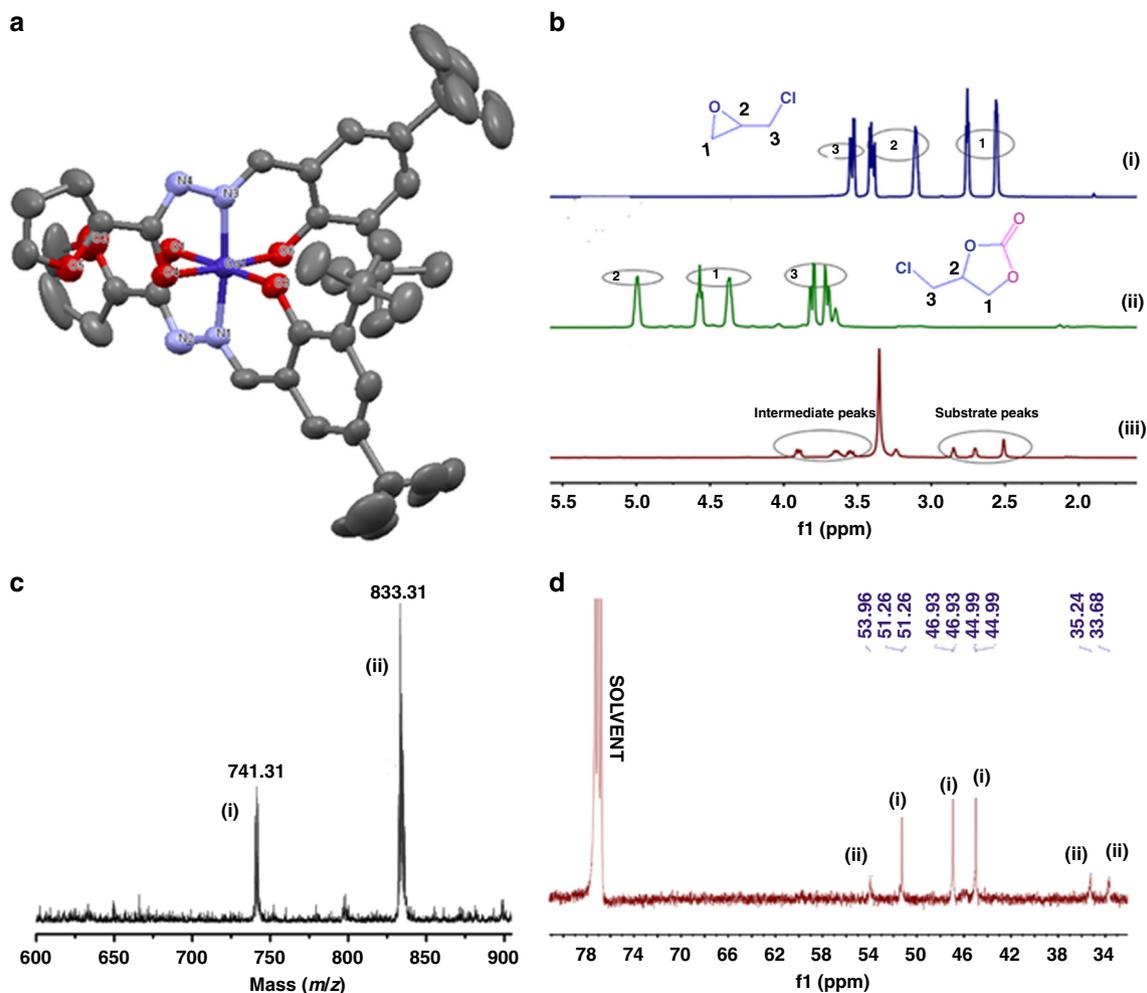


Fig. 1 Crystal structure and mechanistic investigation of complex **2a** catalyzing CO₂ insertion into epoxides. **a** ORTEP diagram of complex **2a** (Labeling of carbon and hydrogen atoms is omitted for clarity). **b** ¹H-NMR spectrum of 'i' ECH 'ii' product and 'iii' intermediate. **c** MALDI-TOF MS spectrum catalyst/substrate molar ratio (1:1) 'i' shows mass of complex 'ii' shows mass of intermediate. **d** ¹³C-NMR spectrum of catalyst/substrate molar ratio (1:1) 'i' represents the peaks of epichlorohydrin 'ii' represents the peaks of intermediate

