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Carbon Dioxide Copolymerization Study with a Sterically Encumbering Naphthalene-Derived Oxide

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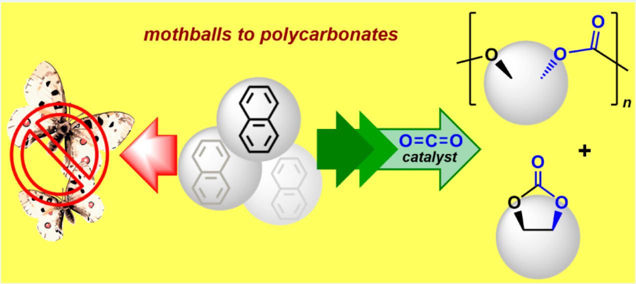
Supporting Information

ABSTRACT: Poly(1,4-dihydronaphthalene carbonate) has been prepared via the catalytic coupling of carbon dioxide and 1,4-dihydronaphthalene oxide using chromium(III) catalysts. The copolymer formation is found to be greatly dependent on the steric environment around the metal center. Traditional (salen)$Cr^{III}X$/cocatalyst systems bearing bulky *t*-butyl groups hinder the approach of the large monomer, significantly diminishing polymer chain growth and providing the entropically favored cyclic byproduct in excess. In contrast, employing the sterically unencumbered azaannulene-derived catalyst, (tmtaa)$Cr^{III}X$/cocatalyst system (tmtaa = tetramethyltetraazaannulene) shows polymer selectivity close to 90% with three times the activity (TOF = 20–30 h^{-1}). With the use of a bifunctional (salen)Cr^{III} catalyst, even higher polymer selectivity (>90%) can be observed. The complete synthesis of a new bifunctional tetraazaannulene ligand for a more effective catalyst is also described herein.



KEYWORDS: *carbon dioxide, 1,4-dihydronaphthalene oxide, polycarbonate, copolymerization, steric effect*

INTRODUCTION

Epoxides employed in the catalytic copolymerization reactions with CO_2 are largely aliphatic and alicyclic in nature for producing polycarbonates.[1] The most common and well-studied in the literature are propylene oxide (PO) and cyclohexene oxide (CHO) along with their functionalized derivatives. Poly(propylene carbonate) (PPC) and poly(cyclohexene carbonate) (PCHC) have been commercialized in recent years and are used as sacrificial binding agents, additives in coatings, and as low-molecular-weight PC-polyol precursors for polyurethane synthesis.[2] Of late, there has been an interest in preparing CO_2-derived polycarbonates that display high thermal resistance comparable to that of the widely applicable industrial standard BPA polycarbonate (T_g = 154 °C). We began work in this area when we first presented poly(indene carbonate) with a T_g of 138 °C as a result of its fused cyclopentene and benzene ring in the polymer backbone (Figure 1).[3,4] Lu and co-workers then described the preparation of CO_2 copolymers with 3,5-dioxaepoxides in which their use of 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO), in particular, gave the respective polycarbonate, PCXC with a T_g of 140 °C.[5]

The copolymerization of indene oxide with CO_2 proved to be a challenge. Our initial attempts with the (salen)Co^{III}-2,4-dinitrophenoxide catalyst, **1** (Figure 2) along with an onium salt cocatalyst at its normal working temperature range (25–40 °C) was met with the production of only the entropically favored product, *cis*-indene carbonate.[3] After lowering the temperature to 0 °C, a polymer selectivity of ~60% was observed with very low TOFs (2 h^{-1}). The tendency to produce the cyclic byproduct is enhanced for epoxides with a π system near the methine carbon as a result of a resonance-stabilized transition state that provides a lower barrier for polymer backbiting, as seen through computations.[6] The use of a bifunctional (salen)Co^{III} catalyst, **2**, then proved fruitful in producing PIC with high selectivity (>99%) at 25 °C.[4] The ammonium side arm of **2** prevents disassociation of the growing anionic polymer chain, keeping it closer to the metal center via electrostatic interactions. This encourages long-chain propagation, averting the detrimental polymer backbiting process leading to cyclic carbonates.[1k] Furthermore, the built-in cocatalyst helps increase the activity at lower loadings along with the thermal stability of the complex. This gave us PIC in higher MWs with M_n reaching 10 000 g/mol. The catalytic activity still remained low, with TOFs of no more than 12 h^{-1}.

We felt the need to improve upon the results described above and decided to look for other aromatic epoxides that could fare well in the catalysis. Our focus then shifted to 2,3-epoxy-1,2,3,4-tetrahydronaphthalene or 1,4-dihydronaphthalene oxide (DNO). There were a few reasons that made DNO an appropriate monomer for the next study: (1) The aromatic ring is one carbon away from both of the methine carbons, which will diminish the electronic effects that lead to polymer backbiting. (2) DNO can be viewed as a benzene fused with a cyclohexene oxide; cyclohexene oxide selectively produces the copolymer because it has a large activation barrier

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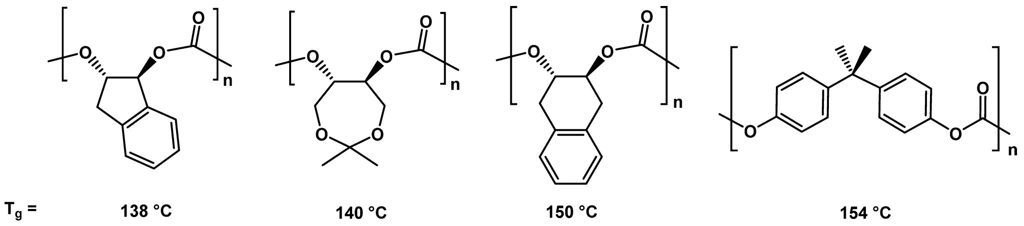


Figure 1. (left to right) CO_2-derived PCs: poly(indene carbonate); PCXC; poly(1,4-dihydronaphthalene carbonate); and the industrial PC derived from phosgene, BPA polycarbonate.

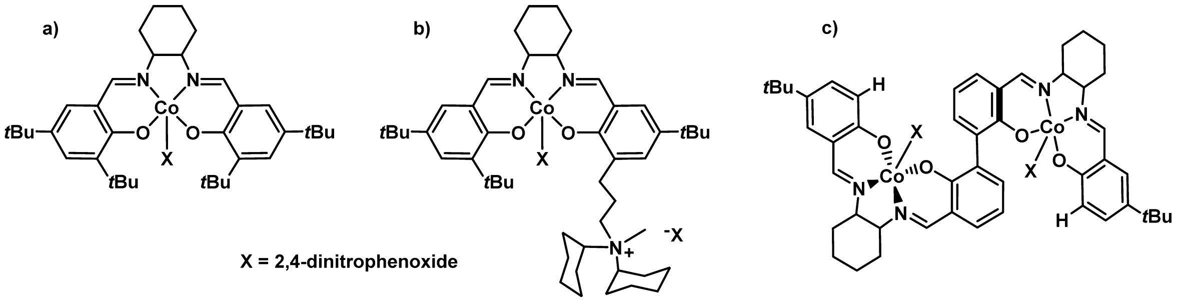
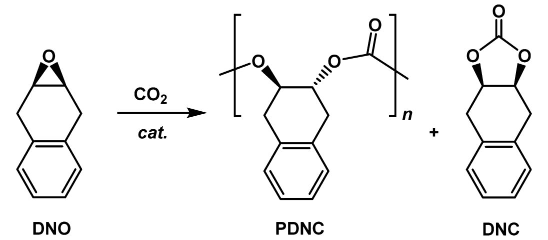


Figure 2. Cobalt(III) catalysts: (a) (salen)Co^{III}-2,4-dinitrophenoxide, **1**; (b) bifunctional (salen)Co^{III}, **2**; and (c) biphenol-linked dinuclear Co^{III} complex, **3**.

for making cyclic carbonate;[6,7] hence, DNO could have an analogous property. (3) The resulting polymer could display a higher glass transition temperature than PIC as a result of its bulkier backbone.

