



REGULAR ARTICLE

Cobalt (II) complex catalyzed polymerization of lactide and coupling of CO₂ and styrene oxide into cyclic styrene carbonate

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Abstract. In the present study, the cobalt (II) complex [Co-HMBED] has been prepared and characterized by spectrochemical techniques, which confirmed its square planar structure. The catalytic activity of the cobalt complex was evaluated towards solvent-free conversion of CO₂ and styrene oxide into cyclic styrene carbonate and polymerization of lactide.

Keywords. CO₂; Styrene oxide; cyclic carbonate; PLA; Schiff base; Cobalt complex.

1. Introduction

Since the early 21st century, modern researchers are searching for bio-renewable resources for the biodegradable, biocompatible and bioassimilable material. Poly(lactic acid)(PLA) is such a polymer,¹⁻³ on degradation it produces environmentally assimilable compounds such as H₂O and CO₂.⁴⁻⁷ PLA is used in biomedical application.^{8,9} And also, CO₂ is an easily available, economical, nonflammable and non-hazardous renewable carbon resource, available as an attractive raw material for the production of cyclic carbonate.¹⁰ These cyclic carbonates have extensive application as electrolytes,¹¹ aprotic solvents,¹² synthesis of polycarbonates,¹³ pharmaceutical intermediate,¹⁴ synthesis of urea derivative,¹⁵ biodegradable materials,¹⁶ etc.

An ideal industrial process should employ non-cytotoxic metals, as complete removal of metal never happens. Therefore, metals having no negative effects on living beings must be taken into consideration. However, although different transition metal complexes were used for the synthesis of PLA¹⁷⁻¹⁹ and cyclic carbonates.²⁰⁻²⁶ Nowadays, cobalt complexes with moderate lewis acidity property have given emphasis for in-depth investigation.

Furthermore, FDA has approved the CO₂ - based polymer such as poly (styrene carbonate), which is

formed from the raw material cyclic styrene carbonate and production of PLA. Presently, we are engaged in synthesizing Schiff base copper complexes,^{27,28} and nickel complexes^{29,30} which efficiently catalyzed the polymerization of lactide. Very few literatures say about the activity of cobalt metal catalysts for lactide polymerization and cyclic carbonate formation. Thus, the present paper reports the catalytic activity of cobalt complexes of HMBED (N,N'-bis (hydroxymethoxybenzaldehyde) ethylenediamine) towards ROP of L-lactide and solventless conversion of CO₂ and styrene oxide into cyclic styrene carbonate. Finally, based on experimental results, a proposed mechanism has been given for lactide polymerization.

2. Experimental

2.1 Materials and characterization

All reactions were executed in dry N₂ ambiance by the use of glove box and Schlenk line. Sodium benzophenone and P₂O₅ were used for drying and distillation of toluene and dichloromethane, respectively. L-Lactide was supplied by Sigma-Aldrich, anhydrous cobalt chloride and ethylenediamine (ED), hydroxymethoxy benzaldehyde (HMB), benzyl alcohol (BnOH), dimethylaminopyridene (DMAP), pyridine (Py),

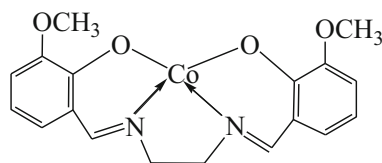
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imidazole (Im), triethylamine (Et₃N), triphenylphosphine (Ph₃P) and styrene oxide were purchased from E-Merck, India and carbon dioxide with the purity of 99.9% was obtained from Kasliwal Brothers supplier, Raipur India.

¹H NMR were recorded on a FT-NMR-Brucker- 400 spectrometer by using DMSO-d₆ as a solvent and tetramethylsilane (TMS) as an internal reference. IR spectra was recorded by Perkin-Elmer 1600 FTIR Spectrophotometer and UV-Vis spectra in the solution phase was obtained by Shimadzu 1601 PC UV-Vis Spectrophotometer. Thermo Gravimetric Analysis was observed by Perkin Elmer Pyris Diamond Thermal Analyzer at a heating rate of 10 °C min⁻¹. Perkin-Elmer 3100 Atomic Absorption Spectrometer was used for AAS at λ_{max} of cobalt ion. The composition of compounds can be determined by Haraeus Carlo Ebra 1108 Elemental Analyzer. Vibrating Sample Magnetometer-155 was used to determine the magnetic moment (μ_{eff}) of cobalt complex. The molecular weight of samples can be determined by Merck VAPRO 5600, Germany, Vapor-pressure Osmometer. The high-pressure reactor BERGHOF, Germany was used for the catalytic part. The GPC by Waters was used to determine the molecular weight and PDI of PLA.

