Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name RSCPublishing

ARTICLE

Highly active Cr(III) catalysts for the reaction of CO_2 with epoxides

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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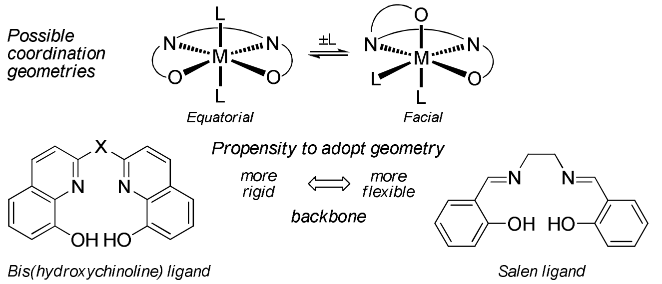
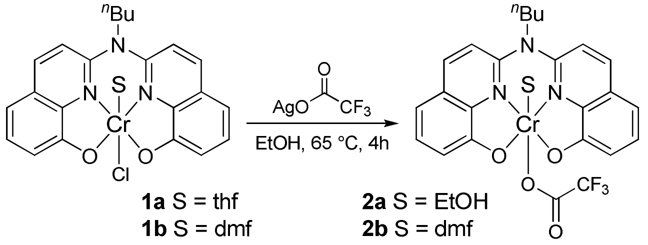
This paper describes the synthesis and characterization of [Cr(babhq)OAc^F(EtOH)] (OAc^{F-} = $CF_3CO_2^-$) as well as application of the complex as catalyst in the reaction of CO_2 with epoxides. While cyclic propylene¬carbonate was obtained as the sole product when propylene oxide was used as epoxide, alternating polycarbonate was obtained with cyclohexene oxide. Following the course of the reaction with *in situ* IR spectroscopy revealed that a direct pathway to the formation of cyclic carbonate prevails in case of propylene oxide whereas the polycarbonate obtained from cyclohexene oxide is prone to degradation to cyclic carbonate. The differences in chemoselectivity are rationalised on basis of the propensity of the ligand to adopt a podand-like structural motif allowing for an inner-sphere mechanism.

Targeted at developing sustainable routes to chemical production, the utilization of carbon dioxide for the synthesis of value added chemicals currently receives remarkable attention.[1] A prime example demonstrating the successful utilization of CO_2 is the reaction of CO_2 with epoxides leading to polycarbonates and cyclic carbonates.[2-3] Complexes of the 3d metals chromium[4] and cobalt[5-6] are among the best catalysts for carbon dioxide – epoxide co-polymerisation,[7] whereby the combination of these three-valent cations with a dianionic salen ligand is the most intensively studied system. Numerous studies focussed on the variation and optimisation of this tetradentate N_2O_2 ligand,[8] yet little is known with respect to variation of the ligand backbone.



Scheme 1. Coordination geometries of tetradentate N_2O_2 ligands to octahedral metal centres and molecular structure of the *bis*(hydroxychinoline) and salen backbone.

Thus, we investigated the use of a *bis*(8-hydroxyquinolinyl)-butylamine (babhq) as novel N_2O_2 ligand template for the reaction of CO_2 with epoxides to aliphatic polycarbonates and cyclic carbonates. Recently, we had applied this ligand successfully in the cobalt catalysed carbonylation of nitroarenes and aromatic amines for the sustainable synthesis of carbamates,[9] another technically important class of carbonic acid derivatives. The babhq ligand is a more rigid N_2O_2 chelate ligand compared to salen (Scheme 1), while it is still flexible enough to adopt two different geometries,[10] when coordinated to a metal atom with octahedral ligand sphere: upon dissociation of one of the axial ligands, the equatorial N_2O_2 chelate can switch to a podand-like facial chelate,[11] whereby one chelate oxygen atom and the remaining N_2O donor atom set are mutually in *cis* coordination. This renders two neighbouring coordination sites accessible during the catalytic cycle. A further advantage of *bis*(hydroxyquinoline) ligands is their much higher stability against hydrolysis and oxidative degradation compared to salen ligands.[12-13]



Scheme 2. *Bis*(hydroxychinoline) complexes explored in this study for their catalytic activity in the reaction of carbon dioxide and epoxides.

