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Carbon Dioxide Fixation

Aldimine-Thioether-Phenolate Based Mono- and Bimetallic Zinc Complexes as Catalysts for the Reaction of CO_2 with Cyclohexene Oxide

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Abstract: A synthetic strategy for the preparation of a new class of ligands is introduced. The bis(aldimine-thioether-phenolate) ligands bear two anionic oxygen donors from phenolate moieties, two neutral sulfur donors and two neutral nitrogen donors belonging, respectively, to thioether and aldimine functionalities. The so designed OSNNSO ligands show two coordinative pockets and thus should be able to host two metallic centers. Instead, the aldimine-thioether-phenolate OSN ligands are tridentate ligands which may form monometallic complexes. Two OSNNSO and one OSN ligands of this class, have been synthesized. Satisfyingly, by direct reaction of the ligands with one or two equivalents of the zinc precursor, the corresponding bimetallic Zn(II) complexes were prepared from the bis(aldimine-thioether-phenolate) ligands, while the monometallic zinc complex was prepared from the tridentate ligand. These zinc amido complexes act as single component catalysts in the reaction of CO_2 with cyclohexene oxide by furnishing polycyclohexene carbonate, while adding PPNCl as cocatalyst to the reaction medium, cyclohexene carbonates were obtained as the main products.

Introduction

The presence of CO_2 in the atmosphere makes possible life on Earth. On the other hand, its uncontrolled growth, mainly due to human activities, is causing several problems to the whole ecosystem. For this reason, the fixation of massive quantities of CO_2 as a C1 building block into useful products is a challenging goal.[1] The reaction with highly energetic molecules allows to overcome the high thermodynamic stability of CO_2. In particular, the relief of ring strain associated with epoxides is the driving force for chemical conversion of CO_2 into cyclic carbonates and/or polycarbonates.[2] To date, polycarbonates made from carbon dioxide have been mainly used as binders, sacrificial materials and as polyols in the manufacturing of polyurethane; while cyclic carbonates find applications as non-protic polar solvents, electrolyte in lithium ion batteries and as precursors for the synthesis of drugs and polymers.

The formation of both products requires the presence of a catalyst to reduce the energy demand of the whole process.[3] The behaviour of a homogeneous catalyst basically depends on the metal and on the ancillary ligand, which remains bound to the metal through the whole catalytic cycle and allows to modify the reactivity of the catalyst. Inexpensive and biorelevant metals, such as zinc,[4] constitute a valid choice to obtain catalysts to be used in sustainable processes. As for the ancillary ligand, salen ligands show several advantages since they are easy to synthesize, cheap and may be easily sterically and electronically modified.[3b,3c]

Salen-type zinc complexes have been reported by some authors as active catalysts for the production of cyclic carbonates.[3c,5] On the other hand, polycarbonate synthesis has been obtained by employing bimetallic zinc complexes bearing different classes of ligands. Starting from seminal works of Coates which showed, for β-diiminate zinc complexes, the fundamental role of a binuclear transition state to obtain the polycarbonate products,[6] a number of different dizinc complexes active in the fixation of CO_2 in polycarbonates have been reported in the literature.[7–9]

With the aim to combine the advantages of salen ligands and zinc metal in a new catalytic system potentially active in the production of polycarbonates, we tried to synthesize bimetallic salen-based zinc complexes by increasing the length of the bridge between the two nitrogen atoms of the ligand skeleton, a strategy which worked well with aluminum complexes bearing salen,[10a,10b] salan[10c] and also salalen ligands.[10d] Unfortunately, in the case of the zinc complexes, the monometallic derivative was always obtained, reasonably because zinc centers in the dimetallic complexes would be tricoordinated while the monometallic derivatives fix the zinc metal in a tetracoordinate environment.[11] Following this reasoning we designed a new class of ligands which resemble salen ligands, thus preserving some of their advantages, yet present two additional sulfur atoms as neutral donors.

In this paper we describe the synthetic strategy conceived for the preparation of these new bis(aldimine-thioether-phenol-

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ate) OSNNSO ligands and the corresponding aldimine-thioether-phenolate OSN ligands, the synthesis and the characterization of the corresponding zinc complexes and, finally, catalytic experiments employing the zinc complexes in the reaction of CO_2 with cyclohexene oxide under different reaction conditions.

Results and Discussion

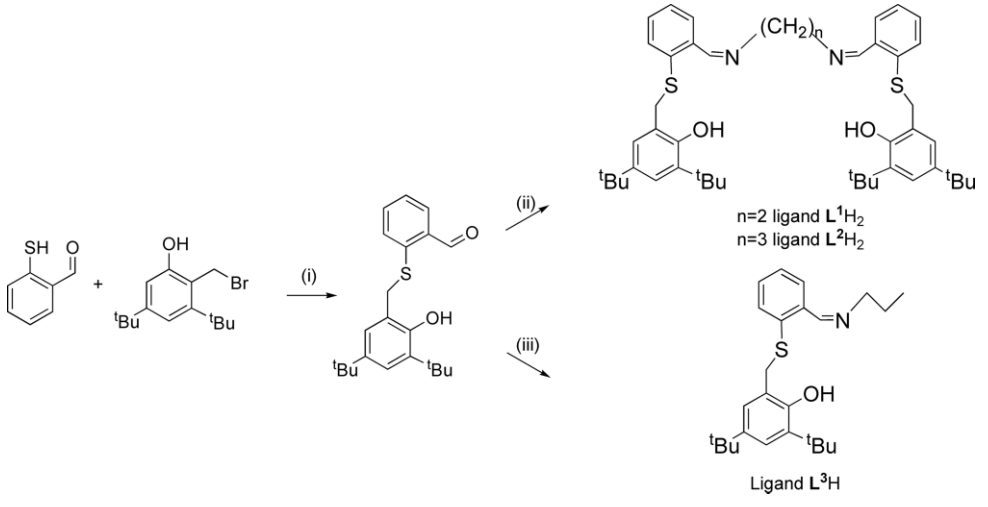
A three step procedure (Scheme 1) was designed to prepare the new class of OSNNSO ligands showing two anionic oxygen donors from phenolate moieties, and four neutral donors: two sulfur atoms and two nitrogen atoms belonging, respectively, to thioether and aldimine functionalities. The proper choice of the amine reagents in the third step allows the obtaining of tridentate OSN ligands by the same synthetic strategy.

