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Introduction

As petroleum resources are depleting, there has been a significant interest to attain an alternative feedstock for fuel and to search for new routes to basic valuable chemicals from renewable carbon resources such as CO₂.¹ The Keeling curve demonstrated that ever since the industrial revolution, there has been a steady rise in CO₂ levels in the atmosphere. The rise was about 280 ppm in 1850 while 391 ppm in 2011 and continues to increase at an accelerating rate of 1.9 ppm per year.² The anthropogenic accumulation of CO₂ primarily originates from fossil fuel combustion for energy requirements. In an effort to mitigate global warming, carbon sequestration technologies were introduced to limit the amount of CO2 entering the atmosphere from industrial processes.³ However, carbon sequestration is discouraged by industries due to the ambiguity in the process feasibility and high energy demand.⁴ Therefore, utilization of CO2 has the additional environmental benefit of maintaining climate change if the process is implemented at an industry level.⁵

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Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{*N*-(2,6diisopropylphenyl)iminomethyl}pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis†

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The syntheses of Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H **1** and their catalytic activities in CO₂ fixation are reported. The structures of these complexes were characterized by IR, ¹H, ¹³C NMR and single crystal X-ray diffraction techniques. The catalytic activities of these complexes for the cycloaddition of CO₂ to an epoxide under one atmosphere of pressure and mild temperature conditions to yield cyclic carbonate have been studied. Among the four complexes synthesized, the Zn(II) and Cu(II) complexes were found to be versatile whereas the Cu(II) complex was more selective in the conversion. They were highly effective for the conversion of monosubstituted terminal epoxides, disubstituted terminal and internal epoxides to their corresponding cyclic carbonates with good to high yields.

> CO_2 is a cheap, nontoxic, non-flammable, naturally abundant carbon feedstock. However, CO_2 is a highly oxidized, thermodynamically stable molecule which hinders its utility as a starting material for the synthesis of various compounds. Highly reactive compounds have been explored for the reaction with CO_2 . One such important commercial reaction is the insertion of CO_2 into an epoxide in the presence of a catalyst to generate polycarbonate or cyclic carbonate.⁶ Polycarbonates have potential applications as exterior thermoplastics for engineering parts, safety glasses, eyewear lenses and packaging materials.⁷ Cyclic carbonates have applications in a variety of fields, such as electrolytes in secondary batteries, pharmaceutical intermediates, aprotic polar solvents in paint stripping, degreasing and cleaning applications.⁸

> Varieties of catalysts, such as salen complexes⁹ of Zn, Co, Cr, Al, Cu, Mg and Sn, organocatalysts,¹⁰ ionic liquids,¹¹ $InBr_3^{12}$ and other ligand complexes¹³ of Zn, Mo, Pd, Co, and Sn have been reported for the synthesis of cyclic carbonates from epoxide and CO₂. However, these reactions require high temperatures and high pressures of CO₂ to induce the reaction with epoxides. The long-term obligation of the scientific community is to find an alternate efficient catalyst to perform this reaction under mild temperature conditions at atmospheric pressure. Recent reports¹⁴ on the electrosynthesis and utilization of alkylammonium salts, bimetallic aluminium–salen complexes, Zn clusters, ionic liquids and amidine derivatives as catalysts for cyclic carbonate synthesis are promising. However, these systems are highly efficient only to the

[†]Electronic supplementary information (ESI) available: Crystallographic data and structures of complexes **3a**, **3b**, **5a** and **5b**, spectra of all complexes and cyclic carbonates. CCDC 874343 (**3b**), 885290 (**5a**) and CCDC 885291 (**5b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31755a

monosubstituted terminal epoxides. The active catalyst for both mono- and disubstituted epoxides at an atmospheric pressure of CO_2 is rarely reported.¹⁵ We are interested in developing versatile catalysts that are useful for the conversion of both mono- and disubstituted terminal and internal epoxides.

Complexes of the 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H ligand **1** with Cu, Zr, Fe, Co, Al, Cr, alkali-metals¹⁶ and rare earth metals¹⁷ have been reported. Some of these complexes showed catalytic activity for the polymerization of ethene, oligomerisation of ethene and propene and ring opening polymerization of ε -caprolactone. Metal complexes of (DIP₂pyr)H **1** have never been attempted for the cycloaddition of CO₂ to epoxides. Herein, we report the synthesis of Zn(π), Cd(π) and Cu(π) complexes of (DIP₂pyr)H **1** and their efficient catalytic activities for the synthesis of cyclic carbonate from epoxide and CO₂ at atmospheric pressure and under mild temperature conditions.

Results and discussion

Synthesis and characterization

Bis(aryliminomethyl)pyrrole derivatives have received considerable attention in organometallic catalysis due to their diverse bonding modes and easy coordination with metals.^{17b-e,18} Metal complexes with a N,N',N"-tridentate coordination mode indicated remarkable activity in the ring opening polymerization of lactones^{17a,19} and ethylene polymerization.^{16b-d,20} However, epoxide/CO₂ coupling using N,N',N''-tridentate ligand complexes is virtually unexplored. The (DIP₂pyr)H ligand 1 was synthesized from pyrrole-2,5-dicarbaldehyde and 2,6-diisopropylaniline via a condensation reaction.^{17a} Syntheses of metal complexes of 1 were carried out using two different methods. In the first approach, complexes 3a and 3b were conveniently prepared from the homoleptic diamido complex $Zn[N(SiMe_3)_2]_2$ 2a or $Cd[N(SiMe_3)_2]_2$ 2b by an amine elimination reaction. Treatment of 2a or 2b with two equivalents of 1 in toluene at 60 °C yielded the corresponding $Zn(\pi)$ 3a or Cd(II) 3b complexes as yellow microcrystalline powders after filtration followed by evaporation of the solvent (Scheme 1). The complexes were purified from the reaction

Toluene

60 °C

3a: M = Zn

3b: M = Cd

Scheme 1 Synthesis of the Zn(II) 3a and Cd(II) 3b complexes.