Here, we report on the synthesis, characterization and use of [Cr(babhq)Cl(H_2O)] (**1a**) and [Cr(babhq)OAc^F(EtOH)] (**2a**, OAc^{F-} = $CF_3CO_2^-$, Scheme 2) as catalysts in the reaction of carbon dioxide and epoxides to cyclic carbonates or aliphatic polycarbonates.

Results and Discussion

Synthesis and characterisation of the catalysts

The complex [Cr(babhq)OAc^F(EtOH)] was synthesized by introducing first the *bis*(8-hydroxychinoline) chelate ligand into the coordination sphere of a suitable Cr(III) precursor followed by exchange of the axial ligand. During the first step of the synthesis, the parent ligand H_2(babhq) was deprotonated with potassium hydride in anhydrous thf. The purple precursor complex [$CrCl_3$(thf)$_3$] was added to the solution to obtain brown [Cr(babhq)Cl(thf)] (**1a**). By adding water to the mixture, the corresponding aqua-complex was precipitated and isolated. Then, the chloride ligand was exchanged with trifluoroacetate using AgOAc^F in ethanolic suspension to obtain [Cr(babhq)OAc^F(EtOH)] (**2a**) as a brown solid in a good overall yield of 73%. Single crystals of [Cr(babhq)Cl(dmf)] (**1b**) and [Cr(babhq)OAc^F(dmf)] (**2b**) suitable for X-ray diffraction analysis were obtained by slow diffusion of diethylether into a saturated solution of the corresponding complex in dmf.

Table 1. Crystal data and structure refinement for [Cr(babhq)Cl(dmf)] and [Cr(babhq)OAc^F(dmf)]

	[Cr(babhq)X(dmf)]	
	X = Cl$^-$ (**1b**)	X = OAc^{F-} (**2b**)
Formula	$C_{28}H_{33}ClCrN_5O_4$	$C_{27}H_{26}CrF_3N_4O_5$
MW [g/mol]]	591.04	595.52
Crystal system	monoclinic	monoclinic
Space group	P 2_1/n	P 2_1/c
a [Å]	9.8802(4)	12.2189(9)
b [Å]	14.1274(4)	13.6109(9)
c [Å]	19.4439(9)	15.9826(11)
α [°]	90	90
β [°]	94.197(3)	102.501(5)
γ [°]	90	90
V [Å^3]	2706.7(2)	2595.1(3)
D_{calcd} [g/cm^3]	1.450	1.524
μ [mm^{-1}]	0.566	0.509
F(000)	1236	1228
Crystal size [mm^3]	0.25 × 0.21 × 0.06	0.15 × 0.09 × 0.03
Reflns collected	22018	19006
Independent reflns	5740	5491
R_{int}	0.0465	0.1021
R indices [I>2σ(I)]	R_1 = 0.0452	R_1 = 0.0437
R indices (all data)	wR_2 = 0.1222	wR_2 = 0.1002

In complexes (**1b**) and (**2b**), the chromium centres assumed an octahedral coordination sphere, whereby the babhq ligand was coordinated to the chromium centre in the equatorial plane in a tetra-dentate fashion with $N_2O_2^{2-}$ coordination sphere. The anion, Cl$^-$ or OAc^{F-}, respectively, and a dmf solvent molecule were located in the axial positions. The bond lengths observed for the two complexes are in the range typically found for 16 electron chromium(III) salen complexes (Table 2).[14]

The chloro complex (**1b**) exhibited a weak doming effect with the chromium atom lying 0.099(1) Å shifted towards the anionic ligand Cl1 with respect to the plane represented by N1, N2, O1, and O2.[†] In consequence, the ligand is slightly folded along the axis Cr1-N3 giving rise to a dihedral angle of 17.1(1)° between the two planar quinolinole units. The twist in the ligand adumbrates a later rearrangement to a podand-like facial coordination during the catalytic cycle (*vide infra*). The axis Cl1–Cr1–O3 (deviating 0.6° from linearity) is almost perfectly perpendicular with respect to the equatorial plane defined by N1, N2, O1, and O2.