conditions, such as temperature, pressure, mole ratio, and time, were optimized using epichlorohydrin as a model substrate without and with co-catalyst. The precursors used in the synthesis of the Co complexes such as Co(CH₃COO)₂ salt and the free ligands were examined individually for their catalytic potential for the CO₂ cycloaddition into epichlorohydrin to form cyclic carbonates. No cyclic carbonate formation was observed, due to the well-known fact of the high exothermic nature of this reaction, hence suggesting the need for activating the catalyst, which diminishes the activation energy for the synthesis of cyclic carbonates.

Subsequently, the catalytic activity of these complexes was examined to further optimize the effect of various reaction parameters. No yield was obtained at room temperature and a very low conversion was monitored at 50 °C (Table 1, entries 1, 2) in spite of the long reaction time of 24 h. A gradual increase in conversion was observed at 75 °C (Table 1, entry 3) at 2 bar of CO₂, suggesting the impact of temperature on the activation of the catalyst. A considerable yield was obtained at 100 °C (Table 1, entries 4–8) and an excellent yield at 120 °C (Table 1, entries 9–13) at 2 bar from 6 to 24 h.

The main shortcoming of using CO₂ as a reagent in organic transformations is the facing danger related to operations at high

Table 1 Synthesis of cyclic carbonates from epichlorohydrin and CO₂

Entry	Temp (°C)	Press (bar)	Time (h)	%-conversion ^a
1	RT	2	24	0
2	50	2	24	3
3	75	2	24	10
4	100	2	6	30
5	100	2	10	48
6	100	2	16	59
7	100	2	20	70
8	100	2	24	82
9	120	2	6	52
10	120	2	10	76
11	120	2	16	91
12	120	2	20	96
13	120	2	24	100
14	120	4	6	100

Reaction conditions: **2a** 0.1 mol% (10 mg, 0.01348 mmol)
^aConversion is based on ¹H-NMR. All reactions were conducted without solvent and co-catalyst unless otherwise mentioned.

Table 2 Effect of co-catalyst

Entry	Catalyst	Co-catalyst	%-Conversion ^a
1	2a	TBAI	70
2	2a	TBAB	82
3	2a	TBAC	98
4	2a	DMAP	99
5	2b	TBAI	30
6	2b	TBAB	50
7	2b	TBAC	70
8	2b	DMAP	90
9	2c	TBAI	30
10	2c	TBAB	50
11	2c	TBAC	70
12	2c	DMAP	85

Reaction conditions: Pressure 1 bar, temperature 120 °C, time 3 h, 0.1 mol% catalysts (0.01348 mmol), 0.1 mol% co-catalyst (0.01348 mmol)

^aConversion is based on ¹H-NMR. All reactions were conducted without solvent unless otherwise mentioned.

Table 3 Effect of molar ratio of 2a on Epichlorohydrin

Entry	Cat: Sub (mmol)	Time (h)	% Conversion ^a	TON ^b	TOF (h ⁻¹) ^c
1 ^d	1:1000	3	>99	1000	333
2 ^e	1:10,000	3	>99	9200	3333
3 ^f	1:20,000	3	80	16,000	5333
4 ^g	1:50,000	6	90	45,000	7500
5 ^g	1:50,000	8	95	47,500	5937
6 ^h	1:100,000	12	83	83,000	6916
7 ⁱ	1:200,000	3	17	34,000	11,333
8 ⁱ	1:200,000	6	26	52,000	8666
9 ⁱ	1:200,000	24	55	110,000	4583
10 ⁱ	1:200,000	48	>99	200,000	4166

