



Efficient coupling of CO₂ and epoxides with bis(phenoxyiminato) cobalt(III)/Lewis base catalysts

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ABSTRACT

A series of unbridged bis(phenoxyiminato) cobalt(III) complexes were synthesized and studied as catalysts for the coupling of CO₂ and epoxide. Dimethylamino pyridine (DMAP) and tetrabutyl ammonium bromide (Bu₄NBr), were used as co-catalysts in the reaction. Both Co(III)/DMAP and Co(III)/Bu₄NBr systems showed high catalytic activity and selectivity in the coupling of *n*-hexyl oxide and CO₂, resulting in *n*-hexyl carbonate. Several mono- and di-substituted terminal epoxides were also tested. The reaction mechanism of the Co(III)/DMAP system was investigated in detail using ESI-MS revealing that in addition to the main product, cyclic carbonate, traces of oligomers are formed.

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1. Introduction

The conversion of carbon dioxide to desirable, economically competitive products has received much attention because of its potential use as an abundant C1 resource and its indirect role as an environmental pollutant [1–3]. The synthesis of cyclic carbonate by the coupling of CO₂ and epoxides is one of the most interesting reactions in this area (Scheme 1), and in recent decades numerous catalyst systems have been developed for this transformation [4–9]. Apart from a number of efficient Zn complexes [10–12], the most common catalyst precursors reported for the synthesis of both cyclic carbonates and polycarbonates are based on salen and porphyrin complexes of Co(III) [4,5,12–17], Cr(III) [6,18–22,19,23] and Al(III) [7,18,24–28]. Square pyramidal geometry is characteristic of both salen and porphyrin complexes. This involves planar coordination of the ligand framework around the metal center with the square pyramid coordination sphere being completed by a halide at the apical position. As an augmentation for these previous studies, we report herein a convenient method of cyclic carbonate synthesis by utilizing catalysts based on unbridged bis(phenoxyiminato) cobalt(III) complexes.

2. Experimental

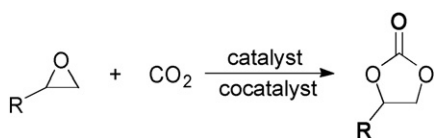
2.1. Reagents

The epoxides were purchased from Fluka and Aldrich and used without further purification. Solvents were used after distillation. The carbon dioxide of purity 99.99% was purchased from AGA and used as received. Anhydrous cobalt(II) chloride (CoCl₂), tetrabutyl ammonium bromide (Bu₄NBr), dimethylamino pyridine (DMAP), salicylaldehyde, 2'-hydroxyacetophenone, 3,5-di-tert-butyl-2-hydroxybenzaldehyde, aniline, *p*-toluidine, 4-chloroaniline, benzylamine, 4-fluorobenzylamine, 2-phenethylamine, sodium hydride, iodine were purchased from Aldrich.

2.2. Typical reaction procedure

All of the coupling reactions were conducted in a 50 ml stainless-steel autoclave equipped with a glass liner and a magnetic stirring bar. In a typical reaction set-up the catalyst (0.01 mmol), dichloromethane (0.5 ml), epoxide (16.6 mmol), and co-catalyst (0.04 mmol) were loaded into the glass liner. The reactor was then pressurized with the appropriate amount of CO₂ (10 bar) and heated to desired temperature (145 °C). After the required reaction time (2 h), the reactor was cooled in an ice bath and degassed. For the GC analysis the reaction solution was diluted and a standard (acetophenone) was added. A sample from the reaction solution was taken and analyzed with a gas chromatograph (Agilent 6890N). The product formation and distribution was verified with a mass spectrometer (Agilent 5973).

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Scheme 1. Coupling reaction of CO₂ and epoxides.