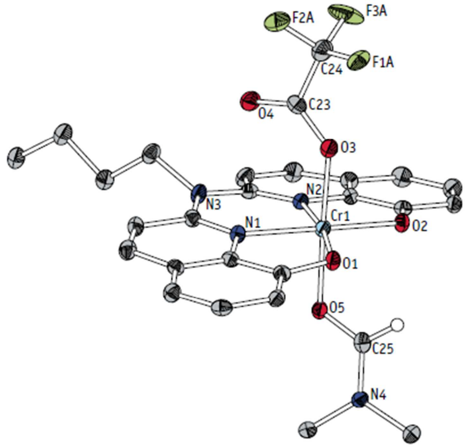


Figure 1. ORTEP drawing of the complex [Cr(babhq)OAc^F(dmf)] (**2b**). Hydrogen atoms and a second dmf solvent molecule are omitted for clarity. Ellipsoids are set at 30% probability.

The doming effect is less notable in case of the trifluoroacetate complex (**2b**) consistent with the weaker anionic donor ability of the OAc^{F-} ligand (Figure 1). Here, the chromium centre is dislocated by 0.061(1) Å towards the anionic ligand OAc^{F-}, which results in a smaller dihedral angle of 10.7(1)° between the two quinolinole units. As in [Cr(babhq)Cl(dmf)], the axis O3–Cr1–O5 (deviating 2.5° from linearity) is almost perfectly perpendicular with respect to the equatorial planes defined by N1, N2, O1, and O2.

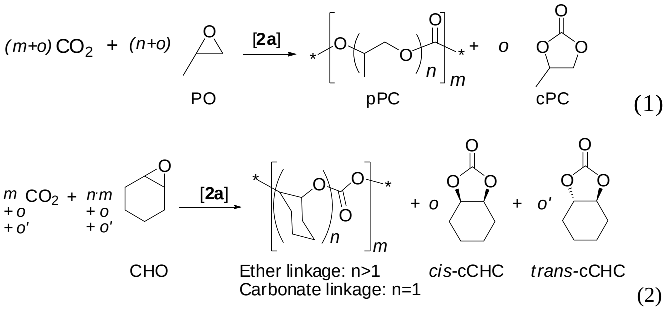
Table 2. Selected bond lengths [Å] for the complexes [Cr(babhq)Cl(dmf)] (**1b**) and [Cr(babhq)OAc^F(dmf)] (**2b**) in comparison to other chromium(III) salen complexes.

Bond	[Cr(babhq)X(dmf)]		Average[a]
	X = Cl$^-$ (**1b**)	X = OAc^{F-} (**2b**)	[Cr(salen)X(L)]
Cr1–O1	1.938(2)	1.929(3)	1.917
Cr1–O2	1.940(2)	1.946(3)	1.922
Cr1–N1	2.012(2)	2.009(4)	2.010
Cr1–N2	2.011(2)	2.008(4)	2.012
Cr1–Cl1	2.323(1)	–	2.292
Cr1–O3/X[b]	–	1.991(3)	2.001
Cr1–O3/O5/L[c]	2.035(2)	2.018(3)	2.104

[a] Average values for 16 [Cr(salen)X(L)] complexes according to a search in the Cambridge Structural Database;[14] [b] O3 for **2b**; X for [Cr(salen)X(L)] with X = N_3^-, CN$^-$, OR$^-$; [c] O3 for **1b**; O5 for **2b**; L for [Cr(salen)X(L)] with L = various neutral ligands.