First, thiophenol, premixed with N,N,N′,N′-tetramethylethylenediamine (TMEDA), reacted with *n*-butyllithium giving the deprotonated product, which subsequently gave the 2-mercaptobenzaldehyde by reaction with dry dimethyl formamide in hexane as solvent.[12] The second step was the reaction of 2-mercaptobenzaldehyde with 2-(bromomethyl)-4,6-di-*tert*-butylphenol, purposely synthesized,[13] using dry dimethyl formamide as the solvent. Finally, the desired ligands were obtained by condensation of two equivalents of the 2-(3,5 di-*tert*-butyl-2-hydroxybenzyl) sulfanyl benzaldehyde (Supporting Information Figures S1–S2) with the opportune diamine in dry acetonitrile. The so designed bis(aldimine-thioether-phenolate) ligands include two coordinative pockets and thus should be able to host two metallic centers. Obviously, to achieve the cooperative action of the two metal centers, their distance is a critical parameter. For this reason, in the first instance, we chose two diamines with a different length of the alkylene chain between the nitrogen atoms: The ligand precursor $\mathbf{L^1}H_2$ is based on ethylenediamine while the ligand precursor $\mathbf{L^2}H_2$ is based on 1,3-propanediamine. In the case of the tridentate ligand $\mathbf{L^3}H$ propanamine was used in the condensation reaction. The OSNNSO ligands and the OSN ligand were characterized by ^1H and ^{13}C NMR in dry C_6D_6 and by MALDI-ToF spectrometry (Supporting Information Figures S3–S11).

The ^1H NMR spectrum of $\mathbf{L^1}H_2$ (Supporting Information Figure S3) shows: a singlet for the protons of the hydroxyl groups at 9.08 ppm, a singlet at 8.17 ppm due to the imine protons, and six signals with predictable multiplicity between 7.45 and 6.43 ppm for the aromatic protons. The methylene protons bound to the sulfur (SCH_2Ar) and to the nitrogen (NCH_2) were observed as two singlets, each integrating for 4 protons, respectively at 3.96 ppm and 3.40 ppm. Finally, two singlets, each integrating for 18 protons, were observed at 1.72 and 1.30 ppm for the protons of the *tert*-butyl groups. As expected, the ^1H NMR spectrum clearly indicated a high symmetry for the described ligand. The number of the signals observed in the ^{13}C NMR spectrum was coherent with this observation (Supporting Information Figure S4). As for the ligand precursor $\mathbf{L^2}H_2$, both the ^1H and the ^{13}C NMR (Supporting Information Figures S6 and S7) suggest a situation similar to that observed for $\mathbf{L^1}H_2$, with a high symmetry in solution. A detailed assignment is reported in the Supporting Information part.

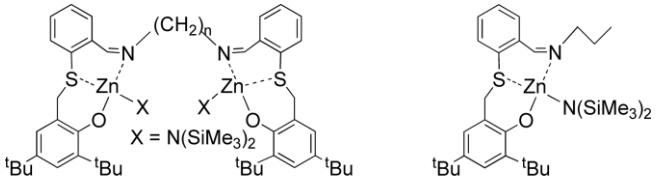
The MALDI-ToF spectrum of $\mathbf{L^1}H_2$ showed three signals (Supporting Information Figure S5): one at 737.417 *m/z* for the molecular ion, another one at 517.234 *m/z* indicating the fragment formed after the break of one of the S-CH_2 bond and, finally, a peak at 299.067 *m/z* indicating the fragment formed after the breaking of both the S-CH_2 bonds. A similar fragmentation pattern was observed for $\mathbf{L^2}H_2$ (Supporting Information Figure S8).

The synthesis of the zinc complexes **1–3** was accomplished by treating the ligands with 2 equivalents ($\mathbf{L^1}H_2$ and $\mathbf{L^2}H_2$) or one equivalent ($\mathbf{L^3}H$) of zinc bis[bis(trimethylsilyl)amide] in benzene. After two hours at room temperature the benzene was removed under vacuum and the product was washed with cold hexane to remove any impurities including the bis(trimethylsilyl) amine formed as a co-product. The zinc complexes **1–3** (Scheme 2) appeared as yellow powders (95 %, 91 % and 97 % yields, respectively). The three complexes were characterized by NMR (Supporting Information Figures S12–S25). The ^1H NMR



Scheme 1. Synthesis of the ligand precursors $\mathbf{L^1}H_2$, $\mathbf{L^2}H_2$ and $\mathbf{L^3}H$. (i) DMF; (ii) 0.5 equivalents of ethylenediamine or 1,3-propanediamine in CH_3CN; (iii) 1 equivalent of propanamine in CH_3CN.

spectrum of complex **1** (Supporting Information Figure S12) showed the disappearance of the OH signal of the ligand and the appearance of two new broad peaks, centered at 0.14 and 0.04 ppm and partially overlapping, integrating to a total of 36 protons, attributable to the protons of the silylamido groups. Moreover, the narrow singlets observed for the methylene protons bound to the sulfur (SCH_2Ar) and to the nitrogen (NCH_2CH_2N) in the ligand spectrum, split in three broad signals at 4.98, 4.51 and 3.57 ppm, integrating, respectively, for two, four and two protons (see assignment in Figure S12 of the Supporting information). All the other signals due to the protons of the ligand skeleton were easily recognizable, most of them shifting downfield with respect to the same signals in the spectrum of the free ligand.



Scheme 2. Zinc complexes **1–3** synthesized in this work.

A similar ^{1}H NMR spectrum was obtained for complex **2** (Figure S17 Supporting Information), but in this case, the peaks of all the methylene protons, bound to the sulfur (SCH_2Ar) or corresponding to the bridge between the nitrogen atoms ($NCH_2CH_2CH_2N$), appear as very broad signals in the range 2.5–4.5 ppm. Moreover, only one broad signal, at 0.08 ppm, was observed for the 36 protons of the silylamido groups.

These observations support, for both complexes, the coordination of two zinc centers to the anionic and neutral donors of the ligand, suggesting a tetravalent coordination sphere for both zinc centers, each of them resulting bound to: the oxygen of the phenolate, the sulfur donor, the nitrogen of the aldimine and the nitrogen of the silylamido labile ligand. The spectra also suggest that the symmetry of the ligands was retained upon the formation of the complexes, at least in solution.