Δr

M{N(SiMe₃)₂}₂

2a: M = Zn

2b: M = Cd



Scheme 2 Synthesis of the Cd(II) 5a and Cu(II) 5b complexes.

mixture by recrystallization from toluene-hexane through a diffusion method and the products were obtained in good yields.

Another approach involved the use of a base. The reaction of anhydrous $CdCl_2$ **4a** or $CuCl_2$ **4b** with two equivalents of **1** was carried out in methanol in presence of triethylamine at 25 °C, as shown in Scheme 2. The reaction mixtures were filtered and the residues were purified by recrystallization from a CHCl₃-MeOH mixture to give the corresponding yellow colored Cd(π) **5a** or brown colored Cu(π) **5b** complexes in moderate yields. However, a similar method with ZnCl₂ yielded a product which degraded during purification.

Spectroscopic study

Complexes 3a, 3b, 5a and 5b were characterized by IR and NMR (¹H, ¹³C) and their molecular structures were determined by single crystal X-ray diffraction techniques. The IR spectra of the complexes revealed stretching frequencies for the presence of coordinated (3a, 1564; 3b, 1567; 5a, 1570; 5b, 1564 cm⁻¹) as well as uncoordinated (3a, 1626; 3b, 1621; 5a, 1630; 5b, 1622 cm⁻¹) imino groups to the metal center. The ¹H NMR spectra exhibited only one set of peaks for -HC=N- (3a, 7.85; 3b, 7.91; 5a, 7.88 ppm) and the isopropyl groups (3a, 0.90 and 3.08-2.86; 3b, 0.89 and 3.08-2.86; 5a, 0.90 and 2.98-2.85 ppm) instead of separate peaks for coordinated and uncoordinated imino groups. This observation disclosed the symmetrical coordination of the ligand to the metals and the free rotation of the 2,6-diisopropylaniline moieties of the ligand in solution. The ¹³C NMR spectra also displayed one set of peaks for -HC=N- (3a, 158.8; 3b, 158.4; 5a, 158.6 ppm) and the isopropyl groups (3a, 3b and 5a, 23.8 and 27.9 ppm). This disparity, when compared to the solid state, confirmed a fluxional behaviour of the ligand in solution, as observed in previous reports.^{16b,17e}

Crystallographic characterization

Recently, the crystal structure of Zn(II) complex **3a** has been reported by Lewinski *et al.*, which was found as a byproduct during oxygenation reactions.²¹ The molecular structures of **3a** and **3b** are isostructural and the structure of **3b** is shown in Fig. 1. The metal center in complexes **3a** and **3b** adopts a four coordinate distorted tetrahedral geometry in which the



Fig. 1 ORTEP of the molecular structure of **3b**. Thermal ellipsoids are shown at 30% probability levels. The diisopropylphenyl moiety and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–N2 = 2.111(4), Cd1–N1 = 2.426(4), Cd1–N4 = 2.235(4), Cd1–N5 = 2.201(4), N2–Cd1–N1 = 73.23(14), N4–Cd1–N1 = 115.89(13), N5–Cd1–N4 = 77.89(14), N2–Cd1–N5 = 113.28(14), N2–Cd1–N4 = 162.53(15), N5–Cd1–N1 = 113.15(13), C10–C11–C12 = 131.4(5), C9–C8–C7 = 133.2(5), C7–N1–C6 = 119.5(4), C12–N3–C13 = 119.5(4), C39–C38–C37 = 130.1(4), C40–C41–C42 = 128.1(4), C42–N6–C43 = 118.9(4), C37–N4–C36 = 118.4(4).



Fig. 2 ORTEP of the molecular structure of **5b**. Thermal ellipsoids are shown at 30% probability levels. The diisopropylphenyl moiety and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–N2 = 2.013(3), Cu1–N4 = 1.941(3), Cu1–O1 = 2.035(3), Cu1–N1 = 2.023(3), N5–Cu1 = 2.738(3), N6–Cu1 = 2.738(3), N1–Cu1–N2 = 83.10(13), N4–Cu1–O1 = 92.37(13), N2–Cu1–N4 = 96.30(12), N1–Cu1–O1 = 88.23(13), N4–Cu1–N5 = 70.76, N4–Cu1–O1 = 88.47, N1–Cu1–N6 = 109.27, N2–Cu1–N6 = 94.38, N5–Cu1–N6 = 141.22, C5–C6–C7 = 132.4(4), C8–C9–C10 = 125.3(4), C10–N3–C11 = 126.6(4), C5–N1–C4 = 114.8(3), C31–C30–C29 = 130.6(3), C29–N5–C28 = 117.8(2), N1–Cu1–N4 = 179.40(13), N2–Cu1–O1 = 171.33(13).