Reaction of CO_2 and epoxides using 2a as catalyst

Complex **2a** with coordinated ethanol was tested as catalyst in the reaction of CO_2 with propylene oxide (PO) and cyclohexene oxide (CHO) as representative epoxides with respect to its catalytic activity and product selectivity (Eq. 1 and 2). As co-catalyst, chloride was employed as the *bis*(triphenylphosphine)-iminium (PPN) or tetrabutylammonium (TBA) salt. To obtain insight into kinetic details, the course of the reaction was followed by *in situ* IR spectroscopy.



* End group of the polymer chain

The reaction of CO_2 with PO provided cyclic propylenecarbonate (cPC) as the sole product in 87% yield (Table 3, Entry 1). In contrast, the reaction of CO_2 with CHO gave polycyclohexenecarbonate (pCHC) in 76 % yield, while only little cyclic cyclohexenecarbonate (cCHC) was formed (0.2%) (Table 3, Entry 2). Later corresponds to a ratio of cyclic carbonate (cCHC) to carbonate linkages in pCHC (*o/m*) of < 0.01. Analysis by ^{1}H-NMR spectroscopy showed that the polymeric product contained a high amount of carbonate repetition units $[C_6H_{10}OC(O)O]_m$ (97%) and few ether repetition units $[C_6H_{10}O]_n$ (3%) corresponding to a ratio of carbonate to ether linkages in the polymer chain (*m/n*) of 34.1 (Eq. 2). Gel permeation chromatography showed that the polymer had a molecular weight of 3831 g/mol with a polydispersity of 1.2.

Table 3 Yield and selectivity in the copolymerisation of CO_2 and epoxides using catalyst [Cr(babhq)OAc^F(EtOH)] **2a** as well as analytic data for the product obtained.[a]

Entry	Epoxide	Time [h]	Yield [%]	Selectivity[b] *o/m*	*o/o'*	*m/n*	M_n[c] [g/mol]	PDI
1	PO[e]	3	87[d]	only cyclic	–	–	–	–
2	CHO[e]	3	76[d]	< 0.01	–	34.1	3831	1.2
3	PO[f]	4.5	> 99	only cyclic	–	–	–	–
4	CHO[f]	6	69[d]	0.30	0.77	30.4	4543	1.2

[a] Reaction conditions: neat, 100 °C, $p_{ini}(CO_2)$ = 20 bar. [b] Determined by ^{1}H-NMR spectroscopy, *o/m* = ratio of cyclic carbonate to carbonate linkages in the polymer; *o/o' = ratio of cis- to trans-cCHC; m/n* = ratio of carbonate to ether units in the polymer; – = not applicable. [c] Determined by gel permeation chromatography against polystyrene of known molecular weight as standard. [d] The concentration profiles indicated **2a** to remain active at the end of the reaction. [e] PPNCl as co-catalyst, **2a**/PPNCl 1/2.5. [f] 1,8-octanediol/TBACl as additive/co-catalyst, **2a**/TBACl 1/3.3.

The kinetics of the **2a** catalysed reaction of CO_2 and PO (Table 3, Entry 1) was followed with *in situ* IR spectroscopy. The intensity of the characteristic signal for PO at 827 cm^{-1} declined rapidly. Consistent with the initial catalyst screening, an increasing intensity of the signals at 1809, 1387, 1352, 1168, 1114, 1074, 1041, 775, and 709 cm^{-1} indicated the formation of cyclic propylenecarbonate as the sole product (Figure 2). Quantitative analysis of the IR profile showed that PO was converted to cPC with an initial reaction rate of 178 $mol_{PO}{\cdot}(mol_{cat}{\cdot}min)^{-1}$. The absence of diffusion limitations across the gas-liquid phase boundary was confirmed by the constant intensity of the characteristic signal at 2339 cm^{-1} for CO_2 (not shown in Figure 2). Closer inspection of the IR profile revealed the absence of the carbonate ν(C=O) stretch vibration characteristic for polycarbonate at 1743 cm^{-1} over the entire course of the reaction. Thus, a direct pathway to formation of cPC must be present.