On the other hand, the broad resonances observed for all the methylene protons in both spectra are consistent with the formation of fluxional species. For this reason, ^{1}H NMR spectra of both complexes were recorded at sub-ambient temperature in toluene-d8. In the ^{1}H NMR spectrum of complex **1** at –10 °C (see Figure S13 in the Supporting Information for the whole spectrum and Figure 1 for an enlargement of the range between 3 and 9 ppm) four sharp and well resolved signals, each integrating for two of the protons of the methylene groups, can be detected in the range 3.5–5.0 ppm. Accordingly, seven signals for the aromatic and imine protons, each integrating for 2H, are observable. This spectrum suggests that, at this temperature, the fluxional process becomes slower than the NMR timescale and that the symmetry of complex **1** is preserved.[14]

A well resolved ^{1}H NMR spectrum of complex **2** was recorded at –50 °C in toluene-d8 (see Figure S18 and S19 in the Supporting Information for the whole spectrum and for an enlargement of the range between 2.5 and 8.5 ppm). In this case, ten signals

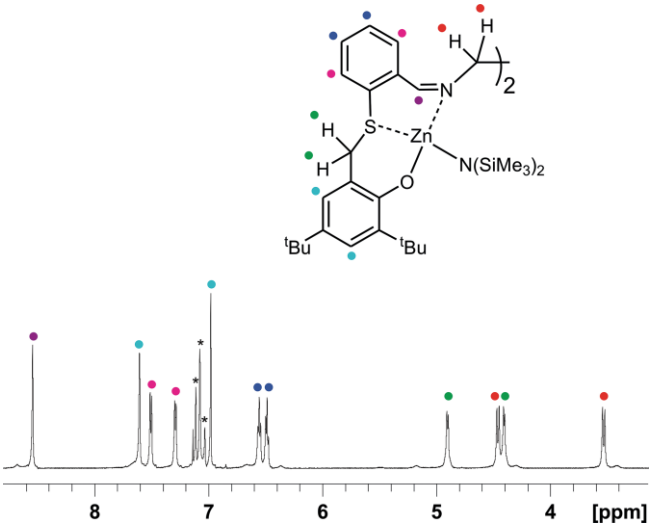


Figure 1. Enlargement of ^{1}H NMR spectrum (600 MHz, tol-d8, –10 °C) of complex **1**. * denotes signals due to toluene-d8 protons.

are present for the methylene protons, among them the four doublets for the two AB patterns of the methylene protons bound to the sulfur (SCH_2Ar) are well recognizable (green circles in Figure S19). Coherently, in the aromatic region, different signals are observable for each proton (see, for example, the two peaks denoted with purple circles for the imine protons and the four signals denoted with light blue circles for the aromatic protons on the phenolate moieties). The whole picture suggests that, in the case of complex **2**, the symmetry is lost at low temperature.

Also in the case of complex **3**, the ^{1}H NMR spectrum (Supporting Information Figure S23) indicated the formation of the desired complex by the disappearance of the hydroxyl proton and the presence of a signal at high field, integrating for the 18 protons of the amido methyl groups and the presence of two broad signals around 3.5 and 4.0 ppm, each integrating to 2 protons, attributable to the methylene protons respectively bound to the sulfur and the nitrogen donors. For complex **3**, a well resolved spectrum was recorded at –40 °C in toluene-d8 (see Figure S24 and S25 in the Supporting Information for the whole spectrum and for an enlargement of the range between 1.4 and 8.0 ppm).

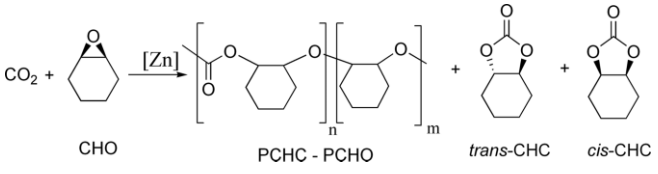
With these three new complexes in hand, their behavior as catalysts for the fixation of CO_2 in organic carbonates was studied.

Firstly, the dizinc complex **1** was tested in the reaction of carbon dioxide and cyclohexene oxide under different reaction conditions (Table 1). This reaction can give different possible products (see Scheme 3): namely, *cis*-cyclohexene carbonate (*cis*-CHC), *trans*-cyclohexene carbonate (*trans*-CHC) and poly(cyclohexene carbonate) (PCHC) eventually containing ether linkages (PCHO). The conversion of the epoxide was measured by ^{1}H NMR spectroscopy by integrating the signal at δ = 4.6 ppm (methine protons of both PCHC and *cis*-CHC), the signal at δ = 4.0 ppm (methine protons of *trans*-CHC) and the signal at δ = 3.5 ppm (methine protons of the ether linkages) with respect to the analogous protons of the CHO (δ = 3.1 ppm).

Table 1. CO_2/CHO reaction promoted by complexes **1–3**.

Entry[a]	Complex	Temp [°C]	Pressure [bar]	Time [h]	Conv[b] [mol-%]	PCHC	*Trans*-CHC	Ether linkages	$M_n^{GPC[c]}$ [kDa]	Đ[c]
1	**1**	80	30	16	10	97	3	<1	8.7	7.0
2	**1**	100	30	16	20	90	3	7	8.3	5.5
3	**1**	120	30	16	29	82	10	8	6.0	3.7
4	**1**	100	30	64	52	93	3	4	6.5	3.3
5	**1**	100	20	16	22	90	2	8	9.4	4.3
6	**1**	100	10	16	13	85	7	8	9.2	4.6
7	**2**	100	30	16	24	91	2	7	10.5	7.2
8	**3**	100	30	16	13	86	5	9	3.7	5.6
9[d]	**3**	100	30	16	26	86	5	9	15.4	7.8
10[e]	**1**	100	30	16	13	85	<1	15	4.5	5.9
11[f]	**1**	100	30	16	32	91	3	6	8.8	6.2

[a] General conditions: Complexes **1–3** = 19.8 µmol (0.05 mol-%), CHO = 40 mmol, (2000 equiv.). [b] The conversion and amount of CHC were determined by integration of methine peaks in the ^1H NMR spectra. [c] Determined by GPC, in THF, using polystyrene standards, for calibration. [d] Complex **3**: 39.6 µmol. [e] 0.05 mol-% of cyclohexane-1,2-diol (CHD) added in the reaction mixture. [f] Freshly bi-distilled CHO was used in this polymerization experiment.



Scheme 3. Possible products generated by the reaction of CO_2 with cyclohexene oxide (CHO).

The product ratio, corresponding to the reaction selectivity, was determined through high-resolution ^1H NMR spectra ($CDCl_3$, r.t., 600 MHz) after removing the residual CHO, by integrating the signals due to the methylene protons of the different products (see, for example, Figure S28 in the Supporting Information).[10d,15] The first reaction trials were carried out in neat CHO, by using complex **1** as a single component catalyst (i.e. no cocatalyst was added to the reaction mixture), at a low catalyst loading (0.05 mol-%) by varying reaction temperature and CO_2 pressure. In all cases poly(cyclohexene carbonate) was obtained as the main product with a selectivity depending on the experimental conditions. In addition, small percentages of ether linkages and *trans*-cyclohexene carbonate were found in the reaction mixture.