 $(DIP_2pyr)^-$ ligand behaves as a bidentate rather than tridentate ligand, which coordinates through two nitrogen atoms (N, N') from each ligand. The smaller ionic radius of the metal center and steric bulkiness of the aryl substituents might influence the coordinated pattern of the ligand. One of the uncoordinated aryl imino moieties (C42–N6–C43) is rotated away from the metal center due to steric repulsion.^{16b,d}

The molecular structures of complexes 5a and 5b are isostructural and the structure of 5b is shown in Fig. 2, which revealed a six coordinate pseudo octahedral geometry about the metal center. The coordination sphere consists of three nitrogen atoms (N4, N5, N6) from one of the (DIP₂pyr)⁻

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Table 1 Crystal data and structural refinement details for 3b and 5b

-		
	3b	5 b
Formula	C ₆₀ H ₇₆ CdN ₆	C ₆₁ H ₈₀ CuN ₆ O
Fw	993.67	976.85
Space group	P2(1)/n	Pnma
Crystal system	Monoclinic	Orthorhombic
a (Å)	10.739	18.870
$b(\dot{A})$	20.900	21.946
c (Å)	23.604	13.737
α (°)	90	90
β (°)	97.12	90
γ (°)	90	90
$V(\mathbf{A})^3$	5257.0	5688.8
Z	4	4
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.255	1.141
$\mu (\text{mm}^{-1})$	0.459	0.428
Temp (K)	100(2)	100(2)
F(000)	2104	2100
θ range (°)	1.31-24.98	1.75 - 25.40
No. of refins	49 217	54 674
Unique	$9219 (R_{int} = 0.0788)$	$5392 (R_{int} = 0.0668)$
Goodness-of-fit on F^2	1.300	1.221
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0754,$	$R_1 = 0.0645,$
2 (73	$wR_2 = 0.1345$	$wR_2 = 0.1377$
R indices (all data)	$R_1 = 0.0887,$	$R_1 = 0.0717,$
	$wR_2 = 0.1392$	$wR_2 = 0.1418$
Largest diff. peak/ hole (e $Å^{-3}$)	1.138/-1.418	0.457/-0.486

ligands, two nitrogen atoms (N1, N2) from another (DIP₂pyr)⁻ ligand and one oxygen (O1) from a solvent methanol molecule. It is interesting to note that in both **5a** and **5b**, one of the (DIP₂pyr)⁻ ligands was coordinated symmetrically to the metal center (Cd(II) **5a**, Cu(II) **5b**) through a *N*,*N'*,*N''*-mode as a tridentate ligand. The apexes of the pseudo octahedral structure were occupied by both arms of the (DIP₂pyr)⁻ ligand coordinated weakly to the metal center (**5a**, N5-Cd1 = 2.716(3) and N6-Cd1 = 2.716(3) Å; **5b**, N5-Cu1 = 2.738(3) and N6-Cu1 = 2.738(3) Å). Another (DIP₂pyr)⁻ ligand coordinated asymmetrically to the metal center *via* one arm through a *N*,*N'*-mode as a bidentate ligand whereas the uncoordinated arm (C10-N3-C11) bent away from the metal center.

In the pseudo octahedral structure, the square planar arrangement around the metal center (N1, N2, N4, O1) was confirmed by the sum of the four angles (360°). The angles between the apexes (N6–M1–N5) are not linear and are about 135.1° (**5a**) and 141.2° (**5b**). These deviations in the angle are probably due to the constrained angle of the coordinated arms. The C27–C28–C29 angle in the coordinating arm of the ligand in **5a** is 132.4°. However, a similar C29–C30–C31 (130.6°) angle in **5b** was contracted by 2° when compared to free ligand (132.6°). Similarly, a subtle change in the Cu1–N5 and Cu1–N6 bond lengths and N6–Cu1–N5 bond angle was observed when compared to those in **5a**. The crystallographic data for complexes **3b** and **5b** are listed in Table 1.

It is worth noting the formation of two different Cd-ligand complexes when the Cd precursor was varied. When Cd- $[N(SiMe_3)_2]_2$ **2b** was used as the Cd source, it yielded a four coordinate complex with a tetrahedral structure (**3b**) whereas when CdCl₂ was used as a source of Cd, it yielded a six

coordinate complex with a pseudo octahedral structure (5a). Complexes **3b** and **5a** were crystallized in monoclinic and orthorhombic crystal systems respectively.

According to Scheme 2, the reaction mixture was purified by recrystallization from a $CHCl_3$ -MeOH mixture to yield **5a**. In order to confirm whether the product **5a** was formed during the reaction or in the crystallization process, a few controlled reactions were attempted, as shown in Scheme 3. On completion of the reaction after 24 h, the reaction mixture was filtered and the residue was dried completely to ensure the absence of solvent molecules. The residue was kept in toluene–hexane for recrystallization. The X-ray quality crystals were obtained after a week and were found to be **3b**.



Scheme 3 Transformation during the recrystallization process

Table 2Screening studies for the synthesis of 7^a

Furthermore, 3b was redissolved in a CHCl₃–MeOH mixture for recrystallization. The product was recrystallized to yield 5a.

From this study, it was found that **5a** was not formed during the reaction but was obtained through a transformation during the crystallization process. In the case of **3b** and **5a**, the formation of the product does not depend on the Cd source starting material but depends on the crystallization process. The same strategy was also attempted for copper but X-ray quality crystals were not formed in non-coordinating solvents.