Co-HMBED complex was synthesized by the method from literature.^{31,32} The yellow-coloured ligand (Yield: 92.6 wt%) (Table S1, Figure S1, Figure S3, Supplementary Information)³³ were refluxed with cobalt chloride (1:1 equivalent) at 60 °C for 5 h to produce the cobalt complex Co-HMBED (Table S1, Figure S2, Supplementary Information). It has been observed from thermogravimetric analysis that, Co-HMBED is more stable than Schiff base. The Schiff base has shown a weightloss of 50.4 wt% and cobalt complex showed 38.6 wt% at 500 °C, indicating more stability of Co-HMBED complex (Figure S4, Supplementary Information).³⁴ The molecular formula of Co-HMBED complex corresponds to C₁₈H₁₈CoN₂O₄ (Anal calcd. for Co-HMBED: C: 56.11; N: 7.27; H: 4.71% Found: C: 56.78; N: 7.93; H: 5.11%). The experimental M_w of Co-HMBED was 386.17 g mol⁻¹ (Calcd 385.28 g mol⁻¹). The magnetic moment of Co-HMBED is 1.91 BM, which confirmed its paramagnetic behavior and square planar geometry with dsp² hybridization.



Co - HMBED (Square planar)

2.2 Co-HMBED catalyzed ROP of lactide

The PLA-50 ([LA]/[Co] = 50) has been synthesized. Co-HMBED (0.077 g, 0.2 mM) in CH₂Cl₂ (20 mL) was mixed to L-lactide (1.44 g, 10 mM) solution under rapid stirring, with 1 equivalent of BnOH. After 25 h, reaction was ceased

and volatile materials were removed under vacuum. The white precipitate PLA was rinsed with n-hexane two times and was desiccated to produce a crystalline white solid.

2.3 Co-HMBED catalyzed coupling of CO₂ and styrene oxide

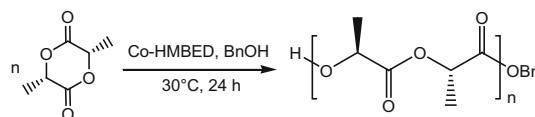
Catalytic experiments have been done in a high-pressure reactor (BERGHOF, Germany) of 100 mL PTFE (polytetrafluoroethylene) crucible attached with a magnetic stirrer. Before ejection of the reaction mixture, the reaction vessel was cleaned and dried. The reaction vessel was charged with Co-HMBED (0.386 g, 1 mM), styrene oxide (1000 mM) and DMAP (0.244 g, 2 mM) without additional organic solvent. The reactor was placed under a fixed pressure of CO₂. Then the reactor containing mixture was heated to requisite temperature with constant stirring. After completion, the crude mixture was collected by adding CH₂Cl₂ and water to separate using separating funnel, then the desired cyclic carbonate was cleaned by adding anhydrous Na₂SO₄. The cyclic carbonate was obtained from the mixture by vacuum distillation. The cyclic carbonate was identified by ¹H-NMR spectrum.

3. Results and Discussion

3.1 Co-HMBED catalyzed ROP of lactide

From literature,^{17,18} it was predictable that Co-HMBED complex was an effective catalyst towards L-lactide polymerization in the presence of benzyl alcohol (BnOH) (Scheme 1). The results of the ROP of lactide were given in Tables 1 and 2. Moderate to high molecular weight of PLA have been found by all the runs. The amount of BnOH affects significantly on ROP of lactide (Table 2, entry 6 & 7).

A systematic study on ROP of lactide by Co-HMBED complex was carried out at 30 °C with [LA]₀/[BnOH] = 150 (Table 1). It was found that Co-HMBED complex is highly reactive in CH₂Cl₂ than other solvents. This variation in catalytic activity may be attributed to the solubility of Co-HMBED complex. The complex is more soluble in CH₂Cl₂ than toluene. But, the ROP rate is low in THF due to formation of dative bond with cobalt complex.