We had previously worked with DNO as early as 2004, at which time we communicated the crystal structure of *cis*-1,4-dihydronaphthalene carbonate (DNC) and showed this cyclic carbonate to be the only isolable product from the catalysis of CO_2 with DNO using a (salen)Cr^{III} catalyst.[8] We have now reexamined this reaction with various chromium(III) catalysts and report here the successful preparation of poly(1,4-dihydronaphthalene carbonate), PDNC (Scheme 1). Parallel to our efforts, Lu and co-workers have very recently communicated their preparation of the same copolymer by employing a dinuclear cobalt(III) catalyst, **3** (Figure 2c).[9] They show high-molecular-weight isotactic PDNC to exhibit a T_g of 150 °C, very close to that of BPA polycarbonate (Figure 1). Their work also substantiates our further findings regarding a strong steric influence from the catalyst when copolymerizing a large monomer such as DNO which is described in detail (vide infra).

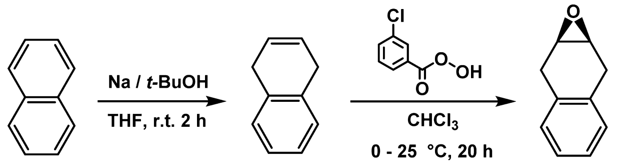
Scheme 1. CO_2 Coupling Reaction with DNO



■ RESULTS AND DISCUSSION

Naphthalene, the readily available polycyclic aromatic hydrocarbon occurring as the largest component in coal tar (10 wt %),[10] can be reduced to 1,4-dihydronaphthalene and epoxidized to 1,4-dihydronaphthalene oxide (DNO) suitable for CO_2 coupling (Scheme 2).[11,12] A pale yellow solid that melts above 40 °C, DNO would require the addition of a solvent such as CH_2Cl_2 or toluene for the copolymerization reaction with CO_2 at ambient temperature, as was previously done with indene oxide (MP = 32 °C). Surprisingly, catalysts **1** and **2** showed no sign of a coupling reaction to produce either cyclic or polycarbonates. Long reaction times (up to 5 days), varying reaction temperature (0−25 °C with solvents; neat reactions with **1** and **2** at 45 and 70 °C, respectively), and varying cocatalyst initiators (2,4-dinitrophenoxide, azide, chloride, trifluoroacetate) under pressures of 25−35 CO_2 bar proved ineffective at our typically employed catalyst loading of 0.2%. However, Lu and co-workers show the catalysis to occur at a higher loading of **1** (0.5%), albeit with a TOF of only 15 h^{-1}.[9] Hence, it was decided to examine the catalysis using the Cr^{III} complexes.

Scheme 2. Preparation of DNO from Naphthalene



Gratifyingly, a reaction at 70 °C with (salen)Cr^{III}Cl, **4** (Figure 3), and an equivalent of PPNCl (PPN = bis(triphenylphosphine)iminium) as cocatalyst at a loading of 0.2% provided poly(1,4-dihydronaphthalene carbonate), PDNC, with a polymer selectivity of 78% and a TOF of 8 h^{-1} (Table 1, entry 4). The working temperatures for chromium catalysts are higher than cobalt (≥70 °C), so the use of solvents can be abated because DNO is a liquid at that temperature. Solvents are known to lower both the conversion and polymer selectivity due to epoxide dilution, and it is also seen here (Table 1, entries 1−3). When the more active bifunctional (salen)Cr^{III} catalyst, **8**, is used at a loading of

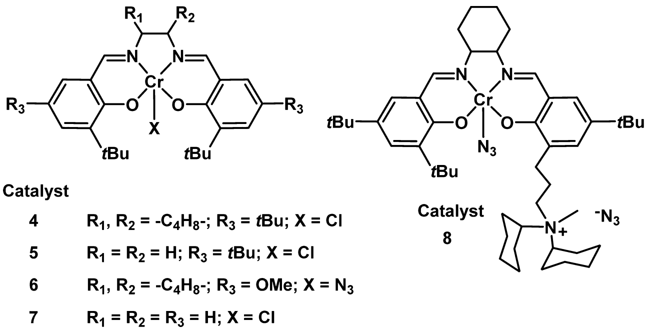


Figure 3. (Salen)Cr^{III} catalysts used for CO_2/DNO coupling.

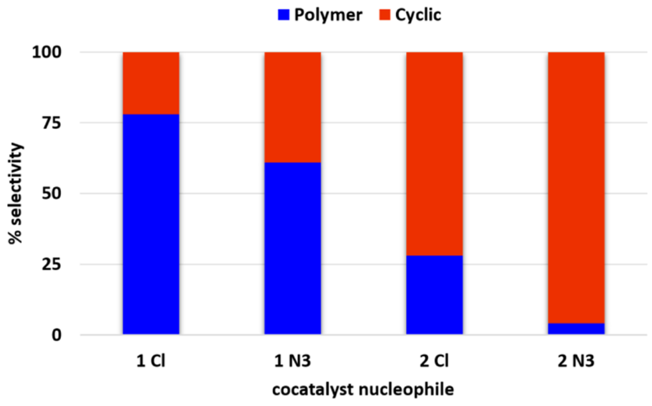


Figure 4. Cocatalyst effect on product selectivity for CO_2/DNO coupling with (salen)CrCl, **4**.

0.13%, both higher polymer selectivity (93%) and TOFs (29 h^{-1}) are observed at 100 °C (Table 1, entry 12). A molecular weight of 6700 g/mol displaying a T_g of 136 °C was noted. Lowering the loading of **8** to 0.1% failed to produce higher MWs (Table 1, entry 13).

Cocatalyst Effects. We noticed an odd occurrence for the catalysis carried out with the binary salenCr^{III} catalyst/cocatalyst systems. Specifically, there seemed to be a large cocatalyst effect on the resulting product ratio based on the identity of the nucleophile and the amount utilized in the reaction (Table 1, entries 4−7). More PDNC was obtained when employing PPNCl vs $PPNN_3$ but changing to 2 equiv of the cocatalysts drastically increased the cyclic product with less than 5% polymer selectivity seen for two azides. Figure 4 depicts this observation more clearly. The role of a cocatalyst is to help initiate the ring-opening of an epoxide, and the addition of 2 equiv can also help accelerate the copolymerization, as was shown previously in a CHO/CO_2 study.[13] On the basis of the data at hand, we believe this trend originates as a result of a steric hindrance from the catalyst. It is now much harder for a bulkier DNO, vs a PO or CHO molecule, to access the metal center surrounded by four *t*-butyl groups in catalyst **4**. In fact, we have shown that a highly sterically encumbered catalyst bearing six *t*-butyl groups, including on the R_1 and R_2 positions of the salen backbone, shows little activity for CHO/CO_2 coupling.[14]