Catalytic studies for cyclic carbonate synthesis

To check the catalytic activities of complexes **3a**, **3b**, **5a** and **5b** for the synthesis of cyclic carbonate from various mono- and disubstituted epoxides (**6**, **9**, and **12**), reactions were attempted at 1 atm of CO_2 under mild temperature and solvent free conditions using tetrabutylammonium bromide (TBAB) as a cocatalyst. First, we examined the reaction of 2-(phenoxymethyl) oxirane **6** with CO_2 (1 atm) using **3a** as a catalyst, according to the scheme shown in Table 2, and the results are illustrated in Table 2. The reaction conditions were optimized by varying the molar ratio, temperature and time at 1 atm of CO_2 (Table 2). 2-(Phenoxymethyl)oxirane **6** was efficiently converted to 4-(phenoxymethyl)-1,3-dioxolan-2-one **7** at 60 °C within 10 h



Entry	Catalyst (mol%)	TBAB (mol%)	$T(^{\circ}\mathrm{C})$	Time (h)	Conversion (%) by NMR		
					7	8	$\operatorname{Yield}^{b}(\%)$ of 7
1	3a (2.5)	_	30	24	_	_	_
2		5.0	30	24	4	_	_
3	_	5.0	60	10	21	_	_
4	_	5.0	105	4	45		_
5	3a (1.0)	1.0	30	24	31		24
6	3a (1.0)	1.0	60	10	51	5	43
7	3a (2.5)	1.0	60	10	63	6	56
8	3a (2.5)	2.5	60	10	72	8	65
9	3a (2.5)	5.0	30	24	49	_	40
10	3a (2.5)	5.0	60	10	84	8	76
11	3a (2.5)	5.0	60	20	60	35	53
12	3a (2.5)	5.0	105	2	59	34	52
13	3a (1.0)	2.5	60	10	73	11	66
14	3a (1.0)	5.0	60	10	78	12	70
15	3b (2.5)	5.0	30	24	18	—	10
16	3b (2.5)	5.0	60	10	51	14	44
17	3b (2.5)	5.0	105	2	55	39	48
18	5a (2.5)	5.0	30	24	14	—	—
19	5a (2.5)	5.0	60	10	48	10	38
20	5a (2.5)	5.0	105	2	49	36	42
21	5 b (2.5)	5.0	30	24	30	—	22
22	5 b (2.5)	5.0	60	10	73	—	67
23	5b (2.5)	5.0	60	20	96	—	91
24	5b (2.5)	5.0	105	2	78	_	70
25	5b (2.5)	5.0	105	4	94	—	90

^a Reaction condition: CO₂ (1 atm, balloon) and solvent free conditions. ^b Purification by flash column chromatography.



					Conversion (%) by NMR		
Entry	Catalyst	$T(^{\circ}C)$	Time (h)	Epoxide 9^{b} (%) by NMR	10	11	Yield ^c (%) of 10
1^d	3a	30	24	100	_	_	_
2^e	_	30	24	96	4	_	_
3^e	_	105	2	62	38		31
4^e	_	105	4	51	49		44
5	3a	30	24	86	14	_	9
6	3a	60	24	11	60	29	53
7	3a	105	2	5	86	9	80
8	3b	30	24	96	4		_
9	3b	60	24	60	22	18	15
10	3b	105	2	19	60	21	54
11	5a	30	24	96	4		_
12	5a	60	24	71	19	10	12
13	5a	105	2	32	58	10	50
14	5 b	30	24	88	12		_
15	5 b	60	24	52	48		41
16	5 b	105	2	25	75	_	70
17	5b	105	4	3	97	_	94

^{*a*} Reaction condition: epoxide **9** (1 mol), catalyst (2.5 mol%), TBAB (5 mol%) under CO₂ (1 atm, balloon). ^{*b*} Unreacted epoxide **9** [%] by NMR. ^{*c*} Purification by flash column chromatography. ^{*d*} Without TBAB. ^{*e*} Without catalyst.

using 2.5 mol% of **3a** and 5 mol% of TBAB under solvent free conditions (Table 2, entry 10). From screening tests (Table 2), better results were achieved with a combination of 2.5 mol% of the catalyst and 5.0 mol% of TBAB. This molar ratio was fixed for further investigations with other catalysts.

When this reaction was examined with catalysts 3b, 5a or 5b (Table 2, entries 15–25), it was observed that the conversion proceeded quickly in the presence of 3a. However, in case of 5b (2.5 mol%), the reaction was neat and cyclic carbonate 7 was obtained selectively (Table 2, entries 21-25) without any diol formation (vide infra). The maximum yield was attained with an extended reaction time and/or with an increased reaction temperature. The reaction was further established for 2-phenyloxirane 9, according to the scheme shown in Table 3. The reaction conditions were investigated with 3a, 3b, 5a and 5b and the results are displayed in Table 3 (entries 5-17). As observed in the previous case, 3a showed a better catalytic activity and yielded (80 %) the corresponding cyclic carbonate 4-phenyl-1,3-dioxolan-2-one 10 at 105 °C within 2 h at 1 atm of CO_2 (Table 3, entry 7). When 5b was used as the catalyst, the maximum yield (94%) of cyclic carbonate 10 was selectively obtained at 105 °C within 4 h (Table 3, entry 17).

In order to confirm the catalytic activities of our catalysts, eight controlled reactions (Table 2 and 3, entries 1–4) at 30 °C, 60 °C and 105 °C were carried out. Cycloaddition reactions did not proceed when only catalyst **3a** was present (Table 2 and 3, entry 1). On the other hand, in the absence of **3a**, TBAB (5 mol%)

alone showed a low catalytic activity (Table 2 and 3, entries 2–4). However, the combination of a catalyst **3a** and TBAB exhibited a high catalytic activity which highlights the necessity for the coexistence of both to effectively catalyze these reactions.