2.3. General procedure for cobalt(II) complexes

The Schiff base ligands were prepared via the simple condensation reaction of a primary amine with either salicylaldehyde or 2'-hydroxyacetophenone in ethanol. The relevant Schiff base ligand was dissolved in dry THF and added via a syringe to a solution of NaH in THF under argon. This solution was stirred for 10 min at room temperature to deprotonate the ligand. CoCl₂ was then introduced to the reaction mixture. The reaction was heated to 60 °C and stirred for 12 h under argon. The reaction solution was subsequently filtered and the solvent was evaporated under vacuum. The residue was then washed either with methanol or a mixture of THF and hexane to remove any unreacted ligand salt and CoCl₂. Finally this mixture was filtered and the solvent was evaporated under vacuum.

Bis(N-phenyl-salicylaldiminato)Cobalt(II): Orange, *Anal. Calc.* for C₂₆H₂₀CoN₂O₂·H₂O: C, 66.53; H, 4.72; N, 5.97%. Found C, 66.48; H, 4.19; N, 5.88%. HRMS (ESI-TOF): *m/z* [C₂₆H₂₀CoN₂O₂] 451 (calculated 451.0840, found 451.0851, error 0.43 ppm) [C₂₆H₂₀CoN₂O₂ + Na] 474 (calculated 474.0749, found 474.0746, error 0.60 ppm) MS(EI⁺): *m/z* (%) 451 (100, M⁺), 255 (51, M⁺–C₁₃H₁₀NO), 196(51, ligand).

Bis(N-4-methylphenyl-salicylaldiminato)Cobalt(II): Red, *Anal. Calc.* for C₂₈H₂₆CoN₂O₂·H₂O: C, 67.60; H, 5.27; N, 5.63%. Found C, 67.99; H, 5.09; N, 5.57%. HRMS (ESI-TOF): *m/z* [C₂₈H₂₆CoN₂O₂] 479 (calculated 479.1164, found 479.1170, error –1.14 ppm) [C₂₈H₂₆CoN₂O₂ + Na] 502 (calculated 502.1062, found 502.1056, error 1.10 ppm). MS(EI⁺): *m/z* (%) 479 (60, M⁺), 269 (18, M⁺–C₁₄H₁₃NO), 210(65, ligand).

Bis(N-4-chlorophenyl-salicylaldiminato)Cobalt(II): Orange, *Anal. Calc.* for C₂₆H₁₈CoN₂O₂Cl₂·H₂O: C, 58.01; H, 3.74; N, 5.20%. Found C, 58.18; H, 3.61; N, 5.04%. HRMS (ESI-TOF): *m/z* [C₂₆H₁₈CoN₂O₂Cl₂] 519 (calculated 519.0072, found 519.0074, error –0.50 ppm), [C₂₆H₁₈CoN₂O₂Cl₂ + Na] 541 (calculated 541.9970, found 541.9968, error 0.35 ppm). MS(EI⁺): *m/z* (%) 519 (77, M⁺), 289(35, M⁺–C₁₃H₉NOCl), 230 (60, ligand).

Bis{2-[(benzylimino)ethyl]phenoxy}Cobalt(II): Green, *Anal. Calc.* for C₃₀H₂₈CoN₂O₂: C, 71.00; H, 5.56; N, 5.52%. Found C, 71.12; H, 5.69; N, 5.31%. (ESI-TOF): *m/z* [C₃₀H₂₈N₂O₂Co] 507 (calculated 507.1477, found 507.1476, error 0.17 ppm) [C₃₀H₂₈N₂O₂Co + Na] 530 (calculated 530.1375, found 530.1376, error –0.10 ppm). MS(EI⁺): *m/z* (%) 507(55, M⁺), 284(88, M⁺–C₁₅H₁₄NO), 225(100, ligand).

Bis(N-benzyl-salicylaldiminato)Cobalt(II): Orange, *Anal. Calc.* for C₂₈H₂₄CoN₂O₂·H₂O: C, 67.60; H, 5.27; N, 5.63%. Found C, 67.61; H, 5.11; N, 5.50%. HRMS (ESI-TOF): *m/z* [C₂₈H₂₄CoN₂O₂] 479 (calculated 479.1164, found 479.1161, error 0.69 ppm), [C₂₈H₂₄CoN₂O₂ + Na] 502 (calculated 502.1062, found 502.1062, error 2.17 ppm). MS(EI⁺): *m/z* (%) 479 (100, M⁺), 269 (100, M⁺–C₁₄H₁₂NO), 211(77, ligand).