Here, when a DNO molecule gets ring-opened and carboxylated, the nucleophilic cocatalysts become increasingly competitive to coordinate and displace the one-mer unit rather than allow chain propagation via ring-opening of another epoxide due to unfavorable steric effects (Figure 5). The displaced one-mer unit can then backbite to give cyclic carbonate. This would explain the observed higher cyclic carbonate selectivity for the more nucleophilic azide cocatalyst versus chloride, a better leaving group, if backbiting were the exclusive reason. Prior results showing only cyclic carbonate formation may well be due to the use of 2.25 equiv of *N*-methyl imidazole (NMI), another good nucleophile (Table 1, entry 8).[8] On the other hand, the lack of catalysis with the cobalt complexes in our earlier attempts can presumably be due to its smaller metal center, more effectively shrouded by the salen ligand toward an approaching DNO molecule. The effective ionic radii of six-coordinate, low-spin Co^{III} and Cr^{III} are 54.5 and 61.5 pm, respectively.[15] Considering spherical volume, which is of a cubic function, Co^{III} is nearly a third smaller than the size of Cr^{III}. Although we note that increased catalyst loading plays a role in enhancing polymer production, as seen with both the Co^{III} catalyst, **1** (our results vs Lu's, vide supra), and the Cr^{III} catalysis (Table 1, entries 3 vs 7), the trend in

Table 1. Copolymerization of 1,4-Dihydronaphthalene Oxide and CO_2 with (salen)Cr^{III} Catalysts

	cat./cocat. [loading][a]	CO_2 (bar)	*T* (°C) [solvent][b]	time (h)	% conv.[c]	% PDNC[c]	TOF (h^{-1})[d]	M_n (g/mol)[e] [theor M_n][f]	PDI	T_g (°C)
1[g]	**4**/$TBAN_3$ [1:2:250]	45	70 [toluene]	6	37	47	16	2600 [7900]	1.06	119
2	**4**/$TBAN_3$ [1:2:250]	30	70 [CH_2Cl_2]	6	36	45	15			
3	**4**/$TBAN_3$ [1:2:250]	25	70	6	47	67	19	4000 [14 800]	1.06	128
4	**4**/PPNCl [1:1:500]	30	70	15	24	78	8			
5	**4**/$PPNN_3$ [1:1:500]	30	70	14	32	61	11	3500 [17 500]	1.07	
6	**4**/PPNCl [1:2:500]	30	70	14	41	28	15			
7	**4**/$PPNN_3$ [1:2:500]	30	70	14	54	4	20			
8[h]	**5**/NMI [4:9:1000]	55	80 [toluene]	12	20	< 1	3			
9	**6**/PPNCl [1:1:500]	30	70	14	25	76	9	3000 [18 200]	1.09	
10	**6**/$PPNN_3$ [1:2:500]	30	70	18	36	5	10			
11	**7**/PPNCl [1:1:500]	30	70	14	17	60	6			
12	**8** [1:750]	25	100	15	58	93	29	5300; 6700[i] [76 200]	1.11	130; 136
13	**8** [1:1000]	25	100	7	17	83	23	3000 [25 300]		

[a] Loading ratio depicts catalyst/cocatalyst/DNO, respectively and catalyst/DNO for last two entries. [b] 1 mL solvent per 1 g of DNO, except entry 8, which used 1.6 mL Tol/g DNO. [c] Determined using ^1H NMR spectroscopy. [d] Turnover frequency of DNO to products (PDNC and DNC) as determined *via* ^1H NMR spectroscopy. [e] Determined via gel permeation chromatography in THF. [f] Theoretical M_n = (*M*/*I*) × (% conversion) × (MW of DNC). [g] $TBAN_3$ used for its solubility in toluene [h] Data based on isolated yields from ref 8. NMI is *N*-methyl imidazole. [i] A low-MW polymer sample was recovered from the CH_2Cl_2/MeOH workup solution after initial precipitation of the high-MW polymer.

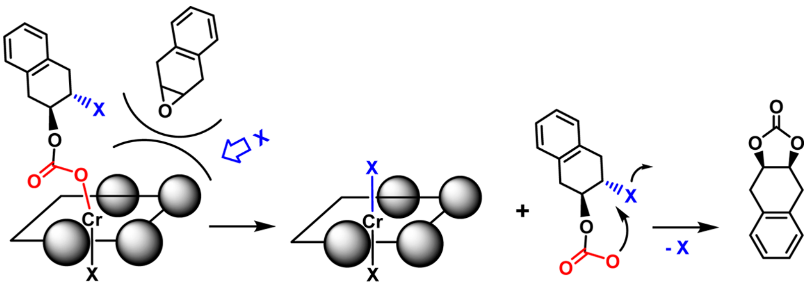


Figure 5. Cartoon representation of the increased nucleophilic competition of a cocatalyst due to the steric hindrance felt by an approaching DNO. The gray spheres depict the *t*-butyl groups of catalyst **4**.

product selectivity because of steric hindrance cannot be ruled out.

Steric Effects. If the observed cocatalyst effect is indeed a reflection of the sterics around the metal center, then a better polymer selectivity and activity should be achieved by using (salen)Cr^{III} complexes bearing smaller substituents. For this purpose, we used catalyst **6** with smaller methoxy groups in the 5-positions with an equivalent of PPNCl, and the resulting polymer selectivity was now 15% higher when compared with catalyst **4** (Table 1, entry 9 vs 5; note: catalyst **6** has a coordinated azide), but if the cocatalyst was switched to 2 equiv of PPNN$_3$, it quickly shut down polymer production, with PDNC selectivity no greater than 5% (Table 1, entry 10). This indicated that the change in the steric environment is slight when reducing the substituent size in the 5-positions alone. Catalyst **7** with hydrogens vs methoxy groups and an ethylene vs cyclohexene backbone did not show any improvements, either (Table 1, entry 11). Replacing all four *t*-butyls with smaller substituents is not a good choice because it results in a poorer solubility of the chromium catalyst in the epoxide medium, thus leading to poorer activity.[14] Facing this limitation with (salen)Cr^{III} complexes, we chose to look at a different ligand altogether for optimizing the polymerization condition.

A tetramethyltetraazaannulene chromium complex, (tmtaa)-Cr^{III}Cl, **9** was shown to be highly active (TOF = 1500 h^{-1}) for the copolymerization of CHO with CO$_2$ by our group in 2007.[16] The less sterically congested and planar motif of this azaannulene ligand seemed to be a suitable candidate in producing PDNC with high selectivity (Figure 6). Upon performing a catalytic run at 0.2% loading of **9** with an equivalent of PPNCl, we found nearly 90% polymer selectivity with three times the activity of the binary (salen)Cr^{III} complex, **3** (Table 2, entry 1 vs Table 1, entry 4). The resulting PDNC also had a MW of 5800 g/mol with a T_g of 136 °C, comparable to that obtained with the bifunctional (salen)Cr^{III} catalyst, **8**. A series of experiments varying the cocatalyst and their loading with **9** further showed that although there was more cyclic product with 2 equiv, it was not a drastic change, as seen with catalyst **4** (Table 2, entries 2–5; Figure 7). Lower catalyst loadings (0.13%) show reduced activity but maintain moderate to good polymer selectivity (Table 2, entries 6, 7). These results suggest that as we expand our epoxide toolset toward bulkier monomers for producing polycarbonates with high thermal resistance, the catalysts we employ need to evolve, as well, particularly taking steric positioning into consideration.