Since **3a** and **5b** displayed better catalytic activities, the scope of these catalysts was further explored for the cycloaddition of CO_2 with different monosubstituted aliphatic terminal epoxides **12a–c** at 1 atm of CO_2 . The results are shown in Table 4 (entries A1–C2). The displayed reaction conditions were optimized for the synthesis of the corresponding cyclic carbonate **13**. All these epoxides selectively yielded cyclic carbonate **13** in the presence of **3a** or **5b** and TBAB in good yields. The reaction of 2-methyloxirane **12a** with CO_2 in the presence of **3a** or **5b** and TBAB yielded 4-methyl-1,3-dioxolan-2-one **13a** at 10 °C in a moderate yield (Table 4, entries A1 and A2).

The catalytic activities of **3a** and **5b** were investigated with disubstituted epoxides **12d–f**. Disubstituted terminal and internal epoxides were successfully converted to the corresponding cyclic carbonates **13d–f** at 1 atm of CO₂. The reaction conditions are detailed in Table 4 (entries D1–F2). It was observed that *cis*-2,3-dimethyloxirane **12e** was efficiently converted to *cis*-4,5-dimethyl-1,3-dioxolan-2-one **13e** with good selectivity (ratio of *cis*:*trans*; 95:5) (Table 4, entries E1 and E2).

It was also interesting to note that *cis*-cyclohexene oxide (CHO) **12f** yielded *cis*-cyclohexene carbonate (CHC) **13f** (ratio

Table 4Scope of catalysts 3a and 5b^a



^{*a*} Reaction condition: epoxide (1 mol), catalyst (2.5 mol%), TBAB (5.0 mol%) under CO_2 (1 atm, balloon). ^{*b*} Purification by flash column chromatography. ^{*c*} Moles of epoxide consumed per mole of catalyst. ^{*d*} Moles of epoxide consumed per mole of catalyst per hour. ^{*e*} *cis* : *trans* ratio (95 : 5), diastereomers were separated. ^{*f*} *cis* : *trans* ratio (96 : 4), diastereomers were separated.

of cis: trans; 96: 4) (Table 4, entry F1 and F2). In the course of the fixation of CO_2 to the epoxide, the formation of cis-CHC from cis-CHO has rarely been reported.^{15,22} In the presence of **3a** or **5b**, even at a moderate temperature, cis-CHO yielded the corresponding cis-CHC with good selectivity. One atmospheric pressure of CO₂, a moderate reaction temperature and co-catalyst loading (5.0 mol%) could have not favored *trans*-cyclohexene carbonate formation (4%).^{15,22} Catalysts **3a** and **5b** proved to be highly active and also selective for the conversion of disubstituted epoxides under mild conditions at 1 atm of CO₂.

In our work, only a few reactions (12 entries out of 48 entries; except the control reactions) required high temperatures while the majority of the reactions proceeded within a temperature range of 30–60 °C. Though a little excess of catalyst/co-catalyst loadings (2.5 and 5.0 mol%, respectively) was required, most of the reactions were selective and proceeded at a lower temperature at one atmosphere of CO_2 . It should be mentioned that there are some literature reports wherein one equivalent of ammonium salts and/or a high pressure of CO_2

was required.⁹⁻¹³ A bimetallic Fe(m) complex¹⁵ was reported to be active for both mono- and disubstituted epoxides at an atmospheric pressure of CO₂, while a bimetallic Al(m) salen complex^{14b} was active for only monosubstituted epoxides. However, the monometallic complexes described here are highly active for both substituted terminal and internal epoxides under mild conditions. It is interesting that all these cycloaddition reactions were carried out in a normal schlenk tube and did not require an autoclave. These facts confirm the usefulness of our catalyst in these conversion reactions. Hence, the present work adds significant improvement to the CO₂ fixation reactions.

During these reactions, glycol formation was also observed in some cases (18 out of 48 entries from Tables 2–4) along with cyclic carbonate in the presence of catalysts 3a, 3b or 5a, especially at higher temperatures even at strictly anhydrous conditions. The reaction mixtures were extracted with CHCl₃ from a water workup and were purified by column chromatography to separate the cyclic carbonates and diols. However,



 Table 5
 Progress of diol 11 formation^a

Entry	Time	Unreacted epoxide 9 (%) by NMR	Conversion (%) by NMR		
			10	11	of 11
1	5 min	94	6	_	_
2	1 h	26	67	5	_
3	2 h	5	86	9	5
4	5 h	_	37	63	56
5	10 h	—	—	99	95

^{*a*} Reaction condition: epoxide **9** (1 mol), catalyst **3a** (2.5 mol%), TBAB (5 mol%) under CO_2 (1 atm, balloon) at 105 °C. ^{*b*} Purification by flash column chromatography.

a similar diol formation was not observed in the presence of catalyst **5b** (Table 2, entries 21–25; Table 3, entries 14–17; Table 4, entries A1–F2).

To further probe the formation of the diol, a set of reactions were carried out with 2-phenyloxirane 9 in the presence of catalyst 3a and TBAB under 1 atm of CO₂ at 105 °C for 5 min, 1 h, 2 h, 5 h and 10 h as independent experiments. The reaction progress was monitored using ¹H NMR spectra. The spectra are shown in Fig. 3 and the results are illustrated in Table 5. When the reaction was stopped at 5 min, cyclic carbonate formation was just commencing and no diol formation was observed. When the reaction was stopped at 1 h, 67% of cyclic carbonate 10 was formed from 2-phenyloxirane 9. In the 2 h reaction, 2-phenyloxirane 9 was almost consumed to yield cyclic carbonate 10 and 5% of diol 11 was isolated. When the reaction was performed for 5 h at 105 °C, cyclic carbonate 10 gradually underwent degradation to yield diol 11 (56% isolated yield). When the reaction was prolonged to 10 h, cyclic carbonate 10 was completely converted to diol 11. These observations show that the diol formation was enhanced with an increase in temperature and time under these conditions. From this monitoring, it was found that diol formation was not due to epoxide cleavage but was a degradation product of cyclic carbonate. The majority of our reactions (30 out of 48 entries from Table 2, 3 and 4) were selective in their activity for cyclic



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Fig. 4 Possible cyclic carbonate formation mechanism

carbonate formation. Specifically, in presence of catalyst **5b**, all the reactions were selective.