Bis(N-4-fluorobenzyl-salicylaldiminato)Cobalt(II): Orange, *Anal. Calc.* for C₂₈H₂₂CoF₂N₂O₂: C, 65.25; H, 4.30; N, 5.43%. Found C, 65.50; H, 4.30; N, 5.31%. HRMS (ESI-TOF): *m/z* [C₂₈H₂₂CoF₂N₂O₂] 515 (calculated 515.0976, found 515.0966, error 1.96 ppm), [C₂₈H₂₂CoF₂N₂O₂ + Na] 538 (calculated 538.0866, found 538.0874, error 1.42 ppm). MS(EI⁺): *m/z* (%) 515 (100, M⁺), 287 (100, M⁺–C₁₄H₁₁NO), 228(55, ligand).

Bis{2-[(phenylethylimino)ethyl]phenoxy}Cobalt(II): Orange, *Anal. Calc.* for C₃₂H₃₂CoN₂O₂: C, 71.77; H, 6.02; N, 5.23%. Found C, 70.71; H, 6.03; N, 5.19%. HRMS (ESI-TOF): *m/z* [C₃₂H₃₂CoN₂O₂] 535 (calcu-

lated 535.1790, found 535.1785, error 1.09 ppm). MS(EI⁺): *m/z* (%) 535 (96, M⁺), 297 (100, M⁺–C₁₆H₁₆NO), 239(100, ligand).

Bis(N-phenylethyl-salicylaldiminato)Cobalt(II): Orange, *Anal. Calc.* for C₃₀H₂₈CoN₂O₂: C, 71.00; H, 5.56; N, 5.52%. Found C, 71.09; H, 5.88; N, 5.47%. HRMS (ESI-TOF): *m/z* [C₃₀H₂₈CoN₂O₂] 507 (calculated 507.1477, found 507.1470, error 1.34 ppm). MS(EI⁺): *m/z* (%) 507 (76, M⁺), 283 (100, M⁺–C₁₅H₁₄NO), 225(46, ligand).

Bis(N-phenylethyl-3-tert-butyl-salicylaldiminato)Cobalt(II): Light green, *Anal. Calc.* for C₄₆H₆₀CoN₂O₂·H₂O: C, 73.67; H, 8.33; N, 3.74%. Found C, 73.63; H, 8.36; N, 3.76%. HRMS (ESI-TOF): *m/z* [C₄₆H₆₀CoN₂O₂] 731 (calculated 731.3981, found 731.3974, error 0.94 ppm). MS(EI⁺): *m/z* (%) 731 (100, M⁺), 395 (50, M⁺–C₂₃H₃₀NO), 336(50, ligand).

2.4. General procedure for cobalt(III) complexes

A previously prepared cobalt(II) complex was treated with a half equivalent of I₂ and dissolved in 5 ml of CH₂Cl₂. The solution mixture was stirred at room temperature for 12 h after which the solvent was evaporated and the excess iodine was removed by sublimation under vacuum for 24 h.

Bis(N-phenyl-salicylaldiminato) Iodo Cobalt(III): **1** Dark red, *Anal. Calc.* for C₂₆H₂₀CoIN₂O₂·2H₂O: C, 50.83; H, 3.94; N, 4.56%. Found C, 50.87; H, 3.22; N, 4.51%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 451 (calculated 451.0851, found 451.0847, error 1 ppm).

Bis(N-4-methylphenyl-salicylaldiminato) Iodo Cobalt(III): **2** Dark red, *Anal. Calc.* for C₂₈H₂₄CoIN₂O₂·H₂O: C, 53.86; H, 4.20; N, 4.49%. Found C, 53.67; H, 3.78; N, 4.57%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 479 (calculated 479.1164, found 479.1165, error 0.25 ppm).