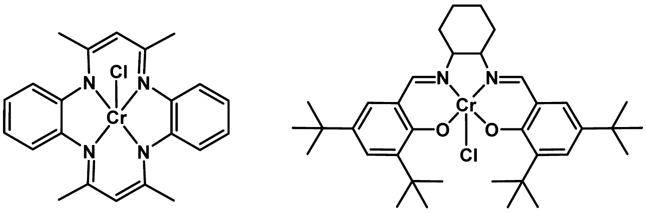


Figure 6. Tetraazaannulene-derived catalyst, (tmtaa)Cr^{III}Cl, **9** (left), vs the sterically crowded catalyst, (salen)Cr^{III}Cl, **4** (right).

With the use of their biphenol-linked dinuclear Co^{III} catalyst, **3**, Lu and co-workers were able to prepare PDNC with high activity and selectivity. For example, at a loading of 0.2% and 2 equiv of PPNDNP as cocatalyst, they observed a TOF of 125 h^{-1}, yielding only the copolymer after 4 h at 25 °C.[9] A TOF of 900 h^{-1} was also noted for a 30 min reaction at an elevated temperature of 50 °C. In a prior work, they have shown the copolymerization with catalyst **3** proceeds via an intramolecular bimetallic mechanism.[17] This involves an alternating chain growth through the carbonate attack of the copolymer from one metal center onto an activated epoxide on the next metal. This cooperative nature gives **3** its superior catalytic rate and polymer selectivity as compared with a monometallic mechanism, as seen with **1**. Important to note here is the ability of **3** to accommodate both the growing polymer chain and an epoxide displaying its open environment with very little steric impact. In fact, on the basis of experimental and theoretical results, it was observed that the substituent size on the dinuclear Co^{III} complex and the width of catalytic cavity (influenced by the linker utilized) clearly dictated the activity of CHO/CO$_2$ copolymerization (Figure 8).[17] The *t*-butyl groups in the 5-positions are found to be remote from the catalytic centers, whereas when the substituents on the 3-positions are changed from an H to *t*-butyl to adamantyl groups, the TOFs drop from 1409 to 1269 to 173 h^{-1}. The activities mentioned go along with the biphenol linker, which displays a fairly wide cavity arising from the large endo phenol−phenol dihedral angle of about 140° (Co−Co distance ≈ 8.2 Å). When a binaphthol bridge is used instead, the opening of the catalytic cavity is reduced as a result of an endo naphthol−naphthol dihedral angle of no more than 90° (Co−Co distance ≈ 6.5 Å). Consequently, the resulting activity is poorer with TOFs around 50 h^{-1} for PCHC production.[17]

Computational Insight. Additional understanding on the formation of the 1,4-dihydronaphthalene carbonates was obtained with the help of computations. Thermodynamically, CHO and DNO behave similarly, having nearly the same calculated enthalpies and free energies of reactions with CO$_2$ to give poly- and cyclic carbonates (Scheme S1). When it comes to kinetics, PCHC has the highest free energy barrier among all polycarbonates toward carbonate backbiting to produce *cis*-CHC.[6] Indeed, very little cyclic byproduct is seen experimentally, which has made CHO an initial benchmark for

Table 2. Copolymerization of DNO and CO_2 with (tmtaa)Cr^{III}Cl, **9**

	cat./cocat. [loading][a]	CO_2 (bar)	T (°C)	time (h)	% conv.[b]	% PDNC[b]	TOF (h^{-1})[c]	M_n (g/mol)[d] [theor M_n][e]	PDI	T_g (°C)
1	**9**/PPNCl [1:1:500]	30	70	14	63	89	23	5800 [53 400]	1.11	136
2	**9**/PPNCl [1:1:500]	30	70	7	40	84	28	4700 [31 000]	1.10	
3	**9**/$PPNN_3$ [1:1:500]	30	70	7	42	85	30	4600 [34 100]	1.10	
4	**9**/PPNCl [1:2:500]	30	70	7	44	58	32			
5	**9**/$PPNN_3$ [1:2:500]	30	70	7	55	71	39	4500 [36 500]	1.11	
6	**9**/PPNCl [1:1:750]	30	70	14	27	80	15	3800 [31 226]	1.09	
7	**9**/$PPNN_3$ [1:1:750]	30	70	14	23	47	13			

[a] Loading ratio depicts catalyst/cocatalyst/DNO, respectively. [b] Determined using ^1H NMR spectroscopy. [c] Turnover frequency of DNO to products (PDNC and DNC) as determined via ^1H NMR spectroscopy. [d] Determined via gel permeation chromatography in THF. [e] Theoretical M_n = (M/I) × (% conversion) × (MW of DNC).

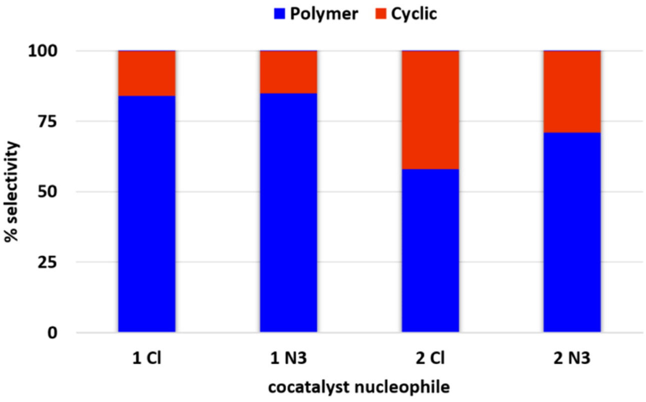


Figure 7. Cocatalyst effect on product selectivity for CO_2/DNO coupling with (tmtaa)CrCl, **9**.

testing new catalysts for CO_2 copolymerization reactions. This is the result of an endergonic conformational change of its cyclohexene backbone from a chair to boat conformation (Δ = 4.7 kcal/mol) prior to achieving its backbiting transition state (Δ = 21.1 kcal/mol). This gives PCHC an overall barrier of 25.8 kcal/mol; other aliphatic polycarbonates exhibit 18−20 kcal/mol.[6] A sketched representation of the conformations are indicated in Figure 9. In the case of PDNC, the benzene ring fused to the cyclohexene ring reduces the latter's flexibility such that the only energy minimum conformation observed is boat-shaped. Hence, the free energy barrier for carbonate backbiting is lower for PDNC at 22.7 kcal/mol. This lower barrier may also explain why some *cis*-DNC (the only isomer seen experimentally) is produced even under the best catalytic conditions thus far with Cr^{III} complexes that work at higher temperatures.

A Bifunctional Azaannulene Ligand. The highest molecular weight of PDNC isolated in the current study is 6700 g/mol, displaying a T_g of 136 °C. Comparing the T_g values to those of low-MW PIC shows PDNC to be greater by ∼5 °C because of its increased bulk (Figure 10). The true measure of a polymer's thermal transition is past 10 000−15 000 g/mol, whereby its T_g becomes independent of the MW. Using catalyst **3**, this was shown to be 150 °C for PDNC.[9] With a similar interest in making higher MWs using Cr^{III} complexes, we began to look into newer and effective ligand designs. We decided to prepare a tetraazaannulene ligand with ammonium side arms, much like the salen bifunctional ligands. With less sterics and the added benefit of the pendant arms that prevent polymer backbiting, a Cr^{III} or even a Co^{III} complex bearing this ligand could prove to be an effective catalyst in producing high-MW PDNC.