The mechanism for the conversion of epoxides to cyclic carbonate in the presence of a bimetallic Al(III) salen complex/ TBAB was previously thoroughly examined.^{14d} The decomposition of the tetraalkylammonium salts and the formation of amine carbamate salts are also well known in the literature.^{1c,7g,14d} Though we could not isolate any intermediate species, based on earlier reports we propose a mechanism for cyclic carbonate formation in the presence of our catalyst system as follows. First, the epoxide could have coordinated to the Lewis acid 3a to form 1 which underwent epoxide ring opening by bromide ions to generate 2. Then, the activated form of CO2 3 was inserted into the Zn-O bond, generating species 4 followed by ring closure by backbiting to give cyclic carbonate and regenerating 3a and TBAB, as shown in Fig. 4. However, to confirm the actual mechanism, further investigations are required.

To check the catalyst reusability, a 2-methyloxirane **12a** system was chosen. After the reaction (Table 4, entry A1), 4-methyl-1,3-dioxolan-2-one **13a** was distilled from the reaction mixture. 2-methyloxirane **12a** was again added to the residue and the process was repeated 6 more times, whereupon the yield started to decrease from 67% to 30%. On adding TBAB (5 mol%) to the system, the yield was restored and the process was repeated 4 more times.

Conclusions

In conclusion, $Zn(DIP_2pyr)_2$ **3a**, $Cd(DIP_2pyr)_2$ **3b**, $Cd(DIP_2pyr)_2$ (CH₃OH) **5a** and Cu(DIP₂pyr)₂(CH₃OH) **5b** were successfully synthesized and were characterized by standard techniques. Two types of structures, **3b** and **5a**, were found for the same Cd(II) metal and (DIP₂pyr)H ligand **1** and the transformation of **3b** to **5a** upon recrystallization was studied. All the monometallic complexes described here were found to be efficient for CO_2 fixation under one atmosphere of pressure at a mild temperature conditions. Our catalyst systems were highly effective for the conversion of monosubstituted terminal epoxides, disubstituted terminal and internal epoxides. The corresponding cyclic carbonates were obtained with good to high yields. Among these complexes, catalysts **3a** and **5b** were found to be versatile.

The epoxide to cyclic carbonate conversion proceeded quickly in the presence of **3a**, whereas in case of **5b**, the reaction was neat and the cyclic carbonate was obtained selectively without any diol formation. Moreover, the catalysts were also selective for the conversion of *cis*-CHO to *cis*-CHC. From time dependant ¹H NMR spectral studies, the diol formation was concluded to be a degradation product of the cyclic carbonate. Catalyst usability studies showed that the catalyst was highly stable and can be recycled 10 times.

Experimental

Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard schlenk techniques under dry nitrogen. All solvents which were used under an inert atmosphere were thoroughly deoxygenated using a freeze-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium benzophenone ketyl (diethyl ether, toluene), Mg-(OMe)₂ (methanol), P₂O₅ (triethylamine), CaCl₂ (chloroform). The compounds, 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H,^{17a,23} Zn[N(SiMe₃)₂]₂²⁴ and Cd- $[N(SiMe_3)_2]_2^{24}$ were synthesized according to the literature procedures. Epoxides 6, 9 and 12a-f (Aldrich) were dried prior to use by refluxing with CaH₂ for 12 h followed by distillation. Tetrabutylammonium bromide (Merck) was dried at 50 °C for 4 h under vacuum.

The structures of all the products were confirmed by IR, ¹H, ¹³C NMR and mass spectroscopy. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrometer using KBr pellets. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. The data were reported in parts per million (δ) using CDCl₃ as the solvent with a TMS internal standard or residual solvent peak as the reference for the ¹H and ¹³C (100 MHz) NMR. Mass spectra were obtained from a Shimadzu-LCMS-2010 at an ionizing voltage of 70 eV using the EI technique. Elemental analysis was carried out using a Thermo Finnigan Flash EA 1112 analyzer. Single crystal X-ray data collection was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo-K α) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-9725 and refined using SHELXL-97.²⁶ All hydrogen atoms were refined anisotropically.

Experimental procedure

General procedure for the synthesis of metal complexes 3a and 3b. A solution of 2,5-bis{*N*-(2,6-diisopropylphenyl)imino methyl}pyrrole 1 (2.4 mmol) in toluene (4 mL) was added to a solution of $M[N(SiMe_3)_2]_2$ (1.2 mmol) in toluene (4 mL) at room temperature. The reaction mixture was stirred for 48 h at 60 °C. The reaction mixture was filtered off and the residue was washed with hexane (3 × 10 ml). The solvent was evaporated to give a yellow powder which was recrystallized from a mixture of toluene–hexane to yield pure crystals for X-ray analysis after a week.