All reactions were conducted without solvent unless otherwise mentioned
Reaction conditions: Pressure 1 bar, temperature 120 °C, catalyst (**2a**)/co-catalyst (DMAP)

^aConversion is based on ¹H-NMR

^bTON = No of mmol of product/No of mmol of catalyst

^cTOF = TON/time

^d0.1 mol%

^e0.01 mol%

^f0.005 mol%

^g0.002 mol%

^h0.001 mol%

ⁱ0.0005 mol%

pressure. Therefore, we were delighted to observe that our catalyst is active at a low pressure of 2 bars without any co-catalyst.

Although an excellent yield was monitored at 120 °C and 2 bar without co-catalyst, we were aiming to develop the best performing catalytic systems at ambient pressure. Therefore, we investigated all three catalysts with various hydrazide side chains with different co-catalysts such as tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium chloride (TBAC), tetra-n-butylammonium iodide (TBAI), and dimethylaminopyridine (DMAP) using a pressure of 1 bar (summarized in Table 2). It is clear that complex **2a** combined with DMAP as a co-catalyst exhibited the highest catalytic performance amongst the three catalysts (Table 2, entries 1–4). We believe this might be due to a more appropriate coordination site available in the complex. Relative low conversions are observed for complex **2b** (Table 2, entries 5–8) and **2c**.

Unexpectedly, TBAB being an excellent co-catalyst for the cycloaddition of CO₂ in most of the reported cases along with almost all transition metal complexes; however, in our system, comparatively low yields were observed with TBAB (Table 2, entries 2, 6, 10) along with TBAI (Table 2, entries 1, 5, 9). Differently, TBAC (Table 2, entries 3, 7, 11) and DMAP (Table 2, entries 4, 8, 12) demonstrated to be a better co-catalysts with almost >99% conversion with 99% selectivity. Because of the hygroscopic nature of TBAC, we selected complex **2a** in combination with DMAP as co-catalyst at 120 °C and 1 bar as the optimized condition for the cycloaddition of CO₂ to epoxides.

Up to now, most catalytic systems of various metal complexes, specifically cobalt complexes reported in the literature for cyclic organic carbonates synthesis, applying a relatively high catalyst loading. Hence, we investigated the effect of catalyst loading on the coupling of CO₂ to epichlorohydrin (Table 3).

We were delighted to obtain the highest TON of 200,000 amongst all the reported cobalt and other metal complexes for the coupling of CO₂ to epoxides at a pressure of 1 bar, which is even the highest reported TON using this pressure. (Table 4)

Finally, the catalytic system was found to be applicable to a variety of other epoxides providing the corresponding cyclic carbonates in nearly quantitative yields and >99 % selectivity. Excellent conversions were obtained with both aliphatic and aromatic epoxides (Fig. 2).

One of the promising results of the above catalytic system is the superior recyclability and the in situ formation of the catalyst in the reaction medium. Reusability of the catalyst, a very important

Table 4 Comparison of TON and TOF of this work with the reported literature

Entry	Catalyst	Co-catalyst	Temp	P (bar)	TOF h ⁻¹	TON	Time (h)	Ref.
1 ^a	Co	DMAP	120	1	4146	200,000	48	This work
2 ^b	Co	DMAP	130	20	662	1986	3	50
3 ^b	Co	–	120	20	122	2930	24	40
4 ^b	Fe	TBAB	120	20	5200	3480	24	27
5 ^b	Fe	–	120	10	7900	7900	1	51
6 ^c	Al	PPN-Br	90	10	36,000	10,000	18	52
7 ^b	Al	PPNCI	120	30	185,000	92,500	0.5	53
8 ^c	Mg ^d	–	120	17	12,000	103,000	24	22
9 ^c	Mg ^e	–	120	17	19,000	138,000	24	54
10 ^c	Mg ^f	–	120	17	46,000	220,000	72	55
11 ^c	Zn	–	120	17	40,000	310,000	120	55
12 ^b	Zn	–	120	17	2000	240,000	120	56