Another advantage of a bifunctional tetraazannulene chromium(III) catalyst would be the range of epoxides that could now be utilized. Previously, we had shown catalyst **9**,

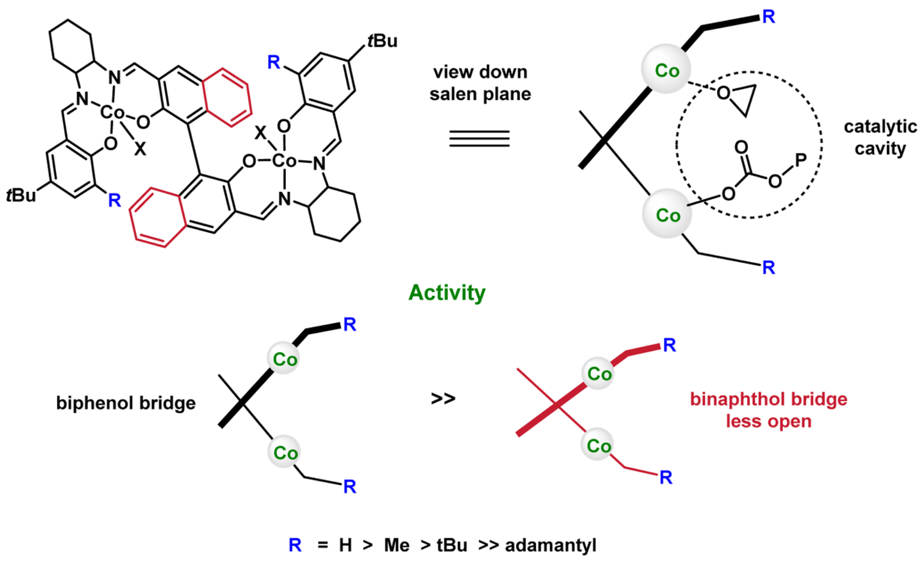


Figure 8. Illustration of dinuclear Co^{III} complexes and its catalytic cavity (top). Higher activity observed when the cavity is more open and bearing smaller substituents.[17]

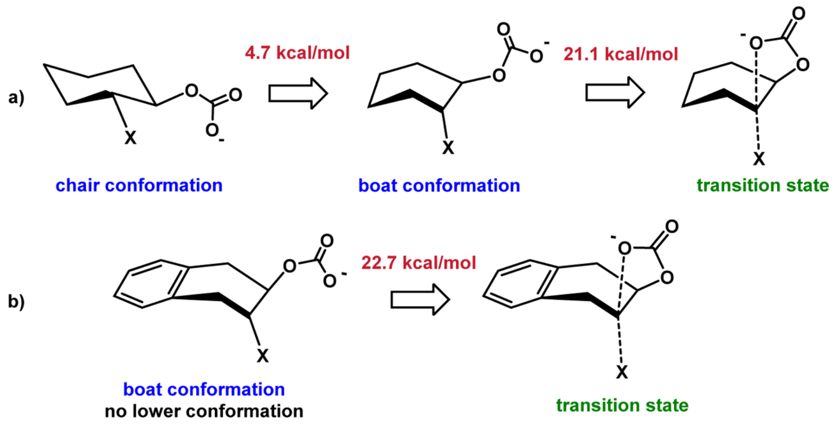


Figure 9. Sketched representations: (a) Total energetic barrier of 25.8 kcal/mol for carbonate backbiting of PCHC from its lowest energy chair conformation. (b) With the boat conformation as the energy minimum, PDNC has a lower backbiting barrier of 22.7 kcal/mol. Free energies calculated using the CBS-QB3 composite method.[6] The anionic polymer chain, X, is modeled as methyl carbonate.

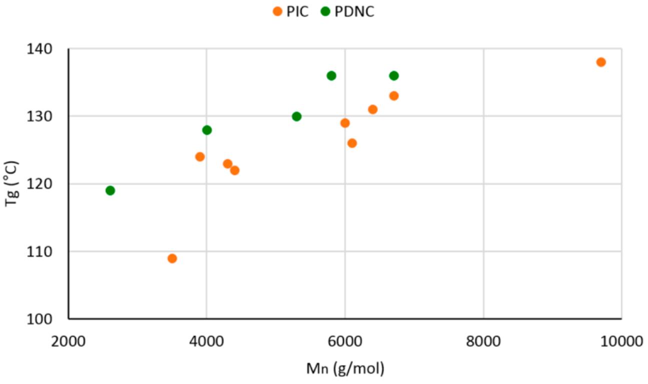


Figure 10. T_g vs MW comparison of PDNC and PIC.

(tmtaa)$Cr^{III}Cl$, to be successful in producing polycarbonates with high selectivity and activity for CHO and 4-vinyl-CHO, but other epoxides such as PO and styrene oxide (SO) produced mostly the cyclic carbonate product.[16] This is a result of a more electron-rich metal center bearing four nitrogen donors. The growing anionic polymer chain is thus not as tightly bound, leading to a higher propensity to backbite. Electrostatic interactions with the ammonium side arms of a bifunctional catalyst can then mitigate this process. CHO is unaffected because it is reticent toward backbiting, as described in the previous section.

The first step toward preparing this new ligand involves the synthesis of a dihydroxytetraazaannulene, dhtaa, compound via the ring-opening and condensation reaction of 3,4-dihydro-2*H*-pyran-5-carbaldehyde and *o*-phenylenediamine (OPD) as shown previously by Breitmaer and co-worker (Scheme 3).[18] This results in a tetraazaannulene bearing two propyl arms with an OH group at the end, which can be further transformed for our purposes. Mesylation of this dihydroxy compound provides the dimesylatetetraazaannulene (dmtaa) in near quantitative yields. We found the use of ionic liquids, 1-butyl-3-methylimidazolium chloride and bromide salts, ([BMIM]X; X = Cl, Br) to successfully convert the dimesylate compound into the dichloro- and dibromotetraazaannulene, dctaa and dbtaa, as per the protocol developed by Chae and co-workers for transformation of sulfonate esters.[19] Single crystals of dctaa suitable for X-ray diffraction were grown from the slow cooling of a hot MeCN solution; its structure is shown in Figure 11. The final step involves the alkylation of NEt_3 in DMF with the dihalo compounds. Although we did not have success with the dichloro derivative, reaction with the dibromo compound proceeds smoothly, giving us a diammoniumtetraazaannulene (dataa) ligand in a high yield.

