Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bimetallic salen aluminum complexes: cooperation between reactive centers in the ring-opening polymerization of lactide and epoxides.

Florence Isnard,[a] Marina Lamberti,[b] Luana Lettieri,[a] Ilaria D'auria,[a] Konstantin Press,[c] Rubina Troiano [a], Mina Mazzeo [a,*]

A series of dinuclear aluminum alkyl complexes of general formula L-Al_2Me_4, where L are salen ligands with alkyl backbone of different length between the nitrogen atoms (1,3-propylene (**1**), 1,5-pentylene (**2**) and 1,12-dodecaylene (**3**)), have been prepared through alkane elimination reactions between each ligand and two equivalents of $AlMe_3$. The related hemi-salen aluminum complex **4** was prepared by an analogous reaction between a phenoxy-imine ligand and a single equivalent of $AlMe_3$. The activities of these binuclear aluminum complexes in the ring-opening polymerization (ROP) of *rac*-lactide and of several epoxides have been investigated and compared. The dinuclear complex **1**, bearing the salen ligand with the shortest alkyl bridge, was the most active in the ROP of LA producing isotactic enriched PLA. Otherwise, the other complexes (**2** and **3**), in which metal centers are remote, produced atactic PLA with inferior activity. Analogous differences in terms of activity emerged in the ROP of epoxides. The comparison of the catalytic behavior of the dinuclear complexes as well as their mononuclear counterpart suggests the possibility of cooperation between the two reactive centers of the dinuclear species in which these are close together.

Introduction

The salen ligands are ubiquitous in the coordination chemistry of trivalent metals both of main and transition groups and their complexes find wide applications in the field of homogeneous catalysis for several reactions as oxidations, polymerizations, and epoxidations.[1,2]

Salen complexes based on five-coordinate aluminum atoms are among the most successful catalysts in the ring-opening polymerization (ROP) of cyclic esters, such as lactide.[3] Following the initial findings of Spassky,[4] that reported the first example of Salen-Al complexes able to promote a controlled polymerization of *rac*-lactide to moderately isotactic PLA, Feijen,[5] and Coates[6] used chiral salen-type catalysts to mediate the stereoselective polymerization of *rac*-lactide *via* the enantiomorphic site control mechanism.

Subsequently Nomura[7], Gibson[8] and Chen[9] reported achiral salen-aluminum catalysts able to promote isotactic polymerization of *rac*-lactide *via* chain-end control mechanism. At the same time, numerous examples of structurally related dianionic tetradentate ONNO-type ligands such as salan,[10] salalen[11] and dialkoxy-diimino[12] ligands have been deeply investigated as coordination environments for the synthesis of monometallic five-coordinate aluminum complexes active in the ROP of cyclic esters. Some of these complexes displayed uncommon abilities in controlling the stereochemistry in the ROP of *rac*-lactide, producing polymers with improved stereoregularities[13] or original microstructures.[14]

More recently, bimetallic aluminum complexes have attracted great attention as they have different catalytic behaviors in comparison to their related monometallic species because of the presence of two proximal Lewis acidic centers within the same complex that can act in a concerted way.

Bimetallic five-coordinate salen-aluminum complexes have been investigated as initiators for controlled and stereoselective ROP of LA.[15]

On the other hand, the use of dianionic "ONNO" type ligands as binucleating ligands for the formation of bimetallic species in which the aluminum centers are tetra-coordinate is definitively less explored.[16,17]

Carpentier et al. reported enantiomerically pure diphenylethylene salen ligands for the synthesis of monometallic five-coordinate and bimetallic tetra-coordinate aluminum complexes. Both classes of complexes showed the same activity in the ROP of LA but the bimetallic complexes revealed to be inefficient in the stereocontrol of the process.[18]

The same behavior was observed by Ma with mononuclear and dinuclear aluminum complexes supported by 6,6'-dimethylbiphenyl-bridged salen ligands.[19] The same author described binuclear tetra-coordinate salan aluminum complexes as efficient initiators for the copolymerization of L-LA and ε-CL, producing copolymers ranging from blocky to random microstructures, depending on the catalyst structure and the reaction conditions.[20]

Evidences about the cooperation between two metal centers of dinuclear tetra-coordinate aluminum complexes stabilized by

---

[a] Department of Chemistry and Biology "A. Zambelli" University of Salerno. I-84084, Giovanni Paolo II, 132 Fisciano, Salerno, Italy.
[b] Department of Physics "E. Caianiello" University of Salerno. I-84084, Giovanni Paolo II, 132 Fisciano, Salerno, Italy.
[c] School of Chemistry. Raymond and Beverly Sackler Faculty of Exact Sciences. Tel Aviv University. Ramat Aviv, Tel Aviv 69978, Israel.