^aEpichlorohydrin

^bPropylene oxide

^c1, 2 epoxyhexane

^dMono-nuclear

^eDi-nuclear

^fTri-nuclear

Entry	Substrate	Time (h ⁻¹)	Product	*Conversion	# _{yield}
1		3		>99	98
2		8		>99	97
3		8		88	70
4		8		>99	97
5		8		>99	97
6		8		86	70
7		16		86	82
8		20		>99	97

Fig. 2 Insertion of CO₂ to various tested epoxides by complex **2a** and DMAP as co-catalyst. All reactions were conducted without solvent unless otherwise mentioned. Pink color in product represents the CO₂ insertion. Reaction conditions: Pressure: 1 bar; temperature: 120 °C; 10 mg of complex **2a** (0.01348 mmol, 0.1 mol%), 0.01348 mmol of DMAP (0.1 mol%), *Conversion based on ¹H-NMR. #Isolated yield

parameter in catalysis, was conducted for our system under optimized conditions at 120 °C and 1 bar using the procedure reported Rulev et al.³⁷. Reusability was performed by addition of fresh ECH to the reaction mixture in the stainless steel reactor, without separating the complex, after the complete conversion of already added ECH to the carbonates. This was repeated 11 times and no loss of activity was observed after 11 cycles (Supplementary Fig. 25). The ESI-mass spectrometry of the complex showed no deformation in the structure after the reusability test (Supplementary Fig. 26).

An in situ reaction, which is very crucial for reducing the time consumed in the synthetic process of the catalyst, was conducted successfully. Therefore, without a pre-synthesized complex, the free ligand along with the metal salt (Co(CH₃COO)₂·4H₂O), and ECH were charged in a 20 mL stainless steel reactor with a stir bar

under 1 bar at 120 °C. Excellent yields (>99) were obtained after 3 h similar as achieved with the well-defined complex (Supplementary Fig. 27). In order to exclude the possibility of acid hydrolysis of epichlorohydrin to diols in the presence of acetic acid and water from the investigated salt, Co(CH₃COO)₂·4H₂O, the epoxide was charged with (Co(CH₃COO)₂·4H₂O) in a flask under an inert atmosphere at 120 °C. No diol formation was observed according to ¹H-NMR. Similarly, no diol generation was witnessed, when the same reaction was performed under CO₂ in a 20 mL (Supplementary Fig. 28).

Mechanistic investigation. Based on the single crystal analysis, Co(III) is octahedrally coordinated via two ONO tridentate ligands, which differ in their protonation state (Fig. 1a).