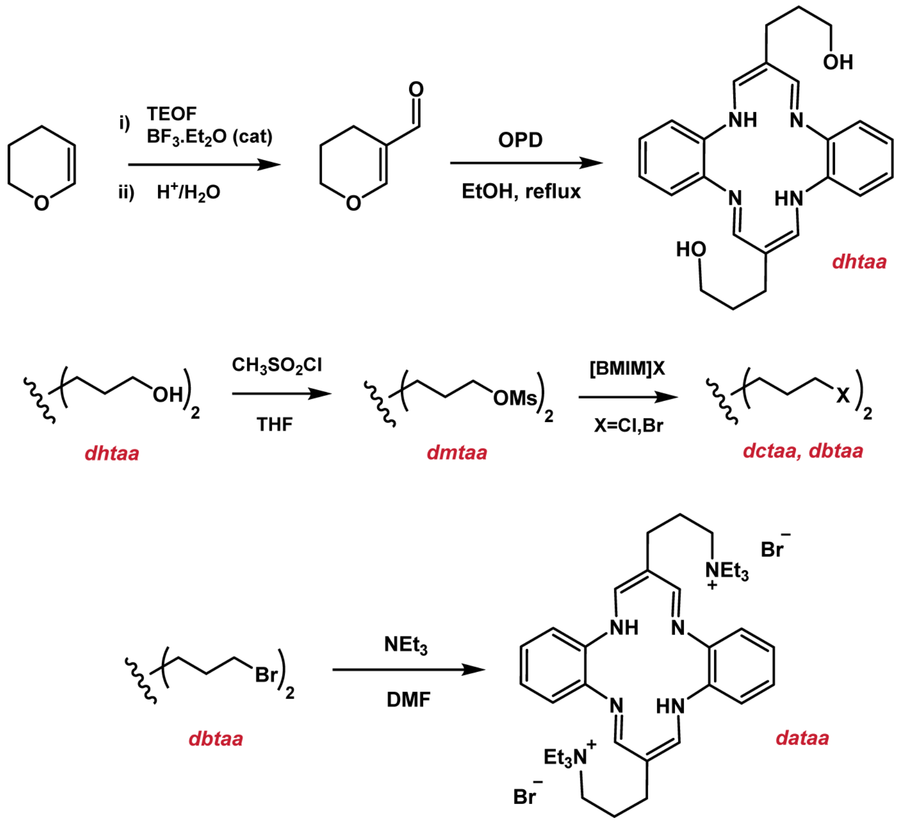
The overall synthesis is relatively quick (5 steps) without any tedious purification as otherwise seen with the preparation of the asymmetrical bifunctional salen ligands.[20] The presence of more than one pendant ammonium arm on the ligand for a bifunctional catalyst has been previously shown to be highly active, as well.[21] This diammonium ligand, dataa, has been fully characterized; a preliminary crystal structure is presented in Figure S1. There is also room for modification of the length of the pendant arms (furan vs pyran derived aldehyde), the electronics (substituted OPDs), and the bulkiness of the onium salt (various tertiary amines), which will make it desirable for optimization studies. Our preliminary work shows the coordination of dataa onto a cobalt center by refluxing with $Co(OAc)_2 \cdot 4H_2O$ in DMF to give the (dataa)Co^{II} complex. Thus far, we have been unable to oxidize the (dataa)Co^{II} complex by various means; however, further work on the preparation of Co^{III} and Cr^{III} complexes and their use in catalysis for copolymerizing various epoxides with CO_2 is being pursued.

CONCLUDING REMARKS

Our renewed interest in exploring the CO_2 coupling reaction with 1,4-dihydronaphthalene oxide was in part due to the demanding but nevertheless a successful catalytic copolymerization observed with a related bicyclic monomer, indene oxide.[3,4] Results from the latter also indicated advantages of using 1,4-dihydronaphthalene oxide over indene oxide. An earlier attempt at making poly(1,4-dihydronaphthalene carbonate) involved the use of a binary (salen)Cr^{III} catalyst/cocatalyst system optimized at that time for making poly(propylene carbonate) and poly(cyclohexene carbonate).[1f,8] This mostly afforded the cyclic byproduct, *cis*-1,4-dihydronaphthalene carbonate, which we assumed to be the result of an electronic difference when compared with its simpler analog, cyclohexene oxide, that primarily provides the copolymer. With a more detailed study, we have shown here that poly(1,4-dihydronaphthalene carbonate) can indeed be produced with high selectivity using chromium(III) catalysts.

The formation of the copolymer is highly dependent on the steric environment provided by the ligands in a catalyst. A

Scheme 3. Five-Step Synthesis of a Diammonium Tetraazaannulene Ligand (dataa)



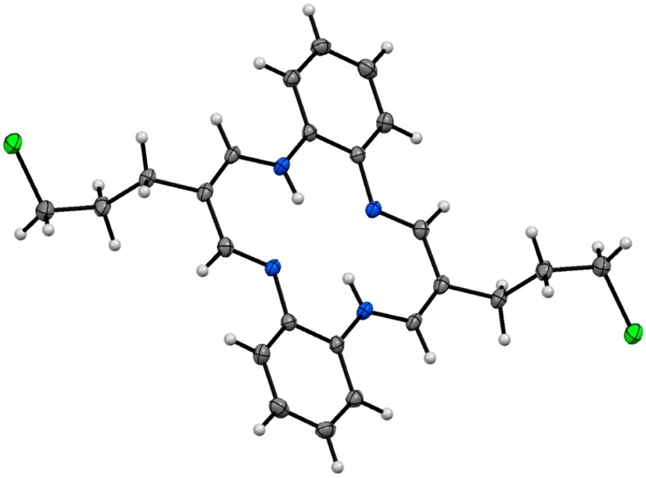


Figure 11. X-ray crystal structure of dctaa. Thermal ellipsoids shown at 50% probability level.

bulkier monomer, 1,4-dihydronaphthalene oxide, now faces a large steric hindrance at a Cr^{III} center surrounded by a salen ligand bearing four *t*-butyl groups. As a result, its chain growth is inhibited because of an increased preference for displacement by the coordination of the smaller cocatalysts. The displaced anionic polymer chain then proceeds to backbite, yielding cyclic carbonate. Increasing the cocatalyst ratio to 2 equiv or employing more nucleophilic anions produces cyclic carbonates almost exclusively.

The use of a less sterically demanding tetramethyltetraazaannulene catalyst, (tmtaa)Cr^{III}Cl, increases the catalytic activity to 3-fold (23 vs 8 h^{-1}) in comparison with (salen)Cr^{III}Cl, with polymer selectivity reaching 90%. The competitive binding of the cocatalyst is also subdued, reflecting the more spacious catalyst. When utilizing a bifunctional salenCr^{III} complex, copolymer selectivity of >90% is achieved, but the molecular weights remain low, around 6500 g/mol. Computations indicate that poly(1,4-dihydronaphthalene carbonate) is somewhat more susceptible to carbonate backbiting, with a lower energy barrier (22.7 kcal/mol) than poly(cyclohexene carbonate) (25.8 kcal/mol). This is a result of the fused benzene ring of the former, which prevents the cyclohexyl ring from adopting the lower-energy chair conformation.

We have also developed a new bifunctional tetraazaannulene ligand that can be easily prepared and further optimized. Supporting two pendant ammonium arms and having less steric hindrance with respect to salen, this ligand can yield a Cr^{III} or Co^{III} catalyst that could display enhanced activity and polymer selectivity. This may then prove fruitful for producing high-molecular-weight polycarbonates from sterically demanding monomers, such as 1,4-dihydronaphthalene oxide, and realizing high thermally resistant properties in CO$_2$ derived polycarbonates.

■ EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Tetrahydrofuran was purified by an MBraun Manual Solvent Purification system packed with Alcoa F200 activated alumina desiccant. Triethylamine (EMD) was freshly distilled from CaH$_2$ prior to use. Naphthalene (Aldrich); *t*-BuOH (Alfa Aesar); *m*-chloroperoxybenzoic acid, mCPBA

(Aldrich); 1-butyl-3-methylimidazolium chloride and bromide salts, [BMIM]X, X = Cl, Br (Alfa Aesar); methanesulfonyl chloride (Acros); and dry *N*,*N*-dimethylformamide (Aldrich) were used as received. (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butyl salicylidene)-1,2-cyclohexane diaminochromium(III) chloride, (salen)CrCl, was purchased from Strem. Other (salen)CrCl derivatives;[14] (salen)CoDNP;[22] bifunctional salen Cr^{III} and Co^{III} catalysts,[20] [PPN]DNP[23] and $[PPN]N_3$,[24] were prepared as per the literature. The tetramethyltetraazaannulene Cr^{III} complex, (tmtaa)CrCl, was synthesized per a modification of Cotton's procedure.[16] 6,13-Bis(3-hydroxypropyl)-dibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine or dihydroxytetraazaannulene (dhtaa) was prepared starting from 3,4-dihydro-2*H*-pyran.[18,25] Research grade 99.999% carbon dioxide supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Airgas. The CO_2 was further purified by passing through two steel columns packed with 4 Å molecular sieves that had been dried under vacuum at ≥200 °C.

Measurements. NMR spectra were recorded on either a Varian INOVA 300 or 500 MHz spectrometer. Infrared spectra were obtained on a Bruker Tensor 27 FTIR spectrometer. Elemental analyses were determined by Atlantic Microlab (Norcross, GA). Molecular weight determinations (M_n and M_w) were carried out with a Malvern Modular GPC apparatus equipped with ViscoGEL I-series columns (H + L) and a model 270 dual detector consisting of RI and light scattering detectors. T_g's were measured using a Mettler Toledo polymer DSC equipped with a liquid nitrogen cooling system and 50 mL/min purge of dry nitrogen gas. Samples (~8 mg) were weighed into 40 μL aluminum pans and subjected to two heating cycles. The first cycle covered the range from 25 to 200 °C at 10 °C/min and was then cooled to 0 °C at −10 °C/min. Midpoint T_g data were obtained from the second heating cycle, which ranged from 0 to 300 °C at a heating rate of 5 °C/min.

2,3-Epoxy-1,2,3,4-tetrahydronaphthalene or 1,4-Dihydronaphthalene Oxide (DNO). The first step involving reduction of naphthalene was prepared per the literature:[11] Sodium (11.6 g, 0.504 mol) as small cut and flattened pieces was added over a period of 15 min to a solution of naphthalene (25.0 g, 0.195 mol) in THF (250 mL). After stirring for 30 min, the blue solution was chilled in an ice bath and treated dropwise with *t*-BuOH (47 mL, 0.491 mol) dissolved in THF (50 mL) over the next 20 min. The solution was allowed to stir for 2.5 h, and the THF was removed in vacuo after removing the excess sodium pieces. The resulting pinkish red oil was taken into 150 mL of Et_2O and washed with distilled H_2O (5 × 100 mL) until the organic layer turned clear yellow. *Caution*: The first addition of water needs to be done very slowly as the flask heats up, causing Et_2O to boil when the salt dissolves. The organic layer was further washed with brine (3 × 50 mL) and dried over anhydrous $CaCl_2$ by stirring overnight. Note: $CaCl_2$ also removes excess *t*-BuOH. Filtration and removal of Et_2O give a viscous yellow oil. ^1H NMR on the crude product showed ~80% 1,4-dihydronaphthalene, and the rest is made up of the 1,2-isomer and tetralin. The product composition varies depending on the amount of excess sodium and reaction time involved, but the crude product can be used for the next step without additional purification.

Epoxidation of 1,4-dihydronaphthalene was carried out in a manner similar to a literature preparation:[12] mCPBA (17.5 g, 0.101 mol) was added slowly to an ice-cooled solution of 1,4-dihydronaphthalene (16 g, 0.123 mol) in $CHCl_3$ (100 mL). It was then treated with a saturated aqueous $NaHCO_3$ solution (80 mL), and the biphasic medium was allowed to stir at room temperature for 4 h. The solution was chilled again and treated with additional $CHCl_3$ (100 mL) and mCPBA (14.0 g, 0.081 mol). Continued stirring for 17 h resulted in the complete conversion of starting material, as seen via TLC. The reaction mixture was transferred to a 1000 mL Erlenmeyer flask, and the acid generated was neutralized by addition of more $NaHCO_3$ solution (70 mL), stirring until bubbling ceased. Excess mCPBA was then destroyed with a saturated sodium thiosulfate solution (150 mL, added in 50 mL increments and tested with starch paper). Finally, distilled water (50 mL) was added, the mixture was stirred, and the organic layer was allowed to separate. The organic layer was further washed with water (3 × 70 mL) in a separation funnel, dried with anhydrous $MgSO_4$, and filtered to give a clear yellow solution. Following removal of solvent, the crude epoxide was purified via flash chromatography with gradient elution of ethyl acetate in hexane on a silica column using Teledyne ISCO's CombiFlash R_f 150. DNO was obtained as a pale yellow solid (14 g) with a total yield of about 50%. Characterizations match that previously reported.[8] mp = 40−42 °C. NMR in $CDCl_3$: ^1H δ 3.15−3.40 (m, 4H, CH_2), 3.50 (s, 2H, CH), 7.05−7.27 (m, 4H, aromatic H); $^{13}C\{^1H\}$: δ 29.7, 51.7, 126.5, 129.2, 131.4. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.25; H, 6.90.

Poly(1,4-dihydronaphthalene carbonate) (PDNC): Representative Coupling Reaction of CO_2 and 1,4-Dihydronaphthaleneoxide. A stir bar, (tmtaa)CrCl (3.0 mg, 7.0 μmol), PPNCl (3.8 mg, 6.6 μmol), and 1,4-dihydronaphthalene oxide (0.500 g, 3.42 mmol, 500 equiv) were added to a 12 mL stainless steel autoclave reactor that had been previously dried at 150 °C for 6 h. The reactor was pressurized to 27 bar and heated to 70 °C in an oil bath with magnetic stirring. After 7 h, the reactor was cooled in an ice bath and depressurized slowly. Sublimated epoxide was observed on the inside of the reactor cap, but it was very minimal (10−30 mg). A ^1H NMR spectrum of the reaction mixture was taken immediately. The crude mixture was dissolved in CH_2Cl_2 and added dropwise to an acidified methanol (10% HCl) solution to precipitate the polymer. The polymer was collected via filtration and purified twice more by precipitation from CH_2Cl_2/MeOH. The pale yellow to off-white PDNC was dried in vacuo before further analysis by GPC and DSC. Note: A 50/50 mix of C_6D_6 and $CDCl_3$ was used to obtain a well-resolved NMR spectrum to determine the polymer/cyclic carbonate ratio in the crude mixture. The peaks of both species overlap in $CDCl_3$, making it harder to do so, and using only C_6D_6 underestimates the amount of polymer because it is not completely soluble in benzene. See Figure S2. NMR in $CDCl_3$: ^1H δ 3.05 (br s, 2H, CH_2), 3.40 (br s, 2H, CH_2), 5.23 (br s, 2H, CH), 7.05−7.31 (m, 4H, aromatic H); $^{13}C\{^1H\}$: δ 31.3, 73.7, 126.5, 128.6, 131.7, and 153.5; ^1H NMR ($C_6D_6/CDCl_3$): δ 2.75 (br s, 2H, CH_2), 3.13 (br s, 2H, CH_2), 5.06 (br s, 2H, CH), 6.70−7.00 (m, 4H, aromatic H). IR (CH_2Cl_2): 1753 cm^{-1}. Anal. Calcd for $(C_{11}H_{10}O_3)_n$: C, 69.46; H, 5.30. Found: C, 69.36; H, 5.48.