The position of the carbonate ν(C=O) stretch vibration assigned to cPC shifted from 1809 cm^{-1} (t = 0 min) to 1784 cm^{-1} (t = 10 h) indicating that specific intermolecular interactions in the reaction mixture change. Comparison with the position of the carbonate signal in mixture with a typical polyether (1000 g/mol, 115 g_{cPC}/l, 1817 cm^{-1}) as well as of the neat compounds (cPC 1782 cm^{-1}, polypropylenecarbonate 1743 cm^{-1}) suggests that mutual interactions between the carbonate groups weaken the C=O band in the highly polar environment of cPC and give rise to the shift of the carbonate vibration to lower wave numbers during the reaction.

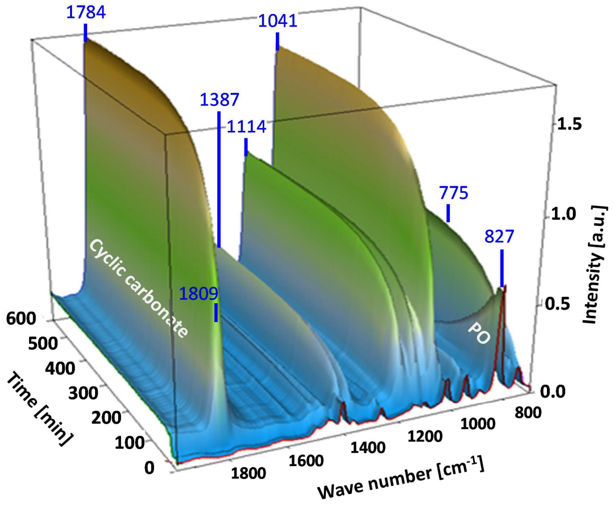


Figure 2. Time-resolved IR spectra of the reaction of CO_2 and PO with [Cr(babhq)OAc^F(EtOH)] (**2a**) at 100°C.

The kinetics of the **2a** catalysed reaction of CO_2 and cyclohexene oxide (Table 3, Entry 2) was also followed with *in situ* IR spectroscopy (Figure 3). The intensity of the characteristic signals for CHO at 1436, 890, 875, 835, 779, 746 cm^{-1} declined over 12 h, while the intensity of the signals at 1749, 1325, 1276, 1226, 1159, 1020, 987, 966, 933, 850 cm^{-1} increased consistent with the formation of pCHC.[15] Quantitative analysis of the IR profile showed that CHO was converted to pCHC with an initial reaction rate of 61 $mol_{CHO}{\cdot}(mol_{cat}{\cdot}min)^{-1}$. The absence of diffusion limitations across the gas-liquid phase boundary was confirmed by the constant intensity of the characteristic signal at 2336 cm^{-1} for CO_2 dissolved in the reaction mixture. Also in case of pCHC as product, the signal for the carbonate ν(C=O) stretch vibration shifted to lower wave numbers (from 1749 to 1743 cm^{-1}), although the red shift was less pronounced.