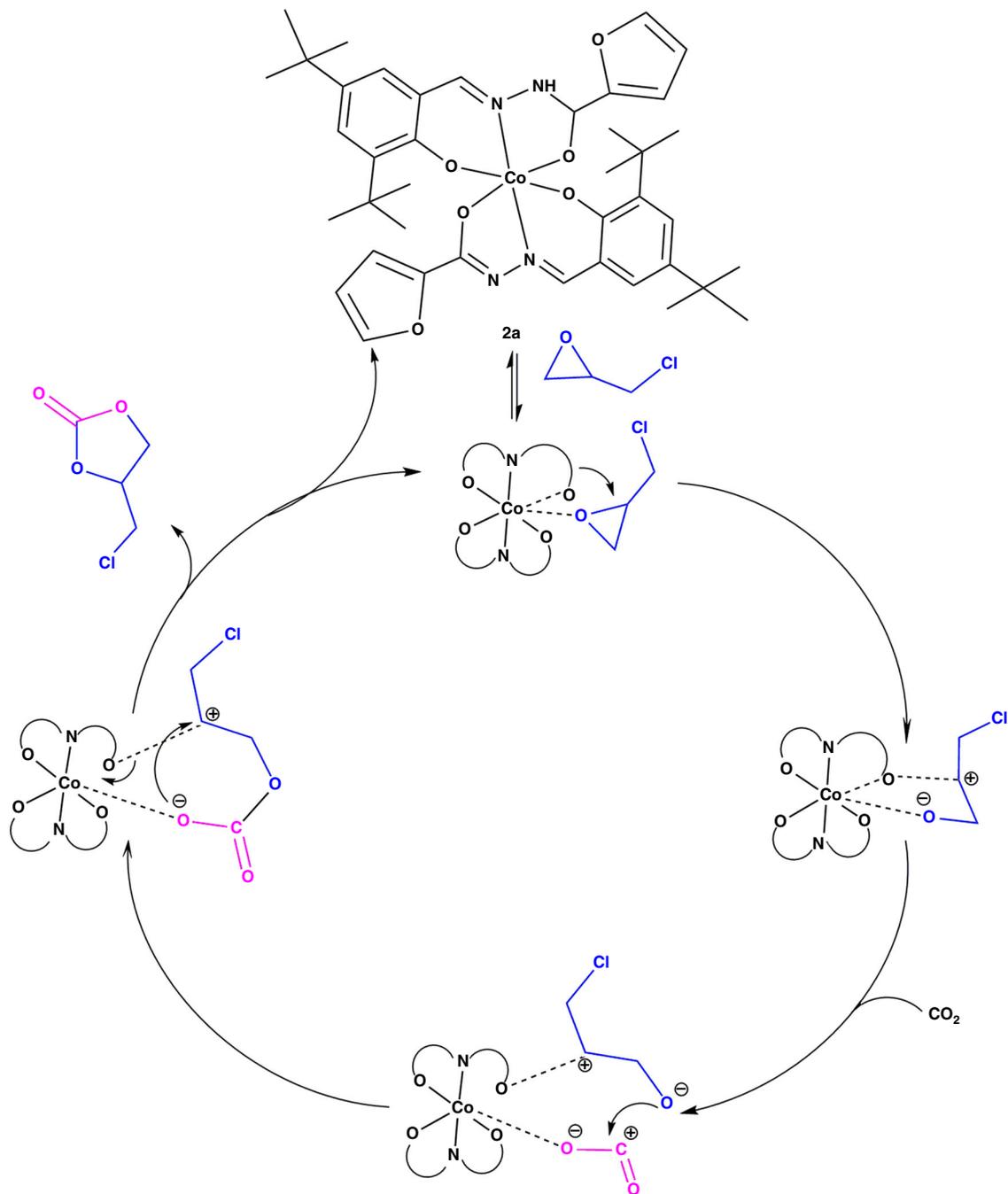


Fig. 3 Proposed mechanism using Co-complex **2a**. Coordination of complex to epoxides followed by generating a phenoxide from complex and ring opening of epoxides. Metal-bound alkoxide ion attacks carbon dioxide followed by cyclization to liberate cyclic product and starting complex. Blue color represents ECH and pink color represents CO₂

Combined with the catalytic outcome, we propose a possible mechanism (Fig. 3) for the coupling of CO₂ and epoxides using the hexacoordinated octahedral Co(III) complexes, where dissociation of one of the Co–O bond of the phenolate is expected to occur, providing a vacant site for either substrate to coordinate.