***cis*-1,4-Dihydronaphthalene Carbonate (*cis*-DNC).** Pure *cis*-DNC was obtained after removal of the acidified methanol filtrate from a polymer workup under reduced pressure and recrystallization of the residue from methanol/hexane. Characterization of the white product matches that previously described.[8] mp = 155 °C. ^1H NMR in $CDCl_3$: δ 2.90 (s, 2H, CH_2), 3.15 (s, 2H, CH_2), 5.19 (s, 2H, CH), 7.20−7.30 (m, 4H, aromatic *H*); in $C_6D_6/CDCl_3$: δ 2.22 (s, 2H, CH_2), 2.62 (s, 2H, CH_2), 4.36 (s, 2H, *CH*), 6.75−7.05 (m, 4H, aromatic *H*). IR in CH_2Cl_2: 1807 (s), 1794 (sh); in THF: 1811 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.47; H, 5.49.

Synthesis of 6,13-Bis(3-methanesulfonylpropyl)-dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine or Dimesylatetetraazaannulene (dmtaa). A 500 mL round-bottom flask was charged with dhtaa (0.955 g, 2.36 mmol) and dry THF (250 mL). To this red mixture, NEt_3 (2.0 mL, 14 mmol) followed by methanesulfonyl chloride (1.0 mL, 13 mmol) were added using a syringe. The reaction was stirred at room temperature until complete conversion of the dihydroxy compound was observed via TLC (24−32 h). The solvent was removed under reduced pressure, and the crude mixture washed thoroughly with distilled H_2O (150 mL) to remove triethylammonium chloride. Further washings using MeOH (50 mL) and Et_2O (50 mL) and drying in vacuo gives the orange-red product (1.28 g, 97%). ^1H NMR (DMSO-d_6): δ 1.89 (p, 4H, $-CH_2-$), 2.32 (t, 4H, $-CH_2-$), 3.19 (s, 6H, CH_3), 4.24 (t, 4H, $-CH_2-$), 6.90 (m, 4H, aromatic H), 7.28 (m, 4H, aromatic H), 7.85 (m, 4H, *CH*), 13.61 (t, 2H, *NH*). Poor solubility precluded the collection of ^{13}C NMR. ESI-MS (*m*/*z*): 561.20 (MH^+). mp = 198 °C (dec). Anal. Calcd for $C_{26}H_{32}N_4O_6S_2$: C, 55.70; H, 5.75; N, 9.99. Found: C, 54.79; H, 5.86; N, 9.55.

Synthesis of 6,13-Bis(3-chloropropyl)-dibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine or Dichlorotetraazaannulene (dctaa). A 30 mL tall vial with a stir bar was packed with dmtaa (0.600 g, 1.07 mmol), followed by [BMIM]Cl (1.92 g, 11.0 mmol) on top. The vial was placed in a 90 °C oil bath to let the ionic liquid melt (∼15 min). Stirring was then begun, and after 24 h, TLC showed complete conversion of the dimesylate to the dichloro compound. Note: If needed, some acetonitrile can be used to rinse down the sides of the vial during the course of the reaction to achieve complete mixing after lowering the temperature to 80 °C. The resulting brown sludge was taken into CH_2Cl_2 (125 mL), washed with 20% aqueous NaCl solution (3 × 100 mL), and dried with magnesium sulfate. The solvent was then removed in vacuo, and the residue was washed with Et_2O (75 mL) to give a brown product after drying in vacuo (0.325 g, 69%). NMR in $CDCl_3$: ^1H δ 1.95 (p, 4H, $-CH_2-$), 2.41 (t, 4H, $-CH_2-$), 3.63 (t, 4H, $-CH_2-$), 6.92 (m, 4H, aromatic H), 7.05 (m, 4H, aromatic H), 7.63 (m, 4H, *CH*), 13.71 (t, 2H, *NH*); $^{13}C\{^1H\}$: δ 29.8, 34.5, 43.9, 106.0, 113.5, 124.3, 137.5, 147.0. ESI-MS (*m*/*z*): 441.18 (MH^+). mp = 224 °C (dec). X-ray quality crystals were grown via slow cooling of a hot MeCN solution.

Synthesis of 6,13-Bis(3-bromopropyl)-dibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine or Dibromotetraazaannulene (dbtaa). Prepared in a manner similar to that for dctaa described above by using [BMIM]Br. A brownish red product was isolated in >60% yield. Characterizations matched those previously reported.[26] ^1H NMR (DMSO-d_6): δ 2.02 (p, 4H, $-CH_2-$), 2.34 (t, 4H, $-CH_2-$), 3.55 (t, 4H, $-CH_2-$), 6.91 (m, 4H, aromatic H), 7.28 (m, 4H, aromatic H), 7.85 (m, 4H, *CH*), 13.61 (t, 2H, *NH*). Anal. Calcd for $C_{24}H_{26}Br_2N_4$: C, 54.36; H, 4.94; N, 10.57. Found: C, 55.22; H, 5.23; N, 10.42.

Synthesis of 6,13-Bis[3-(*N*,*N*,*N*-triethylammonium)-propyl)]-dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine Dibromide or Diammoniumtetraazaannulene (dataa). A 100 mL Schlenk flask charged with dbtaa (0.365 g, 0.688 mmol) was treated with 50 mL of DMF and NEt_3 (10 mL, 72 mmol) and placed in an oil bath set at 50 °C. The dark red solution was allowed stir for 3 days, after which the solvents are removed under reduced pressure. The resulting red residue was washed down the sides of the flask with CH_2Cl_2 (<5 mL) and treated with THF (50 mL). It was stirred for a few minutes, filtered, and dried in vacuo to give the product as a red solid (0.462 g, 92%). NMR in DMSO-d_6: ^1H δ 1.17 (t, 18H, NCH_2CH_3), 1.81 (m, 4H, $-CH_2-$), 2.27 (t, 4H, $-CH_2-$), 3.13 (m, 4H, $-CH_2-$), 3.25 (q, 12H, NCH_2CH_3), 6.93 (m, 4H, aromatic H), 7.31 (m, 4H, aromatic H), 7.91 (m, 4H, *CH*), 13.64 (t, 2H, *NH*); $^{13}C\{^1H\}$: δ 7.31, 23.7, 28.8, 52.2, 55.6, 106.7, 114.1, 124.4, 136.9, 148.0. ESI-MS (*m*/*z*): 286.22 [$(M - 2Br^-)^{2+}$]. Anal. Calcd for $C_{36}H_{56}Br_2N_6 \cdot 3H_2O$: C, 54.96; H, 7.94; N, 10.68. Found: C, 54.12; H, 7.29; N, 10.54. X-ray quality crystals were grown via vapor diffusion of methyl *t*-butyl ether into a MeOH solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01375.

ORTEP of the preliminary structure of dataa, calculated enthalpies of reaction, and NMR spectra of PDNC and DNC (PDF)

X-ray structural data for dctaa (CIF)

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Notes

The authors declare no competing financial interest.

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