At 80 °C and under 30 atmosphere of CO_2 pressure, a conversion of 10 % was obtained (Table 1, entry 1). By increasing the reaction temperature, the conversion increased (cf entries 2 and 3 with entry 1) but at 120 °C an increase in the *trans*-CHC product was also observed. *Trans*-CHC are usually generated by back-biting reaction which can occur at the end of the free or metal-bound copolymer, a process that is usually accelerated at higher temperature.[2a]

Prolonging the reaction time, the conversion increased showing that catalyst **1** is still active after 64 h of reaction (entry 4).

Two catalytic reactions were carried out under 20 and 10 bar of CO_2 pressure at 100 °C. In these conditions, the conversions decreased with respect to the reaction carried out at 30 bar under the same reaction temperature (cfr entries 5 and 6 vs. entry 2) while the percentage of polycarbonate product decreases, mainly in favor of *trans*-CHC. Both effects can be reasonable attributed to the decrease in the concentration of CO_2 in solution.[2a]

The activity of complex **1** in the reaction of CO_2 with CHO can be expressed in terms of TOF (TurnOver Frequency) which is calculated as the mole epoxide converted to product, per mole metal per hour. From the results reported in Table 1, complex **1** showed TOF up to 36 h^{-1} under the explored conditions, indicating a moderate activity, according to the basis used by Coates and Moore.[3a]

Subsequently, complexes **2** and **3** were tested in the reaction of CO_2 with CHO under the same conditions of entry 2 (0.05 mol-% of catalyst, 30 atm of CO_2, 100 °C, 16 h). In both cases, polycyclohexene carbonate was the most abundant product (see entries 7 and 8), with complex **2** showing a double activity with respect to complex **3**. In order to have the same concentration of metallic centers for the mono- and bi-metallic complexes, another polymerization experiment (entry 9) was carried out by doubling the mole amount of complex **3**. Under these conditions, the activity of complex **3** was comparable to those obtained with both complexes **1** and **2** (cf entries 2, 7 and 9). This result suggests the absence of a cooperative effect in the case of the bimetallic complexes **1** and **2**, indicating that each metallic center works independently from the other one.

GPC analysis of the polycarbonates showed, in all cases, low molecular weights (M_n = 3.7-15.4 kDa) and broad molecular weight distributions (Đ = 3.3-7.8, see Figure S29 in the Supporting Information) which could indicate either the formation of multiple active centers and/or the occurrence of post-copolymerization reactions (such as hydrolysis, decarboxylation or other degradation).[16]

Accordingly, the MALDI-ToF spectra showed the presence of several molecular weight distributions. The MALDI-ToF spectrum of the PCHC obtained in entry 2 shows three main distributions centered around 1050, 3970 and 6100 Da (Supporting Information Figure S30). However each distribution is the result of the overlapping of several series. A careful analysis of the observed peaks was conducted allowing the identification of three different end groups, namely trimethylsiloxide, cyclohexanol and cyclohexenolate together with the presence of cyclic chains (Supporting Information Figure S31). In addition, three

other minor peaks were observed corresponding to the trimethylsiloxide, cyclohexanol and cyclohexenolate terminated chains with one additional cyclohexenoxide unit (that is, a missing carbon dioxide unit) in agreement with the presence of ether linkages observed in the NMR spectra.

As previously proposed in the literature, the reaction of the amido ligand with CO_2, followed by migration of a trimethylsilyl group and extrusion of trimethylsilylisocyanate, leads to the formation of trimethylsiloxide end groups (pathway A in Figure S32).[6b] The formation of cyclohexanol $H[OC_6H_{10}]_m[CO_2]_nOC_6H_{10}OH$ end groups has been previously ascribed to two different pathways. Either they can be due to the presence of cyclohexane-1,2-diol (CHD, produced by hydrolysis of CHO) which, acting as a chain transfer agent, leads to the formation of a diol initiating species (pathway B in Figure S32),[8d] or by the release of a CO_2 molecule from the polycarbonate through a mechanism generating cyclohexenolate $H[OC_6H_{10}]_m[CO_2]_nOC_6H_9$ and cyclohexanol end groups (pathway C in Figure S32).[16b] The observation of the cyclohexenolate end group in the MALDI-ToF spectrum supported the occurrence of the latter mechanism, yet the first mechanism cannot be ruled out. To get insight on the formation of cyclohexanol end group by reaction of the zinc center with CHD, a new polymerization experiment was carried out by adding one equivalent of CHD (vs. complex **1**) to the reaction mixture before the addition of CO_2 (entry 10 in Table 1). The MALDI-ToF spectrum of the polymer sample obtained in this experiment, compared with the spectrum of the reaction carried out under the same conditions but in the absence of the CHD (entry 10 vs. entry 2 in Table 1, Supporting Information Figure S33), showed an increase of the peak due to the cyclohexanol terminated chain, supporting the occurrence of pathway B detailed in Figure S32. Finally, intramolecular transesterification at carbonate functionalities along the polymer chains (i.e. different from the last inserted one) may explain the formation of cyclic structures $[OC_6H_{10}]_n[CO_2]_m$ (pathway D in Figure S32). In this respect, the presence of *trans*-CHC in the product mixtures, indicates that the back-biting mechanism of the polymer chain is operative, thus corroborating pathway D.

Further information from the MALDI-ToF analysis, stems from comparing the spectra of samples obtained under different conditions. For example, the comparison of spectra of entries 1–3 (Supporting Information Figure S34), shows the predominance of the trimethylsiloxide end group (pathway A) at 80 °C, while, by increasing the temperature, the relative intensity of the other end groups is increased, indicating that the collateral reactions (i.e. hydrolysis of CHO, decarboxylation and transesterification, described in pathways B-D) are favored by increasing the temperature.