Zn(*DIP*₂*pyr*)₂ (*3a*). The compound was prepared from Zn-[N(SiMe₃)₂]₂ (0.46 g, 1.2 mmol) using the general procedure to yield **3a** (0.74 g, 75%). M.p. 214 °C (toluene–hexane); IR (KBr pellet, ν_{max}/cm^{-1}): 1626, 1564, 1325, 1167, 1099, 1049, 858, 688. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (d, *J* = 6.4 Hz, 48H, CH (*CH*₃)), 3.08–2.86 (m, 8H, *CH*(CH₃)), 6.97 (s, 4H, 3, 4-pyr), 7.05 (s, 12H, Ph), 7.85 (s, 4H, *C*=*NH*). ¹³C NMR (100 MHz, CDCl₃): δ 23.8, 27.9, 118.9, 123.4, 125.1, 140.0, 141.8, 146.6, 158.8; Anal. Calcd for C₆₀H₇₆N₆Zn: C, 76.12; H, 8.09; N, 8.88. Found: C, 76.32; H, 7.96; N, 8.75.

Cd(*DIP*₂*pyr*)₂ (*3b*). The compound was prepared from Cd-[N(SiMe₃)₂]₂ (0.55 g, 1.2 mmol) using the general procedure to yield **3b** (0.84 g, 71%). M.p. 236 °C (toluene–hexane); IR (KBr pellet, ν_{max}/cm^{-1}): 1621, 1567, 1353, 1162, 1096, 1036, 855. ¹H NMR (400 MHz, CDCl₃): δ 0.89 (d, *J* = 6.8 Hz, 48H, CH(*CH*₃)), 3.08–2.86 (m, 8H, C*H*(CH₃)), 6.90 (s, 4H, 3, 4-pyr), 7.05 (s, 12H, Ph), 7.91 (s, 4H, C=N*H*). ¹³C NMR (100 MHz, CDCl₃): δ 23.8, 27.9, 119.1, 123.3, 124.9, 139.8, 141.0, 147.2, 158.4. Anal. Calcd for C₆₀H₇₆N₆Cd: C, 72.52; H, 7.71; N, 8.46. Found: C, 72.45; H, 7.78; N, 8.36.

General procedure for the synthesis of metal complexes 5a and 5b. Triethylamine (3.0 mmol) was added to a solution of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole 1 (0.88 g, 2 mmol) in methanol (20 mL), and heated to 50 °C with stirring. To this clear solution, a solution of MCl₂ (1.0 mmol) in methanol (5 mL) was added. The reaction mixture was cooled to room temperature and stirred for 24 h. The reaction mixture was filtered off and the residue was washed with methanol (30 ml). The residue was recrystallized from a mixture of CHCl₃-MeOH to yield pure crystals for X-ray analysis after a week.

Cd(*DIP*₂*pyr*)₂(*MeOH*) (*5a*). The compound was prepared from anhydrous CdCl₂ (0.18 g, 1.0 mmol) using the general procedure to yield **5a** (0.67 g, 65%). The residue was recrystallized from a mixture of CHCl₃–MeOH–acetone to yield pure crystals for X-ray analysis after a week. M.p. 230 °C (CHCl₃–MeOH– acetone); IR (KBr pellet, ν_{max}/cm^{-1}): 1711, 1695, 1630, 1570, 1352, 1161, 1097, 1037, 842. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (d, *J* = 6.8 Hz, 48H, CH(CH₃)), 2.18 (s, 6H, CH₃COCH₃), 2.98–2.85 (m, 8H, CH(CH₃)), 3.14 (s, 3H, CH₃OH), 6.89 (s, 4H, 3, 4-pyr), 7.06 (s, 12H, Ph), 7.88 (s, 4H, C=NH). ¹³C NMR (100 MHz, CDCl₃): δ 2.3.8, 27.9, 30.95, 50.83, 119.1, 123.3, 124.9, 139.9, 141.0, 147.3, 158.6. Anal. Calcd for C₆₁H₈₀CdN₆O: C, 71.41; H, 7.87; N, 8.20. Found: C, 71.55; H, 7.81; N, 8.15. $Cu(DIP_2pyr)_2(MeOH)$ (5b). The compound was prepared from anhydrous CuCl₂ (0.13 g, 1.0 mmol) using the general procedure to yield 5b (0.76 g, 78%). M.p. 202 °C (CHCl₃/MeOH); IR (KBr pellet, ν_{max}/cm^{-1}): 1622, 1564, 1342, 1170, 1099, 1043, 856. Anal. Calcd for C₆₁H₈₀CuN₆O: C, 75.08; H, 8.25; N, 8.61. Found: C, 75.22; H, 8.09; N, 8.53.

General procedure for the synthesis of cyclic carbonate. A dry, pre-evacuated schlenk tube was filled with CO_2 . The epoxide (1 mol), catalyst (2.5 mol%) and tetrabutylammonium bromide (5.0 mol%) was then added and a CO_2 balloon was connected. The reaction mixture was stirred at the required temperature under CO_2 (balloon). After the reaction time, water was poured into the reaction mixture and extracted with chloroform. The organic layer was separated and evaporated to give the crude product which was purified by flash column chromatography to yield the cyclic carbonate.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (7). ¹H NMR (400 MHz, CDCl₃): δ 4.14 (dd, J = 10.6 and 3.2 Hz, 1H, PhOCH₂), 4.24 (dd, J = 10.6 and 3.9 Hz, 1H, PhOCH₂), 4.57–4.50 (m, 1H, OCH₂), 4.66–4.58 (m, 1H, OCH₂), 5.00–4.98 (m, 1H, CH₂), 6.91 (d, J = 7.84 Hz, 2H, C₆H₅), 7.02 (t, J = 7.36 Hz, 1H, C₆H₅), 7.31 (t, J = 8.36 Hz, 2H, C₆H₅). ¹³C NMR (100 MHz, CDCl₃): δ 66.3, 66.9, 74.1, 114.6, 122.0, 129.7, 154.7, 157.8. m/z (EI) 194 (M⁺, 100).