Last but not least, the reaction of CO_2 with epoxides (PO and CHO) was performed in the presence of 1,8-octanediol to study the extent of chain transfer, which is rapid for, *e.g.*, Zn-[16] and Al-[17] based catalysts. In the presence of an alcohol, similar results were observed with respect to substrate specificity. As shown in Table 3, Entry 3, the reaction of CO_2 and PO provided cyclic propylenecarbonate (cPC) in high yields (>99%). Unexpectedly, in the reaction of CO_2 and CHO the chemoselectivity had changed significantly. A mixture of 77% polycyclohexene-ethercarbonate and 23% cyclic cyclohexenecarbonate was obtained, which corresponds to a ratio *o*/*m* of 0.30. The enhanced cCHC formation can be attributed to the degradation of growing polymer chains by back-biting,[18-19] which might be induced by the higher polarity of the medium due to the use of 1,8-octanediol (*vide infra*). Analysis of the polymeric product by ^{1}H-NMR spectroscopy showed the ratio of carbonate linkages to ether linkages in the polycyclohexenecarbonate (*m/n* 34.1) to be similar to the product obtained in the absence of 1,8-octanediol (30.4). Thus an equally high amount of carbonate repetition units $[OC_6H_{10}OC(O)]_m$ was incorporated into the polymer (97%). The comparable molecular weight of 4543 g/mol and a mono-modal molecular weight distribution (polydispersity 1.2) suggests that the living character of the polymerisation reaction prevails over chain transfer reactions.

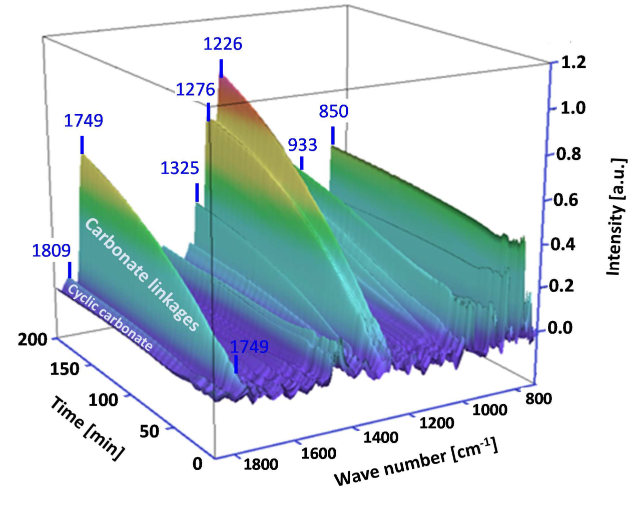


Figure 3. Time-resolved IR spectra of the reaction of CO_2 and CHO with $[Cr(babhq)OAc^F(EtOH)]$ at 100°C.

Closer inspection of the time-resolved IR spectra showed that the formation of pCHC was followed by an increasing intensity of bands at 1817 and 1804 cm^{-1} assigned to the ν(C=O) stretch vibration of *trans*-cCHC and *cis*-cCHC, respectively (Figure 4).[20] This is indicative of consecutive reaction pathways leading to the formation of cCHC.

For analysis, let us start with the mechanism for the copolymerization of CO_2 and CHO shown in Scheme 3. Analogous to the cobalt counterpart,[21] the reaction is most likely initiated by insertion of CO_2 into the cobalt-ethanol bond of **2a**