The molecular weight of the polymer obtained after 64 h (entry 4 in Table 1) is lower than that obtained after 16 h (entry 2 in Table 1), suggesting that some kinds of chain transfer reactions occur during the long polymerization times. Accordingly, a decrease of the dispersity value is observed (Đ = 3.3 and 5.2 respectively for entries 4 and 2). The comparison of the MALDI-ToF spectra of these polymers (Supporting Information Figure S35) shows the prevalence of the cyclohexanol end groups in the spectrum of the polymer obtained after 64 hours (entry 4), suggesting that during longer polymerization times, the adventitious presence of water can hydrolyze an increasing amount of CHO, generating CHD and thus promoting the formation of PCHC end-capped with two hydroxyl groups. This conclusion was in agreement with the ^{1}H NMR spectrum of the same copolymer: in addition to the main signals for the protons of the copolymer chains, two peaks at 3.60 and 4.45 ppm were observed, which have been assigned to the methine protons adjacent to the hydroxyl end groups[7f] (Supporting Information Figure S36). Signals of other end groups were not detectable by NMR.

In order to minimize the chain transfer reaction due to the presence of traces of water, a copolymerization experiment was carried out in the same conditions of run 2 but using freshly bi-distilled CHO (run 11, Table 1). However, in spite of an increase in the reaction conversion (cf entries 2 and 11 in Table 1) the results of these two copolymerization reactions (in terms of product selectivity, molecular weights and dispersity) did not show any significant difference.

The microstructure of the PCHC obtained in entry 2, was studied by ^{13}C NMR spectroscopy (Supporting Information Figure S37). In the carbonyl region, a peak at 153.94 ppm for the *m*-centered tetrads and two peaks at 153.43 and 153.27 ppm for the *r*-centered tetrads were observed.[17] The comparable intensities of these two sets of peaks denotes that the obtained polycarbonate is atactic.

Subsequently, we explored the effect of the addition of a cocatalyst to complex **1** (Table 2). In particular, by adding one equivalent of PPNCl (bis(triphenylphosphine)iminium chloride) (i.e. 0.5 equivalents per Zn center) to the reaction carried out at 100 °C and under 30 bar of CO_2 (entry 12) the conversion decreased while the selectivity of the catalyst changed and a mixture of PCHC, *cis*-CHC, *trans*-CHC and ether linkages in the ratio 25:23:48:4 was obtained (to facilitate the comparison, entry 2, carried out under the same conditions of entry 12 but in the absence of PPNCl, was reported again in Table 2). A plausible explanation is related to the ability of the nucleophile to favor the displacement of the growing chain and so favoring the backbiting of the free copolymer, i.e. not-bound to the metal (for the metal-bound carbonate and alkoxide, the backbiting reaction was found to have higher barriers).[18]

Table 2. CO_2/CHO reaction promoted by complex **1**/PPNCl.

Entry[a]	PPNCl [equiv.]	Conv[b] [mol %]	PCHC	*Cis*-CHC	*Trans*-CHC	Ether linkages
2	0	20	90	<1	3	7
12	1	6	25	23	48	4
13	2	10	20	59	20	1
14	4	40	6	81	13	<1

[a] General conditions: Complex **1**: 19.8 μmol (0.05 mol-%), CHO = 40 mmol (2000 equiv.), temperature = 100 °C, P_{CO2} = 30 bar, reaction time = 16 hours. [b] The conversion and the product ratio were determined through high-resolution ^{1}H NMR spectra ($CDCl_3$, 600 MHz).

Accordingly, by increasing the amount of PPNCl to two equivalents (i.e. one equivalent per Zn center) (entry 13 in Table 2) the total percentage of cyclic carbonates increased with respect to the polymer. Furthermore, in the presence of 4

equivalents of PPNCl, the main product was *cis*-CHC (entry 14 in Table 2). As known, *cis*-CHC may also be formed independently from chain growth (or even in alternative), that is, following initial epoxide opening by an anionic initiator and the subsequent CO_2 insertion.[18] The same change in selectivity by adding a cocatalyst to the reaction mixture was already observed by other authors both with iron based[19a,19b] and zinc based[19c] catalysts. As already observed in some cases, the activity of the catalytic system does not depend linearly on the amount of the cocatalyst.[19a]

Finally, we explored the scope of complex **1** in the reaction of CO_2 with other epoxides, namely propylene oxide (PO) and styrene oxide (SO) representative of terminal and aromatic epoxides, respectively. Carrying out the reaction in the same conditions of entry 2 and in the presence of 2900 equivalents of PO and 2000 equivalents of SO (see Table S1 in the Supporting Information for more details) complex **1** showed no activity. This is not surprisingly since, except for BDI-Zn complexes, no homogeneous Zn-based systems have been reported to be active for the copolymerization of CO_2/PO.[2e] Rieger ascribed the inactivity of a binuclear BDI tethered-zinc complex to the formation of an energetically highly stable intermediate generated in the presence of CO_2 and PO.[9c]

Conclusion

In this paper we describe the synthetic strategy to prepare new bis(aldimine-thioether-phenolate) OSNNSO ligands, which present two anionic oxygen donors and four neutral donors, such as two nitrogen atoms and two sulfur atoms, the same strategy works also to prepare the related aldimine-thioether-phenolate ONS ligands.

The first ONS ligand and two OSNNSO ligands, with a different length of the alkyl bridge between the nitrogen atoms, have been synthesized and characterized. A monometallic complex was obtained by reaction of the tridentate ligand with one equivalent of the zinc precursor while two bimetallic zinc complexes were successfully prepared by direct reaction of the bis(aldimine-thioether-phenolate) ligands with two equivalents of the zinc precursor. The NMR characterization indicated that the complexes are flexible in solution at room temperature.

Complex **1** was able to convert CO_2 and CHO in the corresponding polycarbonate product with a good selectivity (up to 97 %) and a moderate activity (TOF up to 36 h^{-1}). The catalyst did not require the use of an external nucleophile and/or of a solvent. The obtained polycarbonates showed low molecular masses (M_n: 3.7–15.4 kDa) with broad dispersities (Đ = 3.3–7.8). The MALDI-ToF analysis of the obtained polymers allowed the observation of some terminal groups, thereby indicating both the formation of multiple active centers for the explored catalytic systems and the occurrence of post-copolymerization reactions.

By adding PPNCl as a cocatalyst, the selectivity diverted towards the formation of cyclic carbonates (up to 94 % of *cis*- and *trans*-CHC in the presence of two equivalents of PPNCl per zinc center) with a slightly higher activity (TOF = 50 h^{-1}).

By comparing the behaviour of the bimetallic complex **1**, having an ethylene bridge between the nitrogen atoms, with complex **2**, having a propylene bridge between the nitrogen atoms, and with complex **3**, a monometallic analogue, only small differences were observed both in the activity and in the selectivity of the catalysts in the CO_2/CHO reaction. This could be reasonably due to the observed flexibility of the bimetallic complexes in which, as a consequence, the two metallic centers may act independently.