Bis(N-4-chlorophenyl-salicylaldiminato) Iodo Cobalt(III): **3** Brown, *Anal. Calc.* for C₂₆H₁₈CoICl₂N₂O₂: C, 48.25; H, 2.80; N, 4.33%. Found C, 48.24; H, 2.72; N, 4.45%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 519 (calculated 519.0072, found 519.0070, error 0.42 ppm).

Bis{2-[(benzylimino)ethyl]phenoxy} Iodo Cobalt(III): **4** Green, *Anal. Calc.* for C₃₀H₂₈CoIN₂O₂·H₂O: C, 55.23; H, 4.63; N, 4.29%. Found C, 55.19; H, 4.53; N, 4.33%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 507 (calculated 507.1477, found 507.1453, error 1.32 ppm).

Bis(N-benzyl-salicylaldiminato) Iodo Cobalt(III): **5** Green, *Anal. Calc.* for C₂₈H₂₄CoIN₂O₂: C, 55.46; H, 3.99; N, 4.62%. Found C, 55.04; H, 3.85; N, 4.72%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 479 (calculated 479.1164, found 479.1163, error 0.29 ppm).

Bis(N-4-fluorobenzyl-salicylaldiminato) Iodo Cobalt(III): **6** Dark green, *Anal. Calc.* for C₂₈H₂₂CoIF₂N₂O₂: C, 52.36; H, 3.45; N, 4.36%. Found C, 52.28; H, 3.42; N, 4.04%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 515 (calculated 515.0976, found 515.0972, error 0.77 ppm).

Bis{2-[(phenylethylimino)ethyl]phenoxy} Iodo Cobalt(III): **7** Dark green, *Anal. Calc.* for C₃₂H₃₂CoIN₂O₂: C, 58.02; H, 4.87; N, 4.23%. Found C, 58.18; H, 4.97; N, 4.05%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 535 (calculated 535.1790, found 1794, error 0.75 ppm).

Bis(N-phenylethyl-salicylaldiminato) Iodo Cobalt(III): **8** Dark green, *Anal. Calc.* for C₃₀H₂₈CoIN₂O₂·H₂O: C, 55.23; H, 4.63; N, 4.29%. Found C, 55.62; H, 4.28; N, 4.32%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 507 (calculated 507.1477, found 507.1478, error 0.23 ppm).

Bis(N-phenylethyl-3-tert-butyl-salicylaldiminato) Iodo Cobalt(III): **9** Dark brown, *Anal. Calc.* for C₄₆H₆₀CoIN₂O₂·H₂O: C, 63.01; H, 7.13; N, 3.19%. Found C, 63.22; H, 7.23; N, 3.08%. HRMS (ESI-TOF): *m/z* (%) [M⁺–I] 731 (calculated 731.3981, found 731.3993, error 1.58 ppm).

3. Result and discussion

3.1. The unbridged bis(phenoxyiminato) cobalt complexes

For this study a series of Co(III) bis(aldiminato) and bis(ketiminato) complexes were synthesized. Although resembling

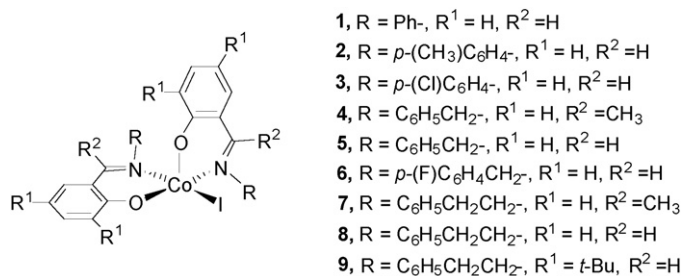


Fig. 1. Schematic structure of the unbridged bis(phenoxyiminato) cobalt(III) complexes used as catalyst precursors in this study.