Scheme 1. Polymerization of lactide [Co-HMBED]/[Benzyl alcohol] = 1/1.

Table 1. ROP of lactide by Co-HMBED.

Sl. No.	Solvent	Conversion (%) = $[(W_{\text{polymer}}/W_{\text{monomer}}) \times 100]$	M_n (Theory) (g mol^{-1}) = $[(\text{[Lactide]}_0/\text{[Benzyl alcohol]}) \times 144.13 \times \text{conversion \%} + 108.14]$	M_n (VPO) ^a (g mol^{-1})	M_n (GPC) ^b	PDI ^b
1	CH ₂ Cl ₂	84.2	18300	19300	21200	1.08
2	Toluene	72.9	15800	12200	13400	1.06
3	THF	53.5	11600	8300	10900	1.11

[Lactide]₀ = 20 mM, at 30 °C, Time 24 h, [Lactide]₀/[Co-HMBED]/[Benzyl alcohol] = 150/1/1.

^a M_n by Vapour Pressure Osmometer³⁴.

^bDetermined by 0.58 times of GPC values and calibrated by polystyrene.

Table 2. ROP of lactide by Co-HMBED in presence of benzyl alcohol.

Sl. No.	[Lactide] ₀ /[Co-HMBED]/[Benzyl alcohol]	Time (h)	Conversion(%) = $[(W_{\text{polymer}}/W_{\text{monomer}}) \times 100]$	M_n (Theory) (g mol^{-1}) = $[(\text{[Lactide]}_0/\text{[Benzyl alcohol]}) \times 144.13 \times \text{conversion \%} + 108.14]$	M_n (VPO) ^a (g mol^{-1})	M_n (GPC) ^b	PDI ^b
1	100:1:0	24	< 5	– ^c	– ^c	– ^c	– ^c
2	50:1:1	24	74.1	5400	7200	8000	1.09
3	100:1:1	24	79.3	11500	14100	15700	1.12
4	150:1:1	24	84.2	18300	19300	21200	1.08
5	200:1:1	24	86.5	25000	25800	27100	1.13
6	100:1:2	20	80.3	5900	7600	8200	1.08
7	100:1:4	15	87.7	3300	4000	5000	1.13

[LA]₀ = 20 mM, at 30 °C, solvent CH₂Cl₂.

^a M_n by Vapour Pressure Osmometer³⁴.

^bDetermined by 0.58 times of GPC values and calibrated by polystyrene.

^cData not found.

Several structure-activity relationships may be determined from the data given in Table 2. It has been found that Co-HMBED catalyst is very efficient towards the polymerization of lactide. It has also been observed from Table 2 (entry 2, 3, 4 & 5) that ROP of lactide follows ‘living polymerization’ with immortal behavior and narrow molecular weight distribution varying from 1.08 to 1.13. The linear plot M_n Vs [Lactide]₀/[BnOH]₀ ratio (Figure 1) also emphasizes the living character. Assessment of two or four equivalent ratios of BnOH (Table 2, entry 6 & 7) has provided evidence for ‘immortal’ character. In the absence of BnOH, the conversion is almost negligible (< 5%) (Table 2, entry 1), whereas its presence changes the activity of Co-HMBED significantly. With an increase in the concentration of BnOH, conversion increases in less time (Table 2, entry 6 & 7), as BnOH actively participate in the reaction.

¹H NMR (Figure 2) confirmed the mechanism. PLA-50, represents [LA]₀/[BnOH] ratio is 50. From its ¹H NMR spectrum, it is evident that on one end benzyl group is attached with polymer chains and on the other

side, a hydroxyl group is present. From ¹H NMR, it was found that the ratio of H_e and H_b is 5:1, which indicates that reaction proceeds through the insertion of benzyl alkoxy group to lactide.^{36,37} Based on literature report,³⁵ PLA with $M_n = 2200\text{--}6500 \text{ g mol}^{-1}$, has been produced by the use of different copper complexes at 160 °C, which suggests that the present result is much superior (Table 2).

ROP of *L*-lactide with Co-HMBED complex (Figure 3) and benzyl alcohol {[Co-HMBED]/[LA]₀/[BnOH] = 1/100/1}, has been carried out to investigate the kinetic behavior. Figure 3 shows a linear graph among $\ln[M]_0/[M]_t$ vs time, indicating first-order kinetics with the apparent rate constant (k_{app}) was found to be 0.02022 h^{-1} .