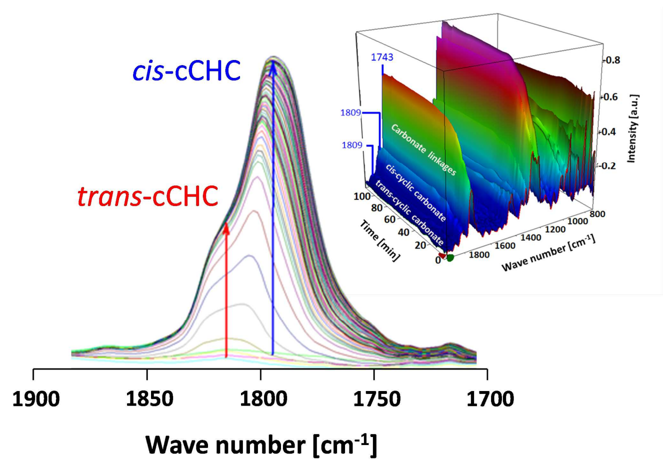
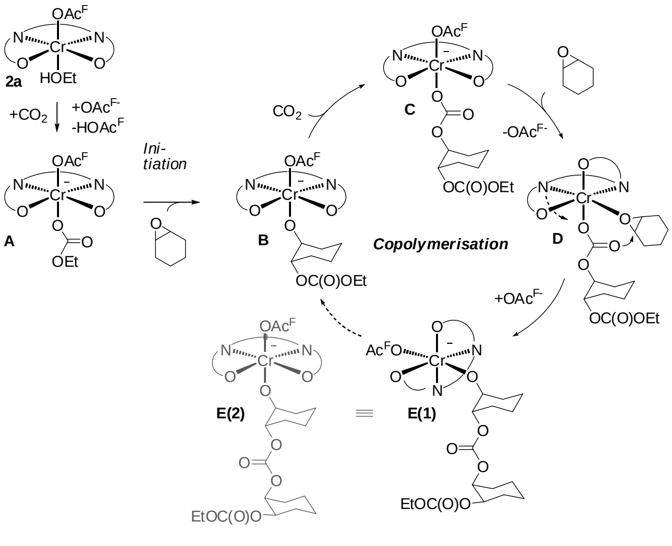


Figure 4 Analysis of the region characteristic for the cCHC ν(C=O) stretch vibration in the time-resolved IR spectra recorded during the reaction of CO_2 and CHO with $[Cr(babhq)OAc^F(EtOH)]$ in the presence of 1,8-octanediol.

under concomitant release of one proton to give complex **A** followed by insertion of cyclohexene oxide (**B**). Insertion of the next CO_2 molecule into the metal-alcoholate bond provides the coordinated carbonate complex **C**. Subsequent coordination of an epoxide molecule to the central chromium atom accompanied by dissociation of an OAc^{F-} anion triggers the rearrangement of the coordination geometry to the distorted podand-like facial geometry of complex **D**. The preference of the babhq ligand to adopt an equatorial coordination sphere facilitates the succeeding intramolecular insertion of the epoxide molecule into the growing polymer chain according to an inner-sphere mechanism.[22] The vacant coordination site is filled by simultaneous coordination of an OAc^{F-} anion to the chromium atom providing complex **E(1)** being equivalent to **E(2)**. Insertion of another CO_2 molecule into the chromium alcoholate bond starts

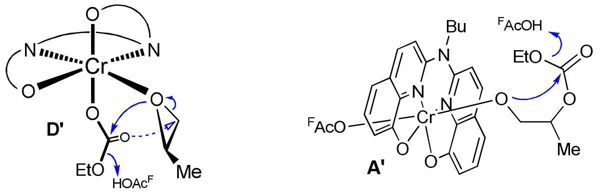


Scheme 3. Inner-sphere mechanism proposed for the copolymerisation of CO_2 and cyclohexene oxide.

the next copolymerization cycle. Note that the stronger tendency of the *bis*(hydroxyquinoline) ligand to return to an equatorial coordination geometry compared to Salen ligands destabilises intermediate **D** and the associated short life-time may be the reason for the high activity of complex **2a**.

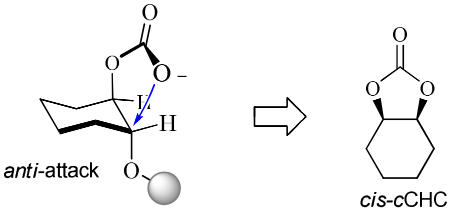
The differences in the propensity to form cyclic carbonate during the **2a** catalysed reaction of CO_2 with epoxides must be related to the diverging geometric constraint of the two epoxides,[23] as PO and CHO bind with essentially equal strength to metal centres.[24-25]