the salen type complexes, unbridged bis(phenoxyiminato) cobalt complexes have not been so far reported for the activation of CO₂ (Fig. 1). According to performed quantum chemistry calculations, the unbridged bis(phenoxyiminato) Co(III) complexes prefer a distorted square pyramidal geometry wherein iodide lies in the main plane and one of the oxygens from the phenoxy groups is at the apical position (Fig. 2). The main difference between the unbridged bis(phenoxyiminato) and salen type transition metal complexes is that in later ones the ligand usually adopt the thermodynamically more favored planar configuration [29]. However, in the chemical transformations catalyzed by salen type complexes the actual configuration catalytic species could often be far different from planar [29–31]. In this account, the unbridged bis(phenoxyiminato) Co(III) and salen type complexes [4] would have similar catalytic behavior in CO₂ activation reactions.

3.2. Coupling reaction of CO₂ and *n*-hexyl oxide

Complexes **1–9**, when used together with tetrabutyl ammonium bromide (Bu₄NBr) or dimethylamino pyridine (DMAP) showed high catalytic activity and selectivity and turnover numbers of up to 1500 were recorded for the coupling of CO₂ and *n*-hexyl oxide in 2 h (Fig. 3). Catalysts **4** and **7** bearing the bis(ketiminato) ligands without tert-butyl substituents were found to be slightly more active than the aldiminato complexes. In general, differences in the ligand substitution pattern in the unbridged bis(phenoxyiminato) complexes do not have a great effect on catalytic activity. This suggests that the overall coordination sphere in these unbridged catalyst precursors is favorable for the efficient coupling reaction and the nature and size of ligand substituents in the series have only a minor influence on the course of the reaction. It is worth mentioning that Bu₄NBr and DMAP alone can also catalyze the coupling of CO₂ and epoxides, but their activities remained moderate in the absence of cobalt complexes.

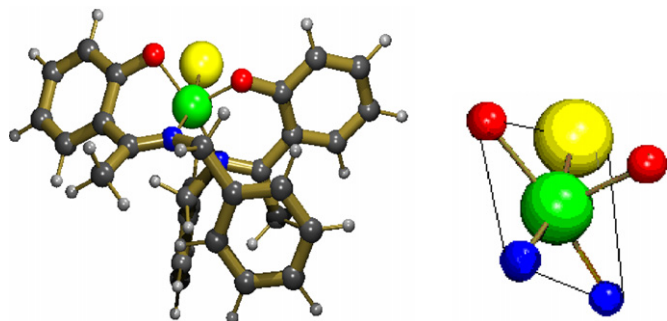


Fig. 2. Calculated structure of bis(salicylaldiminato) complex **4** (left) shows a distorted square pyramidal coordination geometry for Co(III) (right).

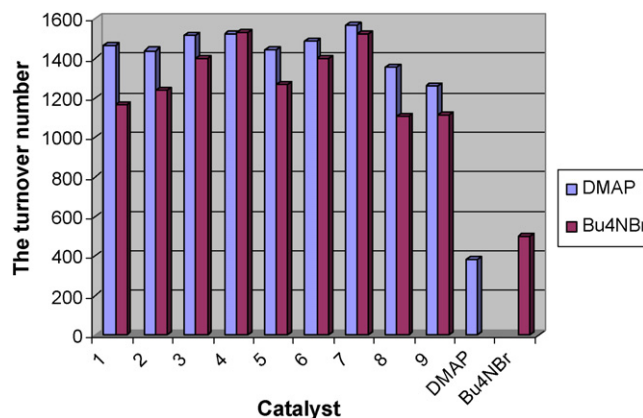


Fig. 3. Catalytic activity of unbridged bis(phenoxyiminato) cobalt(III) complexes **1–9**.

3.3. Different substrates

In addition to *n*-hexyl oxide, the **4**/DMAP and **4**/Bu₄NBr catalytic systems were studied with a range of terminal and cyclic epoxides. Using **4**/Bu₄NBr catalyst the corresponding cyclic carbonates were obtained in pure state with good yields. While having a similar activity to **4**/Bu₄NBr, **4**/DMAP tends to produce oligomeric side products particularly with cyclohexyl oxide and cyclopentene oxide (Table 1).