Electronic Supplementary Information (ESI) available: [Synthesis of proligands, NMR spectra of complexes and of the propagating specie, MALDI-TOF spectrum]. See DOI: 10.1039/x0xx00000x

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

bis amine-phenolato ligands were recently discussed by Yao and Yuan.[21]

In this work we report the synthesis and the study of the catalytic behavior of dinuclear aluminum complexes ligated by salen-type frameworks in order to explore the possibility of the cooperation between the two aluminum centers. Since the distance between the metal centers is a critical parameter to have cooperation between them, three bimetallic tetra-coordinate aluminum complexes supported by salen – type ligands, designed to feature two coordinative tasks at varying distances from one another, were prepared. The related hemi-salen aluminum complex was also synthesized.

All complexes were tested as initiators in the ROP of *rac*-LA and several epoxides.

Results and discussion

Aluminium complexes.

The reaction between the salen ligands and two equivalents of $AlMe_3$ proceeded through the elimination of methane to afford the desired bimetallic aluminum-alkyl complexes [L-Al_2Me_4] (Scheme 1) in quantitative yields.[22]

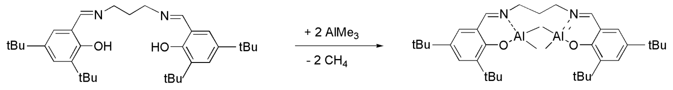
The identity of the complexes was established by ^{1}H, and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectra of the complexes **1**-**3** in C_6D_6 were all consistent with the presence of two aluminum atoms per ancillary ligand and pointed to symmetrical structures in solution. Diagnostic resonances in the protonic spectra include sharp singlets in the high-field region (between δ = -0.20 and -0.29 ppm) assigned to the equivalent protons of the Al-Me groups. In the low-field region, singlets (δ = 7.13 and 7.29 ppm) are detected for the equivalent CH=N moieties. The structural characterization reported by Atwood for analogous aluminum complexes, describes aluminum centers adopting a four-coordinate distorted tetrahedral geometry.[22]

Complex **4** was obtained, in almost quantitative yield, by analogous procedure, by reaction of the phenoxy-imine proligand with a single equivalent of $AlMe_3$ (Scheme 5).

Ring-opening polymerization of *rac*-□lactide.

The bimetallic salen complexes **1**-**3** were tested as initiators for the ROP of rac-lactide (Scheme 2). The reactions were performed in toluene solution at 70 °C, in the presence of four equivalents of isopropanol as activator. The obtained polymers were characterized by NMR and GPC. The obtained data are listed in Table 1.



Scheme 1 Synthesis of complexes **1–3**

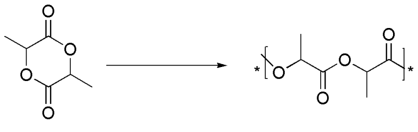
The aluminum complex **1** was active in the ROP of *rac*-lactide promoting the conversion of about 200 equivalents of monomer within 12 hours (run 1, Table 1). This complex showed an activity twice than that showed by the related monometallic species reported by Nomura[7b] and significantly higher than that showed by phenoxy-imine aluminum complexes reported by Carpentier[23] and by Redshow.[24] Unpredictably, complexes **2** and **3** resulted much less active, and analogous conversions were achieved only after 24 hours (cf. runs 2 and 3 with run 1 of Table 1).

All polymerizations proceeded in a controlled fashion, leading to polymers with monomodal and moderately narrow molecular mass distributions (M_w/M_n = 1.09–1.20). The molecular mass of the polymer[25] obtained by **1** was in good agreement with the theoretical value calculated hypothesizing the formation of a single PLA chain per catalyst unit. Differently, the molecular masses of the polymers obtained by **2** and **3** were halved, suggesting that two polymer chains were formed by catalyst unit, one for each metal center.

In terms of activity, complex **1** showed a TOF of 16.7 h^{-1}, much higher than those of complexes **2** and **3** (TOF of 3.5 h^{-1} and 3.1 h^{-1}, respectively) although for complex **1** the growth of a single polymer chain for each catalyst unit is supposed.