Coordination of the metal to epoxides and insertion of CO₂ to metal-bound alkoxide is the most prominent mechanism for the cobalt-catalyzed coupling of CO₂ to epoxides. Jacobson et al.⁴⁶ proposed that the nucleophilic ring opening of epoxides catalyzed by cobalt complexes occurs via catalyst activation of both the electrophilic epoxides and the incoming nucleophile. In the first step, the cobalt complex **2a** may activate the epoxide by coordinating to the ‘O’ of the epoxides forming an intermediate

(supported by ¹H-NMR (Fig. 1b) and MALDI-TOF MS (Fig. 1c)). Dissociation of one of the Co–O bonds (phenolate) may then occur, resulting in the generation of a phenoxide ion. The resulting phenoxide ion may act as an internal nucleophile and attack the less sterically hindered carbon atom of the epoxide, causing the ring opening of the epoxide. The ring opening of epoxide may also be promoted by an external nucleophile, such as the DMAP co-catalyst³⁸. This assumption is supported by experimental observations: the catalyst displayed acceleration in catalytic activity when co-catalyst was present. Mixing the catalyst and epoxide in equimolar ratios, the intermediate formed could be characterized using MALDI-TOF MS and ¹H-NMR. (Fig. 1b, c) The MALDI-TOF MS spectrum showed an ion peak that

corresponds to the formation of the intermediate resulting from the coordination of ECH to the complex. $^1\text{H-NMR}$ further exhibited new peaks that differ from those of ECH and the reaction product, which suggest the coordination of ECH to the cobalt complex as a first step in the catalytic cycle, which is also in agreement with the MALDI-TOF results. In addition, $^{13}\text{C-NMR}$ analysis (Fig. 1d) of the mixture of complex **2a** and ECH (1:10) under inert atmosphere supports the ring opening of the epoxide by an internal nucleophile i.e., phenoxide ion. However, when the complex was kept under a CO_2 atmosphere in toluene as a solvent, using the same conditions as for the catalyst screening, no interaction between the catalyst and CO_2 was observed when monitored by $^1\text{H-NMR}$ or MALDI-TOF MS, which suggests the inability of the catalyst to activate CO_2 before the alkoxide formation, which may have a key role for activating CO_2 and completing the catalytic cycle. This also excludes possible CO_2 coordination as an initial step in the reaction mechanism of our catalytic system.

A tentative mechanism is given in Fig. 3. The metal complex (**2a**) may initiate the coupling reaction by coordinating to the epoxide as evidenced by $^1\text{H-NMR}$ and in MALDI-TOF MS (Fig. 1b, c). Epoxide coordination to the cobalt of the complex may result in de-coordination of one arm of the pincer ligand and generation of a phenoxide ion. As described earlier, the resulting phenoxide ion might act as an internal nucleophile, promoting the ring-opening step, as supported by $^{13}\text{C-NMR}$ (Fig. 1d). In the next step, the metal-bound alkoxide ion formed by the ring opening of ECH in turns may act as a nucleophile and attack the electrophilic carbon of CO_2 , forming a metal carbonate species via CO_2 insertion. However, for the mechanism of CO_2 insertion into cobalt-alkoxide, experimental evidence at the atomic or molecular level is still elusive⁴⁷. In the final step, the metal-bound carboxylate intermolecular cyclization may generate the cyclic carbonate and the starting catalyst via a re-coordination of the phenoxide moiety to the cobalt metal. The high catalytic activity, without using co-catalyst, suggests that the coordination of the metal to the epoxide and ring opening occur simultaneously and that the alkoxide ion might have a crucial role in these two steps. In addition, the ring opening of epoxides can be also accomplished by employing external nucleophiles like (DMAP) as co-catalyst, evidenced by the fast reaction kinetics in the presence of co-catalysts. The later might proceed via a monometallic two-nucleophile mechanism, i.e., both internal nucleophile generated from the complex by de-coordination of one arm of anionic ligand, and via involvement of an external nucleophile such as the co-catalyst (DMAP)⁴⁸. Furthermore, based on kinetic studies, the high catalytic activity without co-catalyst might be due to the formation of anionic six-coordinated intermediates that are superior in chemical reactivity both in terms of ring opening and CO_2 insertion in the epoxide compared to their neutral six-coordinated counterparts⁴⁹.