3-Phenoxypropane-1,2-diol (8). ¹H NMR (400 MHz, CDCl₃): δ 2.54 (br s, 2H, OH), 3.80–3.67 (m, 2H, OCH₂), 4.09–3.99 (m, 2H, C₆H₅OCH₂), 4.26–4.16 (m, 1H, CHO), 6.94–6.86 (m, 2H, C₆H₅), 6.97 (t, J = 7.32 Hz, 1H, C₆H₅), 7.33–7.27 (m, 2H, C₆H₅). ¹³C NMR (100 MHz, CDCl₃): δ 68.8, 69.2, 72.6, 114.6, 121.2, 129.5, 158.5. m/z (EI) 168 (M⁺, 100), 125 (20). HRMS calcd for C₉H₁₂O₃ [M + Na]⁺ 191.0684, found 191.0684.

4-Phenyl-1,3-dioxolan-2-one (10). ¹H NMR (400 MHz, CDCl₃): δ 4.35 (t, J = 8.0 Hz, 1H, OCH₂), 4.81 (t, J = 8.0 Hz, 1H, OCH₂), 5.68 (t, J = 8.0 Hz, 1H, PhCHO), 7.48–7.39 (m, 3H, C₆H₅), 7.39–7.32 (m, 2H, C₆H₅). ¹³C NMR (100 MHz, CDCl₃): δ 71.2, 78.0, 125.9, 129.3, 129.8, 135.8, 154.9. m/z (EI) 164 (M⁺, 100), 139 (10).

1-Phenylethane-1,2-diol (11). ¹H NMR (400 MHz, CDCl₃): δ 2.31 (br s, 2H, OH), 3.66–3.54 (m, 1H, OCH₂), 3.79–3.64 (m, 1H, OCH₂), 5.00–4.92 (m, 1H, CHO), 7.34–7.29 (m, 1H, C₆H₅), 7.43–7.34 (m, 4H, C₆H₅). ¹³C NMR (100 MHz, CDCl₃): δ 68.1, 74.7, 126.0, 128.0, 128.5, 140.5. *m*/*z* (EI) 138 (M⁺, 100), 125 (20).

4-Methyl-1,3-dioxolan-2-one (13a). ¹H NMR (400 MHz, CDCl₃): δ 1.45 (d, J = 6.3 Hz, 3H, CH₃), 3.99 (dd, J = 8.4 and 7.2 Hz, 1H, OCH₂), 4.52 (dd, J = 8.3 and 7.2 Hz, 1H, OCH₂), 4.88–4.78 (m, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 19.4, 70.7, 73.6, 155.1. HRMS calcd for C₄H₆O₃ [M + Na]⁺ 125.0215, found 125.0215.

4-*Ethyl*-1,3-*dioxolan*-2-one (**13b**). ¹H NMR (400 MHz, CDCl₃): δ 1.04 (t, J = 7.5 Hz, 3H, CH₃), 1.91–1.72 (m, 2H, CH₂), 4.09 (dd, J = 8.3 and 7.1 Hz, 1H, OCH₂), 4.53 (t, J = 8.2 Hz, 1H, OCH₂), 4.70–4.63 (m, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 8.5, 27.0, 69.0, 78.0, 155.1. HRMS calcd for C₅H₈O₃ [M + Na]⁺ 139.0371, found 139.0395.

4-Butyl-1,3-dioxolan-2-one (13c). ¹H NMR (400 MHz, CDCl₃): δ 0.92 (t, J = 6.6 Hz, 3H, CH₃), 1.53–1.29 (m, 4H, CH₂), 1.74–1.63 (m, 1H, CH₂), 1.89–1.75 (m, 1H, CH₂), 4.07 (t, J = 7.6 Hz, 1H, OCH₂), 4.52 (t, J = 8.0 Hz, 1H, OCH₂), 4.76–4.66 (m, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 22.2, 26.4, 33.5, 69.4, 77.1, 155.1. HRMS calcd for C₇H₁₂O₃ [M + Na] ⁺ 167.0684, found 167.0696.

4,4-Dimethyl-1,3-dioxolan-2-one (13d). ¹H NMR (400 MHz, CDCl₃): δ 1.52 (s, 6H, CH₃), 4.15 (s, 2H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 26.3, 74.0, 75.8, 155.1. HRMS calcd for C₅H₈O₃ [M + Na]⁺ 139.0371, found 139.0395.

cis-4,5-Dimethyl-1,3-dioxolan-2-one (**13e**). ¹H NMR (400 MHz, CDCl₃): δ 1.36 (d, J = 6.4 Hz, 6H, CH₃), 4.90–4.70 (m, 2H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 76.4, 155.1. HRMS calcd for C₅H₈O₃ [M + Na]⁺ 139.0371, found 139.0395.

cis-1,2-Cyclohexylene carbonate (13f). ¹H NMR (400 MHz, CDCl₃): δ 1.47–1.36 (m, 1H, CH₂), 1.68–1.56 (m, 1H, CH₂), 1.94–1.84 (m, 2H, CH₂), 4.71–4.64 (m, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 19.2, 26.8, 75.7, 155.4. HRMS calcd for C₇H₁₀O₃ [M + Na] ⁺ 165.0528, found 165.0551.

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