- Most likely, propylene oxide inserts into the metal-carbonate bond of complex **A** with similar concomitant rearrangement of the coordination geometry to a distorted facial geometry analogous to complex **D** (Scheme 4, **D'**). Likewise, the epoxide ring is opened by nucleophilic attack of the carbonate carbonyl oxygen. However, in contrast to cyclohexene oxide, the small size of the propylene oxide molecule renders simultaneous formation of a bond between the epoxide oxygen atom and the carbonyl carbon atom feasible. The concomitant release of ethanol is facilitated by transfer of a proton to the terminal group. Last, the cPC formed dissociates from the coordination sphere of the chromium complex followed by coordination of ethanol to regenerate **2a**.
- A direct pathway for the formation of cPC mechanism may involve insertion of the relatively small propylene oxide into the metal-carbonate bond of complex **A** (Scheme 4, **A'**). The flexibility of the initial polymer chain may allow for subsequent formation of cPC *via* an inner-sphere backbiting mechanism.[18,19] Also a dissociative mechanism may account for the formation of cPC (similar to cCHC, *vide infra*). However, even upon exhaustive inspection of the *in-situ* IR spectra obtained under our reaction conditions formation of intermediate polypropylenecarbonate moieties was not detectable.



Scheme 4. Mechanism proposed for the formation of cyclic propylenecarbonate (left) and alternative backbiting mechanism based on an intermediate chromium *O*-ethyl-2-carbonate-2-methylethanolate complex (**A'**, right).

- Regarding the formation of cCHC, the restricted geometry of the cyclohexene ring disfavours such an inner-sphere cCHC formation step. An alternative backbiting pathway may be triggered by dissociation of the polymer chain from the coordination sphere of the chromium complex. *Anti*-attack of a free carboxylate end group on the cyclohexene ring in chair conformation according to a S_N2 mechanism provides *cis*-cCHC (Scheme 5). The propensity of the cyclohexene ring to adopt a boat conformation and nucleophile attack of the terminal carboxylate group in *syn*-position to yield *trans*-cCHC is less favoured due to the high ring strain. Likewise, the parallel formation of *cis*- and *trans*-cCHC in the initial phase of the reaction suggests that an inner-sphere and a dissociative ring closing mechanism may be operative.



Scheme 5. Mechanism proposed for the formation of *cis*-cCHC by backbiting of free poly¬cyclohexene¬carbonate.

Thus, it is the restricted geometry of the polycyclohexenecarbonate chain, which hinders the formation of cCHC *via* backbiting and favours formation of polymeric pCHC.

Conclusions

In this study, we have demonstrated the synthesis and characterization of $[Cr(babhq)OAc^F(EtOH)]$ ($OAc^{F-} = CF_3CO_2^-$) as well as the successful application of the complex as catalyst in the reaction of CO_2 and epoxides to carbonate esters. The use of *bis*(hydroxyquinoline) ligands provides a catalytic system with superior stability against hydrolysis and oxidative degradation compared to salen ligand based catalysts. The kinetic study on the reaction of CO_2 with epoxides reveals a direct pathway to the formation of cyclic carbonate in case of propylene oxide while in case of cyclohexene oxide most of the cyclic carbonate is formed by backbiting of the polycarbonate chain. The differences in chemoselectivity are rationalised on basis of an inner-sphere mechanism. Such molecular insight is the precondition for further tuning of the coordination sphere of catalysts for the reaction of CO_2 with epoxides in regard to substrate specificity, activity and product selectivity.

Acknowledgements

Alexandra Keldenich and Maurice Cosemans are thanked for the experimental support. Marcel Liauw, Dirk Engels and Clemens Minnich are gratefully acknowledged for their contribution to establishing the *in situ* IR spectroscopy on this system. Burkhard Köhler is recognised for suggesting structural variants of the *bis*(hydroxychinoline) ligand and Willem K. Offermans for proofreading the manuscript.

Notes and references

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† Electronic Supplementary Information (ESI) available: [experimental details]. See DOI: 10.1039/b000000x/

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