Experimental Section

Materials and General Methods: All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glovebox or standard Schlenk line techniques. The glassware and autoclave used in the polymerization were dried in an oven at 120 °C overnight. All solvents and reagents were obtained from commercial sources (Aldrich and Merck). The zinc precursor, zinc(trimethyl silyl) amido, were purchased from Aldrich and used as received. Benzene and hexane, were distilled from sodium benzophenone. Cyclohexene oxide (98 %; Sigma-Aldrich), propylene oxide (≥99.5 %; Sigma-Aldrich) and styrene oxide (97 %; Sigma-Aldrich) were dried with CaH_2 for 24 h at room temperature, then distilled under reduced pressure and stored in a sealed flask in a glove-box. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried with activated 3 Å molecular sieves prior to use.

Instruments and Measurements: NMR spectra were recorded on Bruker Advance 300, 400 and 600 MHz spectrometers at 298 K, unless otherwise stated. The chemical shifts (δ) are expressed as parts per million and coupling constants (J) are in Hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ = 7.16 ppm for C_6D_6 and δ = 7.27 ppm for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ = 128.06 ppm for C_6D_6 and δ = 77.23 ppm for $CDCl_3$. The molecular weights (M_n and M_w) and the dispersity (Đ = M_w/M_n) of polymer samples were measured by gel permeation chromatography (GPC) at 30 °C, using THF as the solvent, an eluent flow rate of 1 mL min^{-1}, and narrow polystyrene standards as the reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range: 1000–1000 000 Å). Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were ionized in positive ion mode using the MALDI ion source. The samples of ligands were prepared at a concentration of 1.0 mg mL^{-1} in toluene, while the samples of polymers were prepared at a concentration of 1.0 mg mL^{-1} in THF. The matrix (anthracene for the ligands and trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTB, for polymers) was mixed at a concentration of 10.0 mg mL^{-1} to promote desorption and ionization.

Synthesis and Characterization of the Ligands: A representative procedure for the preparation of ligands is given. Synthetic details and full characterization are reported in the Supporting Information. The synthetic strategy, which allowed the preparation of OSNNSO ligands, involves three steps.

Synthesis of 2-Mercaptobenzaldehyde: The 2-mercaptobenzaldehyde was prepared according to literature procedure.[12]

Synthesis of 2-(3,5 Di-*tert*-butyl-2-hydroxybenzyl)sulfanylbenzaldehyde: To a stirred solution of 2-mercaptobenzaldehyde

(1.041 g, 7.535×10^{-6}) and K_2CO_3 (4.165 g, 30.1 mmol) in DMF (83 mL) at room temperature was added dropwise a solution of 2-(bromomethyl)-4,6-di-*tert*-butyl-phenol (2.255 g, 7.535×10^{-6} mmol) in dry DMF (18 mL). The flask was left to stir at room temperature for 3 h. 50 mL of water and 50 mL of diethyl ether were added. The organic layer was washed with water (3 × 30 mL) and brine (3 × 30 mL). The solution was dried with sodium sulfate and then filtered. The solvent was removed under vacuum yielding a white yellow solid that was recrystallized from pentane as a white solid, and collected by vacuum filtration. Yield 63 %. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.18 (s, 9H, *t*Bu), 1.40 (s, 9H, *t*Bu), 4.15 (s, 2H, S-CH_2), 5.76 (s, 1H, OH), 6.79 (s, 1H, Ar-H), 7.20 (s, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.40 (t, 1H, Ar-H), 7.52 (m, 2H, Ar-H), 7.79 (d, J = 8.05 Hz, 1H, Ar-H), 10.22 (s, 1H, CH=O). ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K): δ = 30.01 (C(CH_3)$_3$), 31.61 (*C*(CH_3)$_3$), 34.47 (C(*C*H_3)$_3$), 35.19 (C(CH_3)$_3$), 37.05 (S-CH_2), 121.70 (Cq),124.40 (CH), 125.96 (CH), 127.67 (CH), 131.86 (CH), 132.68 (CH), 134.35 (CH), 136.21 (Cq), 137.16 (Cq), 139.06 (Cq), 143.07 (Cq), 151.47 (Cq), 191.60 (CH=O).

Synthesis of Ligand Precursor L^1H_2: Compound $\mathbf{L^1}H_2$ was obtained by condensation of two equivalents of the 2-(3,5-di-*tert*-butyl-2-hydroxybenzyl) sulfanyl benzaldehyde (1.628 g, 4.565×10^{-6} mmol) with ethylenediamine (153 µL, 2.289×10^{-6} mmol), in dry acetonitrile (57 mL). The characterization of $\mathbf{L^1}H_2$ was done by means of ^{1}H and ^{13}C NMR and MALDI-ToF mass spectrometry. Yield: 51 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.29 (s, 18H, *t*Bu), 1.71 (s, 18H, *t*Bu), 3.42 (s, 4H, N-CH_2), 3.97 (s, 4H, S-CH_2), 6.44 (t, 2H, Ar-H), 6.67 (t, 2H, Ar-H), 6.82 (d, J = 2.44 Hz, 2H, Ar-H), 7.27 (d, J = 7.84 Hz; 2H, Ar-H), 7.37 (d, J = 7.79 Hz, 1H, Ar-H), 7.44 (d, J = 2.41 Hz, 1H, Ar-H), 8.10 (s, 1H, OH) 9.07 (s, 1H, CH=N). ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 30.48 (C(CH_3)$_3$), 31.82 (C(*C*H_3)$_3$), 34.40 (*C*(CH_3)$_3$), 35.65 (*C*(CH_3)$_3$), 38.65 (N-CH_2), 61.61 (S-CH_2), 123.62 (CH),125.38 (Cq), 125.93 (CH), 129.05 (CH), 130.60 (CH), 135.27 (CH), 135.69 (Cq), 138.09 (Cq), 139.20 (Cq), 143.03 (Cq), 152.36 (CH), 165.19 (CH=N). MS (MALDI-ToF) *m/z* (ion): [M + H$^+$] calcd. for $C_{46}H_{61}N_2O_2S_2$ 737.42, found 737.417; calcd. for $C_{31}H_{37}N_2OS_2$ 517.23, found 517.234; calcd. for $C_{16}H_{15}N_2S_2$ 299.07, found 299.067.