3.2 Co-HMBED catalyzed for the formation of cyclic styrene carbonate

From literature, it was predictable that Co-HMBED complex was an efficient catalyst for the conversion of

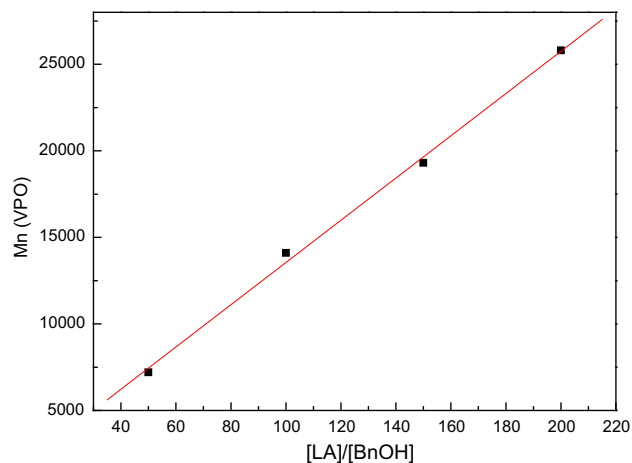


Figure 1. *L*-lactide polymerization by Co-HMBED complex.

CO₂ and epoxide to produce cyclic carbonate. To test the feasibility of our proposed approach, Co-HMBED complex was explored in the reaction of styrene oxide with CO₂ to form cyclic styrene carbonate (Scheme 2).

A systematic study on the formation of cyclic styrene carbonates by using Co-HMBED complex was carried out at 100 °C with [styrene oxide]/[Co-

HMBED] = 1000 and at 1.5 MPa pressure (Table 3). It was found that among dimethylaminopyridine (DMAP), pyridine (Py), imidazole (Im), triethyl amine (Et₃N) and triphenyl phosphine (Ph₃P) co-catalysts; DMAP showed highest activity (89.6%) towards the conversion of styrene oxide and CO₂ (Table 3), which may be due to their low solubility in the styrene oxide.³⁸

It is observed from the experimental results that, the catalytic activity of Co-HMBED is very much sensitive to reaction temperature (Figure 4), which depends on the activation of CO₂. With an increase in temperature from 80 to 100 °C, cyclic styrene carbonate yield increased sharply from 66.1% to 87.1%, and the best result has been found at 100 °C, 1.5 MPa and 3 h. The yield (%) remained almost constant on further increase in temperature (Figure 4).³⁹

Time is also an active parameter for the coupling of epoxide and CO₂ to produce cyclic carbonates. The formation of cyclic carbonate was almost done speedily within the first 3 h, reaching a yield of 64.2% (Figure 5). Thus, 3 h was considered as an optimal condition.⁴⁰ The TOF increases with increasing molar ratios of styrene oxide/catalyst, whereas, yield (%) (100 × TOF (h⁻¹)/molar ratio) of cyclic styrene