Discussion

Herby, we have successfully synthesized a series of hydrazone scaffold-based complexes. These complexes after complete characterization with the aid of various physicochemical techniques were applied as excellent catalysts for carbon dioxide insertion into epoxides to form cyclic organic carbonates at atmospheric pressure. The investigated catalysts exhibit high selectivity (>99) as well as high versatility to all tested aliphatic and aromatic terminal epoxides. A tentative proposed mechanism is presented based on preliminary experimental evidence. Most importantly, besides its general applicability towards various terminal epoxides, the catalyst displays a high turnover number and decent recyclability at atmospheric pressure.

Methods

Materials and instrumentation. See Supplementary Methods for general information regarding chemicals and instrumentation.

Synthesis. Detailed synthetic procedures of ligands and complexes. (Supplementary Fig. 1).

Characterization. Characterization of ligands and complexes $^1\text{H-NMR}$, ^{13}C , 2D-NMR (Supplementary Figures 2–16), FTIR (Supplementary Figs. 17–19), Mass spectrometry (Supplementary Figs. 20–23), Single crystal XRD (Supplementary Tables 1–18 and Supplementary Data 1–3).

Catalysis. $^1\text{H-NMR}$ of the tested epoxides (Supplementary Fig. 24(a–g)), $^1\text{H-NMR}$ and mass spectrum of the catalyst recyclability (Supplementary Figs. 25, 26), $^1\text{H-NMR}$ spectra representing in situ reaction of catalyst (Supplementary Fig. 27), and $^1\text{H-NMR}$ spectra of metal salt used for comparison of the catalytic reactivity of the catalyst (Supplementary Fig. 28).

Ligands and complexes general synthetic procedure. In a typical experiment, hydrazone ligands were prepared in two necked round bottom flask dipped in oil bath equipped with magnetic stir bar charged with equimolar ratio of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (100 mg 0.42 mmoles) and respective hydrazone such as 2-furoic hydrazide (53.81 mg 0.42 mmoles), 2 thiophenecarboxylic acid hydrazide (60.67 mg 0.42 mmoles), and 3-hydroxy-2-naphthoic acid hydrazide (86.20 mg 0.42 mmoles), respectively, in absolute methanol. The reaction mixture was added with few drops of acetic acid and allowed to stir for 12 h at 70°C . The resulted whitish precipitate was washed with cold methanol and recrystallized in ethanol after drying under reduce pressure at 50°C . The complexation of synthesized hydrazone ligands were achieved by refluxing the mixture of respective ligands (2 equiv) and cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) (1.00 equiv) in ethanol as solvent and in the presence of few drops of trimethylamine as a base at 70°C for 12 h. Dark brown solid was obtained after evaporating the solvent by rotary evaporator.

General procedure of catalytic carbon dioxide insertion. In a typical run, the catalytic cycloaddition reactions of CO_2 to epoxides were performed in a 20 mL stainless steel reactor equipped with magnetic stir bar and charged with equimolar ratio of the catalyst and co-catalysts (0.1 mol%) along with respective epoxides at 120°C under atmospheric pressure. The small amount from the crude reaction mixture was taken for $^1\text{H-NMR}$ analysis in deuterated chloroform after cooling the reaction mixture to room temperature and venting slowly. In order to obtain high turnover number (TON), low catalyst experiments were performed using same procedure in 50 mL instead of 20 mL stainless steel reactor. The crude products were purified by column chromatography using mixture of ethyl acetate and petroleum ether. After the complete isolation of products, catalyst was eluted by passing methanol as eluent.

Data Availability

All generated data in the course of the investigated study are available in supplementary information file and can be acquired from corresponding authors on requests. The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1900710 (**1a**), 1900709 (**1b**), and 1900711 (**2a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions

H.U. designed, performed experiments, and wrote the manuscript. B.M. guided in CO₂ fixation experimentation and made corrections in the manuscript. H.A.Y. helped in writing the proposed mechanism and corrections in the manuscript. Z.A.K.K. performed calculations and helped in experimentation. S.C. helped in figure adjustments. S.S. helped in experiments. F.V. supervised the whole project.

Additional information

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