Synthesis of Ligand Precursor L^2H_2: Compound $\mathbf{L^2}H_2$ was obtained by condensation of two equivalents of the 2-(3,5-di-*tert*-butyl-2-hydroxybenzyl) sulfanyl benzaldehyde (0.7050 g, 1.9774×10^{-3} mol) with 1,3-propanediamine (83.3 µL, 9.887×10^{-4} mol), in dry acetonitrile (24 mL). The characterization of $\mathbf{L^2}H_2$ ligand precursor was done by means of ^{1}H and ^{13}C NMR and MALDI-ToF mass spectrometry. Yield: 54 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.23 (s, 9H, *t*Bu), 1.58 (s, 9H, *t*Bu), 2.20 (m, 2H, N-CH_2), 3.72 (t, 2H, N-CH_2), 3.81 (s, 2H, S-CH_2), 6.76 (s, 1H, OH), 6.82, (d, J = 2.36 Hz, 1H, Ar-H), 6.86 (t, 1H, Ar-H), 6.91 (t, 1H, Ar-H), 7.24 (d, J = 7.76 Hz, 1H, Ar-H), 7.39 (d, J = 2.43 Hz, 1H, Ar-H), 7.82 (d, J = 7.90 Hz, 1H, Ar-H), 8.60 (s, 1H, CH=N). ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 30.15(C(CH_3)$_3$), 31.98 (C(*C*H_3)$_3$), 32.39 (*C*(CH_3)$_3$), 34.34 (*C*(CH_3)$_3$), 35.33 (CH_2), 38.47 (N-CH_2), 59.97 (S-CH_2), 122.09 (CH),123.91 (CH), 125.82 (CH), 130.21 (CH), 130.43 (CH), 134.84 (Cq), 136.95 (Cq), 138.05 (Cq), 142.25 (Cq), 152.35 (Cq), 160.09 (CH=N). MS (MALDI-ToF) *m/z* (ion): [M + H$^+$] calcd. for $C_{47}H_{63}N_2O_2S_2$ 751.43, found 751.428; calcd. for $C_{32}H_{39}N_2OS_2$ 531.25, found 531.247; calcd. for $C_{17}H_{17}N_2S_2$ 313.08, found 313.08.

Synthesis of Ligand Precursor L^3H: Compound $\mathbf{L^3}H$ was obtained by condensation of two equivalents of the 2-(3,5-di-*tert*-butyl-2-hydroxybenzyl) sulfanyl benzaldehyde (0.5028 g, 1.41×10^{-3} mol) with propylamine (116 µL, 1.41×10^{-3} mol), in dry acetonitrile (20 mL). The characterization of $\mathbf{L^3}H$ ligand precursor was done by means of ^{1}H and ^{13}C NMR and mass spectrometry. Yield: 62 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.91 (t, 3H, CH_3) 1.23 (s, 9H, *t*Bu), 1.59 (s, 9H, *t*Bu), 1.70 (m, 2H, CH_2), 3.47 (t, 2H, N-CH_2), 3.81 (s, 2H, S-CH_2), 6.77 (s, 1H, OH), 6.81 (s, 1H, Ar-H), 6.85 (t, 1H, Ar-H), 6.91 (t, 1H, Ar-H), 7.25 (d, J = 7.62 Hz, 1H, Ar-H), 7.39, (s, 1H, Ar-H), 7.82 (d, J = 7.55 Hz, 1H, Ar-H), 8.52 (s, 1H, CH=N). ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 12.08 (CH_3), 24.48 (CH_2), 30.12(C(*C*H_3)$_3$), 31.74 (C(*C*H_3)$_3$), 34.32 (*C*(CH_3)$_3$), 35.33 (*C*(CH_3)$_3$), 38.53 (N-CH_2), 64.16 (S-CH_2), 122.09 (Cq), 123.90 (CH), 125.79 (CH), 130.10 (CH), 130.37(CH), 134.68 (Cq), 135.06 (CH), 136.93 (Cq), 138.19 (Cq), 142.22 (Cq), 152.37 (Cq), 159.44 (CH=N). MS (ESI) *m/z* (ion): [M + H$^+$] calcd. for $C_{25}H_{36}NOS$ 398.251, found 398.252.

Synthesis and Characterization of Complexes 1–3*:* The representative procedure for the preparation of complex **1** is given, see Supporting Information for further details for all other complexes.

Synthesis of Complex 1: To a benzene solution (6 mL) of $\mathbf{L^1}H_2$ (0.150 g, 2.03×10^{-4} mol) was added a benzene solution (3.0 mL) of $Zn[N(SiMe_3)_2]_2$ (0.1572 g, 4.07×10^{-4} mol). The reaction mixture was stirred at room temperature for 2 hours. Afterwards the solvent was removed in vacuo and the solid residue was washed with pentane. Complex **1** was obtained as a yellow powder in 95 % yield. Elemental analysis calcd. for $C_{58}H_{94}N_4O_2S_2Si_4Zn_2$: C 58.71, H 7.98, N 4.72, S 5.40; found C 59.02, H 8.02, N, 4.74, S 5.42. ^{1}H NMR (600 MHz, tol-d8, 263 K): δ = –0.01 (s, 18H, Si(CH_3)$_3$), 0.13 (s, 18H, Si(CH_3)$_3$), 1.49 (s, 18H, *t*Bu), 1.86 (s, 18H, *t*Bu), 3.53 (d, J = 11.97 Hz, 2H, N-CH_2), 4.40 (d, J = 7.03 Hz, 2H, S-CH_2), 4.45 (d, J = 11.73 Hz, 2H, N-CH_2), 4.89 (d, J = 7.19 Hz, 2H, S-CH_2), 6.48 (t, 2H, Ar-H), 6.54 (t, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 7.28 (d, J = 7.44 Hz, 2H, Ar-H). 7.49 (d, J = 7.76 Hz, 2H, Ar-H), 7.60 (s, 2H, Ar-H), 8.54 (s, 2H, CH=N). ^{13}C NMR (600 MHz, tol-d8, 263 K): δ = 1.38 (Si(CH)$_3$)$_3$), 3.09 (Si(CH)$_3$)$_3$), 30.45 (2C, C(*C*H_3)$_3$), 32.44 (2C, C(*C*H_3)$_3$), 34.44 (2C, *C*(CH_3)$_3$), 35.80 (2C, *C*(CH_3)$_3$), 53.31 (2C, CH_2), 61.58 (2C, CH_2), 122.37 (2C, CH), 124.57 (2C, Cq) 125.11 (2C, CH), 127.21 (2C, CH) 131.40 (2C, CH), 135.66 (2C, Cq), 136.50 (2C, CH), 139.01 (2C, CH), 150.10 (2C, Cq), 164.71 (2C, Cq), 176.87 (2C, CH=N).