3.4. Mechanism

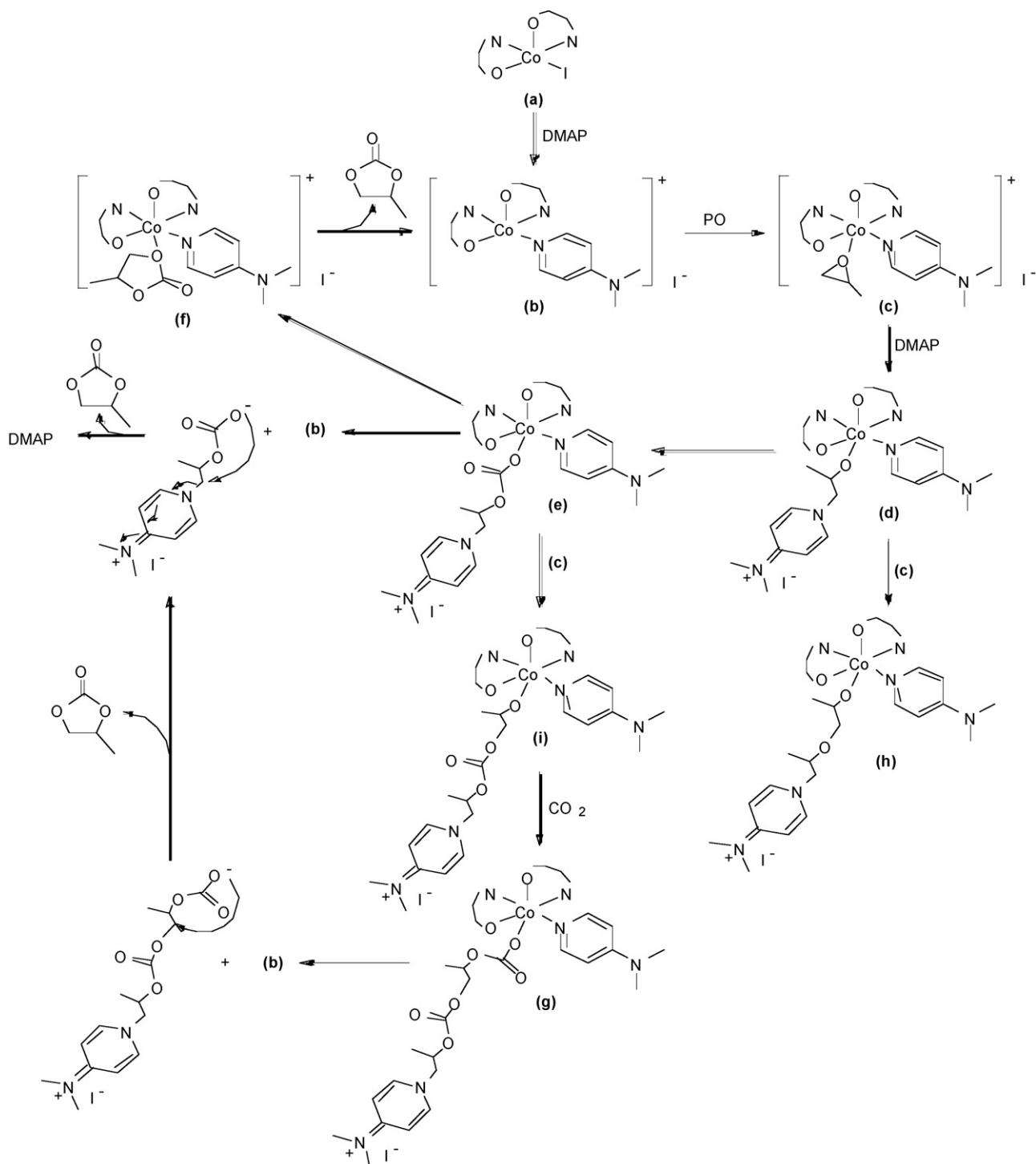
The coupling reaction of propylene oxide (PO) and CO₂ was further investigated using ESI-MS which turned out to be a highly beneficial method to get an insight of the actual processes occurred in course of the catalytic reaction. The original solution containing **8**/DMAP and excess of PO was maintained under CO₂ atmosphere (10 bar) and heated for 1 h. In the resulted mixture, besides cyclic carbonate and the initial cobalt complex, various cobalt(III) cations including [**8** + DMAP]⁺, [**8** + DMAP + PO]⁺, [**8** + 2 ×