To explain these results, we postulate that the proximity of the two metal centers in the bimetallic system **1** does not allow the simultaneous growth of two polymer chains due to an excessive steric hindrance, on the other hand, the cooperation between the two reactive adjacent centers favors a high activity.[26] Otherwise, such interaction cannot take place in complexes **2** and **3** because of the higher distance between the reactive centers, as a consequence of the longer alkyl backbone between the imine functionalities.

The microstructures of the resulting PLAs were determined by the analysis of the methine regions of the homonuclear decoupled ^{1}H NMR spectra. The spectrum of the poly(*rac*-LA) obtained by **1** (Fig. 1) indicated an isotactic multiblock microstructure with a P_m= 82% (where P_m is the probability of a *meso*-linkage between lactide units). The stereochemistry of *rac*-lactide enchainment was evaluated by comparing the integrals at the tetrad level, with calculated values by using Bernoullian statistics (see Table S1 in the ESI†).



Scheme 2 Ring-opening polymerization of *rac*-lactide.

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

Table 1 Opening Polymerization of *rac*-LA by **1-3**.

[a]Run	Cat	Time (h)	Conv. (%)	[b]M_{nGPC} $(\times10^3)$	[c]M_n^{th} $(\times10^3)$	[b]PDI	[d]P_m (%)	[e]T_m
1	1	12	100	22.1	28.8	1.09	82	161.4
2	2	24	85	15.2	24.5	1.20	56	89.0
3	3	24	76	12.0	21.9	1.18	59	89.3

[a]All reactions were carried out with $9.0\ 10^{-6}$ mol of catalyst at 70 °C, in 2 mL of toluene, [cat]/[^{i}PrOH]/[*rac*-LA] = 1:4:200. [b]Experimental M_n (corrected using factor 0.58)[25] and PDI values were determined by GPC analysis in THF using polystyrene standards. [c]Calculated M_n of PLA (in gmol^{-1}) = 144,14 x ([*rac*-LA]/[cat]) x conversion of LA. [d]P_m is the probability of *meso* linkages as determined by ^{1}H NMR homodecoupling experiments. [e] The melting temperature (T_m) was determined from the second heating at heating rate of 10 °C min^{-1}.

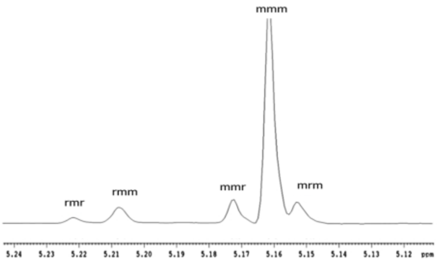


Fig. 1 Homodecoupled ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of a PLA obtained by run 1 of Table 1.

The very good agreement observed suggests that the stereocontrol proceeds *via* a chain end control mechanism, whereby the stereochemistry of the last inserted LA unit in the growing chain induces the stereoselection of the incoming enantiomer. The tacticity of the PLA obtained was comparable to that observed for the PLAs produced by the related monometallic aluminum complexes reported by Gibson and Nomura for which the pentacoordination of the metal center was considered crucial for the stereoselection.[7,8] Analogous stereoselectivity was observed with phenoxy–imine aluminum complexes only for encumbered benzyl–type imino substituents.[23] The stereoregularity of the PLAs obtained by **2** and **3** was significantly lower (P_m = 56 and 59%, respectively) showing the same behavior of analogous tetra-coordinate aluminium complexes bearing bidentate phenoxy-amine[28] or phenoxy-imine[24] ligands. This is coherent with the reduced steric encumbrance around the reactive centers as a consequence of the greater flexibility of the coordination sphere imparted by the longer alkyl bridges.

NMR studies of the active species.

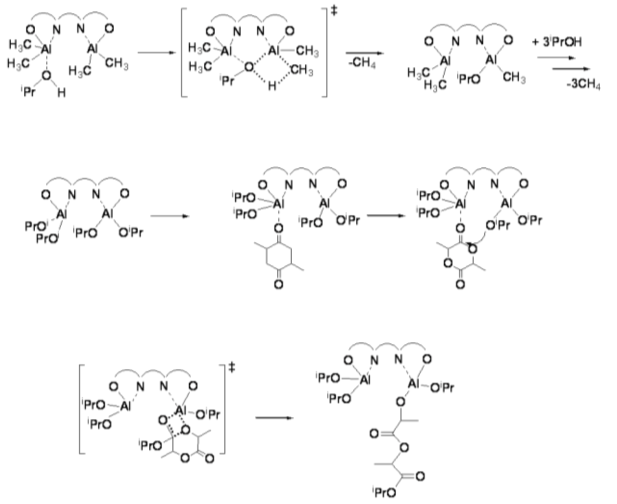
To elucidate the nature of the active species and the role of the two proximal metal centers during the polymerization, some experiments were performed in J-Young tube and followed by ^{1}H, NMR and 2D spectroscopy (^{1}H-^{1}H COSY and NOESY). First, a solution in deuterated benzene containing complex **1**, four equivalents of iPrOH and ten equivalents of L-LA was prepared. After 1 hour at room temperature, no alcoholysis of complex **1** was observed and no conversion of the monomer was achieved. This is consistent with observation reported in the literature, indicating the formation of the alkoxide active species requires an activation energy.[29]

