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Conformationally Flexible Dimeric Salphen Complexes for Bifunctional Catalysis

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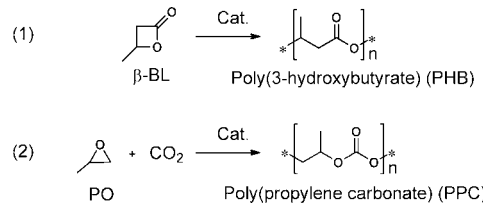
Abstract: Appropriate modification of the salphen ligand allows an easy modular design of flexibly linked dimeric salphen species and their complexes, which can act as bifunctional catalysts. A series of chromium salphen systems including monomeric compound and dimers with different spacer lengths were tested for their catalytic performance in β-butyrolactone polymerization and CO_2/propylene oxide copolymerization toward biodegradable materials. The results clearly show an enhancement in activity upon dimerization, thus underlining the role of bifunctional catalysis in the studied processes and extending the possible strategies for improvement of catalysts in these reactions.

Among metal-based catalysts, complexes with Schiff base ligands belong indisputably to a very important group because of their multifunctionality and versatility.[1] In this regard, salen and salphen derivatives show appropriate activity in oxidation of alkenes and other substrates,[2] Diels−Alder, asymmetric hetero-Diels−Alder, and Michael additions,[3] stereoselective formation of cyanhydrines,[4] stereo- and regioselective ring-opening of epoxides and their copolymerization with CO_2,[5] and ring-opening polymerization (ROP) of β-butyrolactone and lactide.[6] The latter polymerization and copolymerization reactions are of high interest, as they utilize renewable resources like CO_2 and lead to biodegradable materials having a potential to compete with pure oil-based polymers like polypropylene.

One of the proposed mechanisms for the ROP of β-butyrolactone (β-BL) as well as CO_2/propylene oxide (PO) copolymerization using Cr^{III}(salphen) complexes implies a transition state, where the growing chain at one metal center interacts with the activated monomer at another metal center, giving high-molecular-weight polymers.[6a,5e] This kind of bifunctional catalysis is, in general, a widespread reaction mechanism that is currently gaining more and more consideration.[7] As shown in the case of salens, the activity of catalyst in such reactions can be increased by utilization of flexibly linked dinuclear species featuring a higher local concentration of catalytic centers.[5d] To the present, a great number of reports dealing with preparation of di- and multinuclear salens has been published.[8] However, there is still a lack of knowledge on the synthesis and catalytic properties of dimeric salphens. Here, we report on a new synthetic approach to bimetallic salphen systems for bifunctional catalysis which show the effect of dimerization in the ROP of β-BL as well as for CO_2/PO copolymerization reactions (Scheme 1).

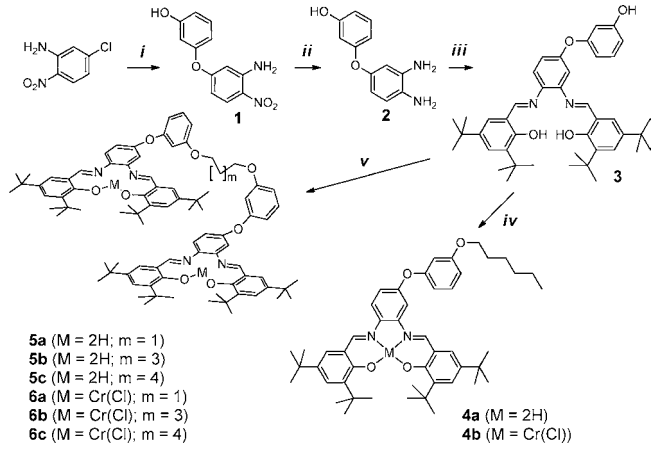
The salphen ligands are typically prepared under conditions where the condensation of amine and aldehyde occurs in fast equilibrium. That is why a stepwise condensation of two different salicylaldehydes with phenylenediamine toward unsymmetrical

Scheme 1. ROP of β-BL (1) and CO_2/PO Copolymerization (2)



salphens yields, in contrast to salens, a nearly statistical mixture of products, unless the synthesis is metal-templated.[9] This makes further derivatization toward dimeric systems extremely complex. For this reason, bridging two salphen units via the phenylenediamine backbone seems to be more affordable. Up to now, only a few dimeric salphen systems, all rigidly bridged via the backbone, have been described in the literature.[10] However, intramolecular interaction of the two catalytic centers in these complexes is unlikely due to their long metal−metal distance. Earlier we successfully demonstrated a modular approach to dimeric phthalocyanines flexibly interlinked by a bis(*O*,*O*′-resorcinato)hexamethylene spacer.[11] Here a similar approach has been adopted to prepare dimeric salphen systems.

Scheme 2. Synthesis of Dimeric and Monomeric Salphen Ligands[a]



[a] Conditions: (i) NaH, resorcin in DMF; (ii) Pd/C, H_2 in ethanol; (iii) 3,5-di(*tert*-butyl)salicyl aldehyde in ethanol; (iv) 1-bromohexane and Cs_2CO_3 in acetonitrile (**4a**) followed by metalation (**4b**); (v) 0.5 equiv of α,ω-dibromoalkane and Cs_2CO_3 in acetonitrile followed by metalation (see experimental details in Supporting Information).

The synthetic route presented in Scheme 2 is completely chromatography-free, granting an advantage for high-scale applications. The readily accessible intermediate **3** is a suitable building unit for modular design of dimeric salphens, where the length of the spacer and the nature of the metal can be easily varied.