Table 1
Reactivity of **4**/DMAP (a) and **4**/Bu₄NBr (b) towards terminal and cyclic epoxides.

Substrate	Product	TOF(a/b), h ⁻¹
		750/900
		760/910
		600/640
		100 ^a /420
		20 ^a /210

Reaction conditions: **4** (0.01 mmol), co-catalyst (0.06 mmol), **4**/DMAP (a) **4**/Bu₄NBr (b) and, epoxide (10 mmol, 1000 equiv.), CO₂ (10 bar), CH₂Cl₂ (0.5 ml), 145 °C, 1 h. Yields were determined by comparing the product with an external standard in GC-Fid.

^a Oligomeric side products.



Scheme 2. Proposed reaction mechanism for Co(III)/DMAP catalyst **8** in PO/CO₂ coupling reaction.

DMAP+PO+CO₂]⁺, [**8**+DMAP+PO+CO₂]⁺ were identified using high-resolution mode (Scheme 2) (see supporting information). The results show that under applied conditions the initial Co complex **8** may coordinate either one dimethylamino pyridine (DMAP) molecule (complex b) or propylene oxide (PO) together with DMAP (complex c), which led presumably to the dissociation of Co–I bond and shift of the iodine atom into outer coordination sphere.

Due to the flexibility of the ligand surrounding of bis(phenoxyiminato) cobalt(III) complexes, the metal center can host both epoxide and DMAP *cis* to each other. Previous reports

on coupling and alternating copolymerization of CO₂ and epoxides catalyzed by salen type systems have shown that the opening of the epoxide is an important step in the mechanism and it proceeds through a bimetallic process [19–22].

As described earlier, nucleophilic attack of an external DMAP or coordinated nucleophile on the less hindered carbon atom of coordinated PO causes the ring opening and apparently leads to the formation of (d) (Scheme 2) [23]. Unfortunately the species (d) was undetectable by ESI-MS. Therefore, the ring opening of epoxide might also occur via bimetallic process. Insertion of CO₂ into

the Co–alkoxide bond affords the carbonate intermediate species (e) and subsequent intramolecular cyclisation generates species (f). Following elimination provides propylene carbonate and regenerates the species (b).

Intriguingly, Co-complexes other than a–f were also identified. The presence of [e+PO] (i), [e+PO+CO₂] (g), as well as [c+PO+DMAP] (h) are clear fingerprints for the leaching of catalyst selectivity (see supporting information). The cyclic carbonate also can be formed from depolymerization of the growing polymer chain by backbiting reaction. In this case the carbonate end groups attack the nearest alkoxy carbon in the chain. During the process of cyclic carbonate formation, the polymer chain may be either free or coordinated to the metal center (from g to e) [23].

4. Conclusion

The results herein underline that activated by either DMAP or Bu₄NBr co-catalysts, the unbridged bis(phenoxyiminato) Co(III) complexes are effective and selective catalysts for the chemical fixation of CO₂ and epoxide leading to the synthesis of the cyclic carbonate. The bis(phenoxyiminato) Co(III) complexes co-catalyzed with Bu₄NBr produced only cyclic carbonate while with DMAP traces of oligomers were formed together with the major product, cyclic carbonate. The proposed mechanism accounts well for the experimental data obtained and corroborates earlier mechanistic proposals as well as sheds light on the new catalytic system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.07.009.

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