Heating the solution at 70 °C, the disappearance of the resonances for protons of Al-Me groups and of the signals corresponding to the lactide monomer was observed in few minutes. The ^{1}H NMR spectrum was very simple (Fig. 2), in the aromatic region six different signals were observed corresponding to four different aromatic protons and two imine protons of the coordinated ligand. In the aliphatic region, five signals were evident corresponding to the diastereotopic protons of the trimethylene bridge between the imine nitrogen atoms. These evidences suggested the loss of the initial symmetry of the metal complex. In addition, three doublets, each integrating for six protons were observed between 0.90 and 0.93 ppm suggesting the presence of three isopropoxy groups bound to the aluminum atoms. An additional doublet was observed at 1.11, for the methyl protons of the terminal isopropoxy group of the growing chain and a quartet was observed for the methine proton of the repeating unit nearest to the aluminum of the growing chain. Finally, methine and methyl protons of the growing chain appeared at 5.09 and 1.37 ppm, respectively.

Subsequently, additional ten equivalents of lactide were added to the solution, after 10 minutes the almost complete conversion of monomer was observed and the pattern of the propagating species resulted unchanged in the ^{1}H NMR spectrum, thus demonstrating the living nature of the active species.

The whole picture is coherent with the formation of an asymmetric propagating species, in which the growth of a single chain occurred on one of the two metal centers of the binuclear complex, although chain transfer phenomena between the two aluminum atoms are plausible. The propagating species revealed to be exceptionally stable since it was stored in benzene solution for several weeks at room temperature and no decomposition was observed.

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.



Scheme 3 Plausible Mechanism for the polymerization of L-LA Initiated by complex **1**- ^{i}PrOH

The same NMR experiment was performed with complex **3**. Differently from what was observed for complex **1**, the alcoholysis of complex **3** proceed slowly even at 70 °C and about two hours were required to obtain the isopropoxy derivative quantitatively.

After this time, the ^{1}H NMR spectrum, although less clear than that discussed for complex **1**, revealed a symmetric structure of the propagating species, as clearly emerged by analysis of the aromatic region of the spectrum. This showed only two signals attributable to the four aromatic protons and a single resonance for the two equivalent imine protons. This corroborates the hypothesis that in the propagating species formed by complex **3** two polymeric chains grew, one for each metal center.

The different reactivity showed by **1** and **3** toward the hexogen alcohol suggests that the cooperation between the two metal centers of complex **1** could have a role both during the formation of the alkoxide derivative and during the propagation reactions. Reasonably, the coordination of the alcohol at one of the acidic aluminum atoms of the bimetallic species promotes the alcoholysis of the Al-Me bonds of the proximal metal atom. According to these evidences and referring to the generally accepted mechanism for the ROP of lactide promoted by metal alkoxides, a mechanism for the aluminum catalyst system **1**, in which the cooperation between the reactive centers is supposed, as shown in Scheme 3.

First, the hexogen alcohol coordinates to the metal centers and reacts exhaustively with the alkyl groups bound to the aluminum atoms of complex **1** to form the catalytically active species. Subsequently, one of the Lewis acidic metal centers binds the incoming monomer and activates it to the attack by the metal alkoxide group of the proximal aluminum atom. The growth of the polymer chain occurs by nucleophilic attach of polymer chain at the coordinated monomer unit by shuttling between the two aluminum centers.