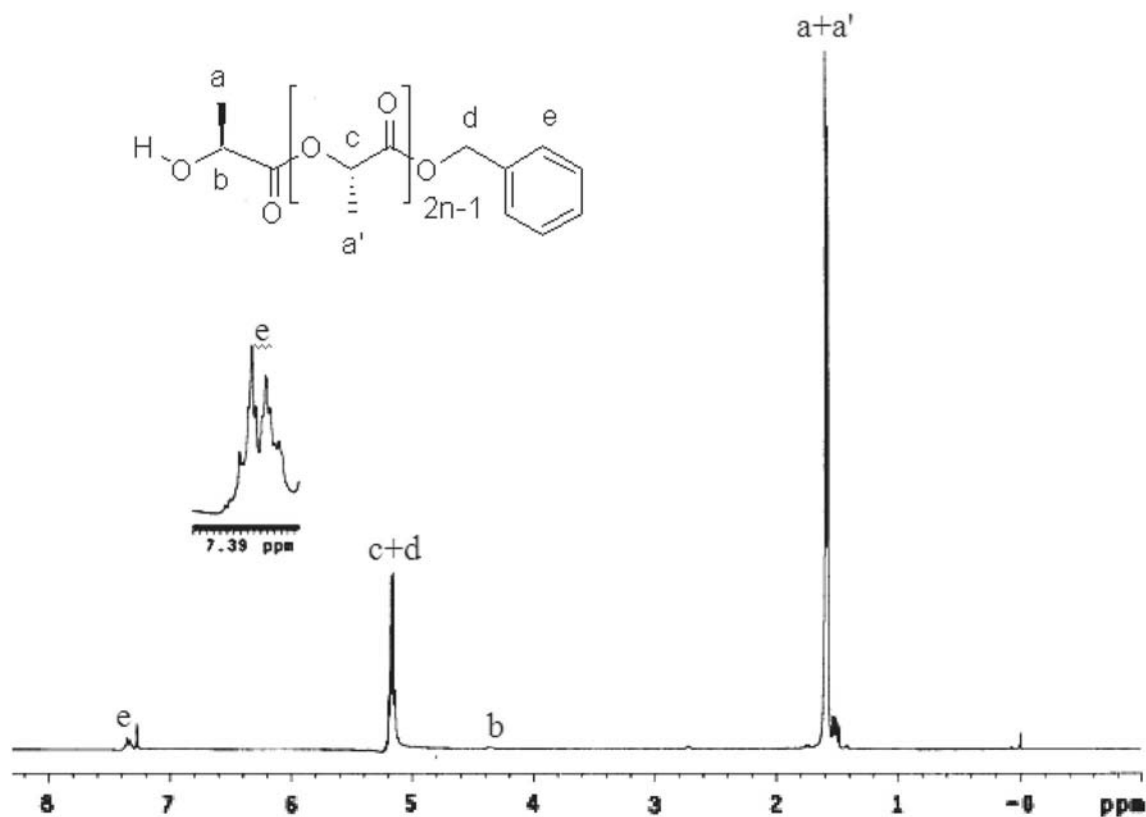


Figure 2. ¹H NMR spectrum of PLA-50.

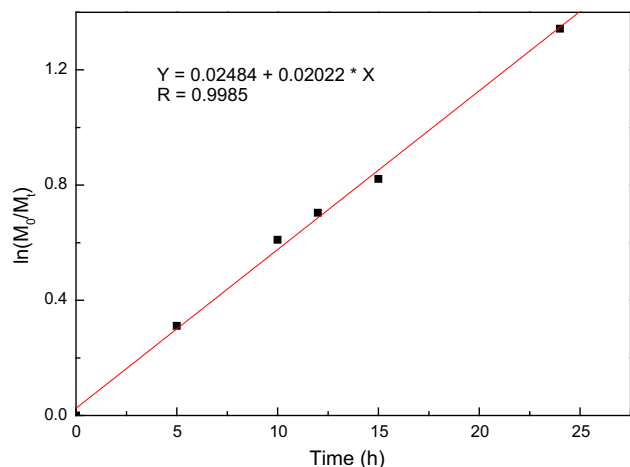
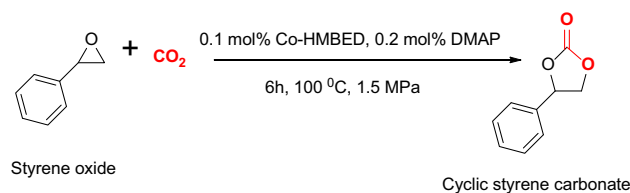


Figure 3. First order kinetics of ROP of lactide catalyzed by Co-HMBED; [Co]/[LA]₀/[BnOH] = 1/100/1.



Scheme 2. Cyclic styrene carbonate formation.

Table 3. Formation of cyclic styrene carbonates.

Entry	Co-catalysts	Yield (%) ^a	TON ^b	TOF ^c (h ⁻¹)
1	DMAP	89.6	871	290
2	Imidazole	72.9	691	230
3	Et ₃ N	70.5	654	218
4	Ph ₃ P	65.3	576	192
5	Pyridine	64.1	549	183

Reaction conditions: Co-HMBED (4.5×10^{-5} M), CO₂ (1.5 MPa), at 100 °C, time 6 h. [Styrene oxide]/[Co-HMBED]/[Co-catalyst] = 1000/1/2.

^aYield (%) by ¹H NMR.