Synthesis of Complex 2: The same procedure used for complex **1** was followed using the ligand precursor $\mathbf{L^2}H_2$ (0.200 g, 2.67×10^{-4} mol) and $Zn[N(SiMe_3)_2]_2$ (0.212 g, 5.33×10^{-4} mol). Complex **2** was obtained as a yellow powder in 91 % yield. Elemental analysis calcd. for $C_{59}H_{96}N_4O_2S_2Si_4Zn_2$: C 59.02, H 8.06, N 4.67, S 5.34; found C 59.29, H 8.07, N, 4.65, S 5.32. ^{1}H NMR (600 MHz, tol-d8, 223 K): δ = –0.01 (s, 18H, Si(CH_3)$_3$), 0.17 (s, 9H, Si(CH_3)$_3$), 0.26 (s, 9H, Si(CH_3)$_3$), 1.59 (s, 9H, *t*Bu), 1.62 (s, 9H, *t*Bu), 1.82 (s, 9H, *t*Bu), 1.92 (s, 9H, *t*Bu), 2.68 (br, 1H, CH_2), 3.37 (m, 2H, CH_2), 3.48 (m, 2H, CH_2), 3.88 (m, 1H, CH_2), 4.29 (d, J = 11.96 Hz, 1H, S-CH_2), 4.31 (br, 2H, CH_2), 4.51 (d, J = 11.76 Hz, 1H, S-CH_2), 6.70 (m, 3H, Ar-H), 6.76 (m, 2H, Ar-H), 6.79 (d, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 7.10 (s, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.69 (s, 1H, Ar-H), 7.82 (t, 2H, Ar-H), 7.91 (s, 1H, CH=N), 8.40 (s, 1H, CH=N). ^{13}C NMR (300 MHz, C_6D_6, 298 K): δ = 2.44 (2C, Si(CH)$_3$)$_3$), 30.52 (2C, C(*C*H_3)$_3$), 32.24 (CH_2), 32.37 (2C, C(*C*H_3)$_3$), 34.31 (2C, *C*(CH_3)$_3$), 35.81 (2C, *C*(CH_3)$_3$), 52.96 (2C, N-CH_2), 58.21 (2C, S-CH_2), 122.18 (2C, CH), 123.07 (2C, Cq) 124.38 (2C, CH), 127.08 (2C, CH), 129.52 (2C, Cq), 131.27 (2C, CH), 135.54 (2C, Cq), 136.99 (2C, CH), 137.97 (2C, Cq), 138.14 (2C, CH), 150.82 (2C, Cq), 164.82 (2C, Cq), 174.69 (2C, CH=N).

Synthesis of Complex 3: The same procedure used for complex **1** was followed using the ligand precursor $\mathbf{L^3}H$ (0.150 g, 3.77×10^{-4} mol) and $Zn[N(SiMe_3)_2]_2$ (0.152 g, 3.77×10^{-4} mol). Complex **3** was obtained as a yellow powder in 97 % yield. Elemental analysis calcd. for $C_{31}H_{52}N_2OSSi_2Zn$: C 59.82, H 8.42, N 4.50, S 5.15; found C 60.18, H 8.47, N, 4.52, S 5.17. ^{1}H NMR (400 MHz, tol-d8, 233 K): δ = –0.08 (s, 9H, Si(CH_3)$_3$), 0.17 (s, 9H, Si(CH_3)$_3$), 0.80 (t, 3H, CH_3), 1.33 (br, 1H, CH_2), 1.40 (s, 9H, *t*Bu), 1.89 (s, 9H, *t*Bu), 2.33 (br, 1H, CH_2), 2.80 (br, 1H, N-CH_2), 3.37 (d, J = 11.86, 1H, S-CH_2), 4.13 (br, 1H, N-CH_2), 4.34

(d, J = 11.88 Hz, 1H, CH_2), 6.74 (m, 3H, Ar-H), 7.56 (s, 1H, Ar-H), 7.62 (s, 1H, CH=N) 7.82 (d, J = 7.27 Hz, 2H, Ar-H). ^{13}C NMR (600 MHz, C_6D_6, 298 K): δ = 2.34 ($Si(CH)_3)_3$), 11.44 (CH_3), 25.73 (CH_2), 30.20 ($C(CH_3)_3$), 32.37 ($C(CH_3)_3$), 34.29 ($C(CH_3)_3$), 35.69 ($C(CH_3)_3$), 52.93 (N-CH_2), 63.13 (S-CH_2), 121.90 (CH), 124.29 (CH), 124.30 (CH), 127.90 (CH), 128.22 (Cq), 129.64 (Cq), 131.08 (CH), 135.36 (Cq), 137.30 (CH), 137.54 (CH), 138.31 (Cq), 172.82 (CH=N).

CO_2/Epoxide Reaction Procedure: In a typical experiment, in a glove-box, the catalyst (19.8 μmol, 0.05 mol-%), and when used, the cocatalyst (PPNCl, from 1 to 4 equivalents) were dissolved in the epoxide (4 mL) and then transferred into the autoclave. The autoclave was pressurized to the appropriate pressure of CO_2 and was heated to the appropriate temperature. The mixture was stirred for the necessary reaction time. After the prescribed time, the reaction mixture was quenched by dipping the autoclave in an ice bath and adding CH_2Cl_2 (0.5 mL) under air and a ^1H NMR spectrum of the crude reaction mixture was used to calculate the conversion. The residual epoxide was removed under vacuum. The polymer was isolated by precipitation in methanol. The precipitated solid was filtered and dried in a vacuum oven overnight at 40 °C.

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Carbon Dioxide Fixation

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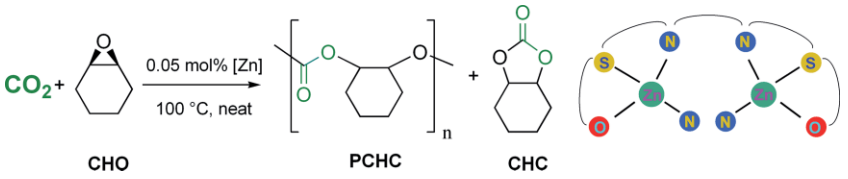
Aldimine-Thioether-Phenolate Based Mono- and Bimetallic Zinc Complexes as Catalysts for the Reaction of CO_2 with Cyclohexene Oxide



A new class of aldimine-thioether-phenolate ligands and the corresponding mono- and bi-metallic zinc complexes have been synthesized. The zinc complexes are active catalysts in CO_2 fixation by reaction with cyclohexene oxide, operating at a low catalyst loading and in the absence of solvents. MALDI, GPC, and NMR analysis of the corresponding polymers are discussed.

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