The alkylation of **3** with excess of 1-bromohexane or with 0.5 equiv of α,ω-dibromoalkanes proceeds selectively at the −OH group of the resorcin moiety. In the dimerization reactions, which require a longer period of time for completion, partial dehydrohalogenation of α,ω-dibromoalkanes and marginal hydrolysis of salphens lead to minor byproducts. Dimeric ligands **5a**−**c** of good purity are readily obtained by reprecipitation from acetonitrile due to a strong difference in solubility of bridged and monomeric ligands in this solvent. Metalation of **5a**−**c** with $CrCl_2$ according to a modified literature procedure gives the corresponding Cr^{III} complexes **6a**−**c** in quantitative yields.[12]

These complexes were first tested for their catalytic performance in the synthesis of poly(3-hydroxybutyrate) (PHB) via ROP of β-BL (Scheme 1). Since the substitution pattern of the salphen ligand plays a crucial role in the activity of the catalyst and changes the characteristics of produced polymer,[13a] an analogous monomeric Cr(III) complex, **4b**, was synthesized for comparison. This highlighted the dimerization effect in the obtained polymerization results (Table 1).

Table 1. Results of Polymerization (100 °C, 1:1000 Cr/β-BL Ratio) of β-BL with Different Complexes

entry	cat.	polymerization time, h	yield of PHB, %[a]	TOF, h^{-1} [b]	M_w, kg/mol	PD
1	**4b**	5	6	12	20	2.0
2	**4b**	24	30	12	25	2.6
3	**6a**	5	35	70	71	1.9
4	**6a**	15	86	57	107	1.9
5	**6a**	24	>99	41	108	1.9
6	**6b**	5	28	56	68	2.2
7	**6c**	5	31	62	70	2.1

[a] Determined by integration of signals in ^1H NMR spectrum. [b] Turnover frequency calculated per Cr center; molar TOFs for dimeric catalysts are twice higher.

Indeed, despite the slightly reduced activities of these new complexes and the lower M_w of the resulting polymers as compared to the best Cr^{III}(salphen)-based catalysts published earlier,[6a] the effect of dimerization on ROP of β-BL in the systems studied herein is clear. The productivity of dimeric complexes is practically independent of the length of the spacer (entries 3, 6, and 7), giving ca. 5 times higher yield and higher molecular weight of PHB in comparison with the monomeric complex (entry 1).

On the other side, polymerization with the complexes studied herein leads to PHB of a relatively narrow polydispersity (PD) close to 2, whereas PHBs of similar molecular weight obtained previously with monomeric Cr^{III}(salphens) display PD in the range of 4−8 and even higher (see also Figure S12 in Supporting Information).[6a,13a] In addition, in ^{13}C NMR spectra of PHBs prepared here, the ratio of *i*- to *s*-signals in the carbonyl region, being a measure of the polymer tacticity,[13b] is below 1.2. This is much lower than in the case of the previously reported Cr^{III}(salphen) catalysts, where it reaches nearly 2.[6a] Investigations to get reasonable experimentally supported explanations of these facts are in progress in our laboratory.

Bifunctional salen catalysts were described recently for the copolymerization of CO_2 and PO to give aliphatic polycarbonate (PPC) (Scheme 1).[14] The similarity of the latter reaction to ROP of β-BL, as well as a high value of PPC for applications and utilization of carbon dioxide, encouraged us to examine the dimeric and monomeric Cr(III) complexes **6c** and **4b** for their activity in such a copolymerization.

As seen from Table 2, the activity of monomeric and dimeric catalysts is comparable at a catalyst/PO ratio of 1/2000 (entries 8 and 9), though there is a drastic influence of dilution on the polymerization results. The monomeric complex **4b** loses its activity in terms of much lower TOF and polymer molecular weight (entry 10), whereas in the case of catalysis with dimeric complex **6c**, these characteristics remain practically unaffected (entry 11). This is consistent with our previous considerations on the mechanism of the CO_2/PO copolymerization.[5e] Additionally, the formation of cyclic propylene carbonate (cPC) becomes noticeable only for monomeric complex upon dilution (entry 10), which can be attributed to an enhanced dissociation of the coordinated polymer chain end from the catalyst, followed by back-biting.[5e] Investigation of polymerization using dimeric catalysts or **4b** in the presence of cocatalysts is in progress.

Table 2. Copolymerization of Propylene Oxide with CO_2 in the Presence of Monomeric and Dimeric Cr^{III}(salphen) Catalysts (60 °C, 40 bar CO_2, 24 h)

entry	cat.	[PO]/[Cr][a]	PO/CO_2[b]	cPC, %[c]	TOF, h^{-1}[d]	M_w, kg/mol	PD
8	**4b**	2000	1.7	<1	67	70	2.0
9	**6c**	2000	2.3	0	49	40	1.8
10	**4b**	20000	1.3	20	7	9	2.0
11	**6c**	20000	2.4	<2	82	46	3.3

[a] Molar ratio of propylene oxide to chromium. [b] Molar ratio of propylene oxide to CO_2 in the polymer (see Supporting Information for details). [c] Weight part of cyclic propylene carbonate. [d] Turnover frequency calculated for consumption of PO per Cr center; molar TOFs for dimeric catalysts are twice higher.

In conclusion, a reliable and versatile synthetic approach toward dinuclear salphen systems was developed. Using the corresponding Cr(III) complexes, an increased activity upon dimerization was demonstrated for such actually important reactions as polymerization of β-butyrolactone and copolymerization of CO_2 with PO, which underlines the role of bimetallic processes in mechanisms of both reactions.

The developed synthetic strategy can be easily adjusted for the preparation of heteronuclear complexes and other multifunctional systems, opening a wide area for different applications. This issue is currently under investigation in our group.

Supporting Information Available: Detailed description of synthesis and characterization of new products and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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