^bTON = Mole of cyclic styrene carbonate/mole of Co-HMBED at 3 h.

^cTOF = Rate = turnovers/h.

carbonate decreases with the increase in molar ratio (Table 4).⁴¹ The formation of cyclic styrene carbonate was confirmed by ¹H-NMR (Figure S5, Supplementary Information).

To investigate the kinetic behavior, the formation of cyclic styrene carbonate with Co-HMBED (4.5×10^{-5} M), CO₂ (1.5 MPa), at 100 °C, [styrene oxide]/[Co-HMBED]/[DMAP] = 1000/1/2, has been carried out. The ln[M]₀/[M]_t vs time plot was found to be a straight line implying first order kinetics²⁹ (Figure S6, Supplementary Information) with apparent rate constant (k_{app}) was 0.4239 h⁻¹.

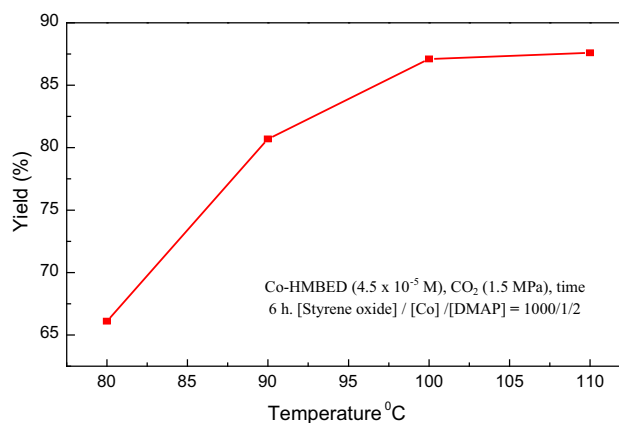


Figure 4. Formation of cyclic styrene carbonate as a function of temperature.

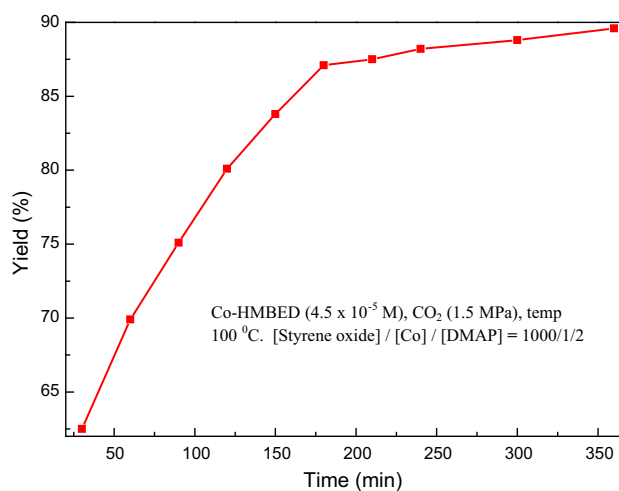


Figure 5. Effects of time (min) on yield (%) of cyclic styrene carbonate formation.

Table 4. Effect of molar ratio of epoxide/catalyst on the conversion of epoxide and CO₂.

Sl. No.	Substrate	[epoxides]/[Co-HMBED]	TOF ^a (h ⁻¹)
1		1000	290
2		2000	576
3		3000	832
4		5000	1270

Reaction conditions: [Co-HMBED]/[DMAP] = 1:2; 1.5 MPa of CO₂, at 100 °C, time 3 h.

^a TOF (h⁻¹): mol of cyclic carbonate/mol of catalyst/h.

4. Conclusions

The Co-HMBED complex was found to be an effective catalyst for the polymerization of *L*-lactide with benzyl alcohol and coupling of styrene oxide and CO₂ into cyclic styrene carbonate in good to excellent yield. Benzyl alcohol shows a significant character for

polymerization of L-lactide. Without benzyl alcohol, cobalt complex has much less activity. Similarly, co-catalyst has significantly affected the formation of cyclic styrene carbonate. DMAP showed the greatest catalytic activity in comparison to other co-catalysts.

Supplementary Information (SI)

This includes data for Electronic spectra and FTIR spectra of Schiff base and Co-HMBED complex, ^1H NMR spectrum cyclic styrene carbonate, kinetics of formation of cyclic styrene carbonate. Supplementary Information is available at www.ias.ac.in/chemsci.

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