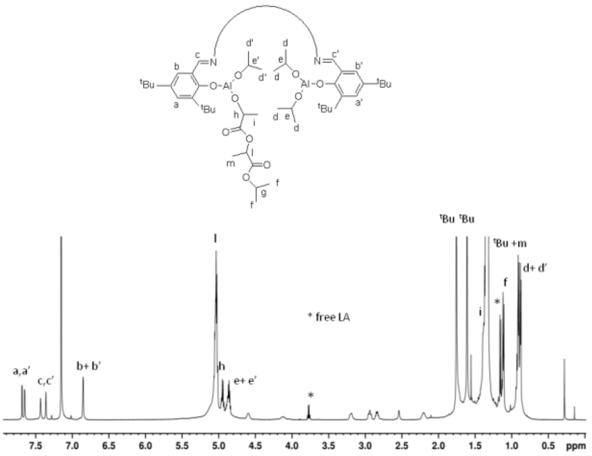


Fig. 2 ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K) of the propagating species **1**-PLA.

Kinetic studies

In order to have more information about the mechanism for polymerization of *rac*-lactide promoted by complexes **1**-**3**, kinetic investigations were conducted. Conversions of monomer in toluene at 70 °C were monitored by ^{1}H NMR spectroscopy at different intervals.

For complex **1**, kinetic studies showed that the polymerization of *rac*-LA obeyed first-order kinetics in monomer with instantaneous initiation (Fig. 4).

Otherwise, the ROP of *rac*-LA promoted by complex **3** showed an induction time of about 2 hours (Fig. 5). After this time, as shown by the second stage of the plot, the conversion of the monomer describes a polymerization of first-order in monomer concentration with a k_{app} of 0.0502 h^{-1}. The existence of an induction period, coherently with that observed by NMR study of the propagating species, is due to a slow reaction between the metal complex and the isopropyl alcohol. The k_{app} for complex **3** is significantly lower than that of complex **1**. As previously discussed, this suggests that the cooperation between the two metal centers has a role both in the alcoholysis reaction for the formation of the metal alkoxides and during the polymerization reaction.

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

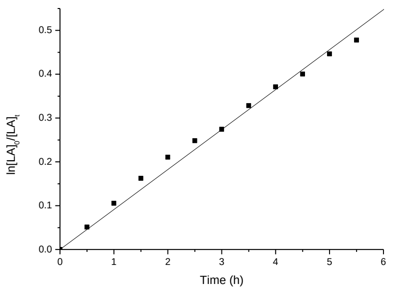


Fig. 4 Kinetic plot for ROP of rac-LA promoted by **1**. The concentrations were determined by ^1H NMR spectroscopy, $[LA]_0$ is the initial concentration of *rac*-LA and $[LA]_t$ the concentration at time t. Pseudofirst-order rate constant is (k_{app} = 0.0912 h^{-1}, R= 0.99689). Reaction conditions: [Cat] = 0.01M; [LA]/[cat] = 100; T=343 K; toluene-d8 as solvent.

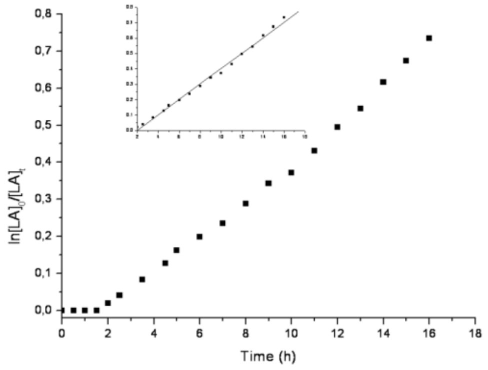


Fig. 5 Kinetic plot for ROP of *rac*-LA promoted by **3**. The concentrations were determined by ^1H NMR spectroscopy, $[LA]_0$ is the initial concentration of *rac*-LA and $[LA]_t$ the concentration at time t. The pseudofirst-order rate constant k_{app}=0.0502 h^{-1}, R = 0.99717. Reaction conditions: [Cat] = 0.01M; [LA]/[cat] = 100; T=343 K; toluene-d8 as solvent.

Table 2 Polymerization of CHO using **1-3**^{a}

^{a}Run	Cat	[CHO]/ [Cat]/	^{i}PrOH (eq)	Time (h)	Temp (°C)	CH_2Cl_2 (ml)	^{b}Conv. (%)	$^c M_{nGPC}$ (×10^3)	$^d M_n^{th}$ (×10^3)	^{e}PDI
1	1	250	-	48	25	2	22	398.7	10.8	1.43
2	1	250	-	0.33	25	-	40	256.6	19.6	1.72
3	2	250	-	0.33	25	-	40	223.7	19.6	1.77
4	1	250	4	48	25	2	27	18.4	13.2	1.66
5	1	500	-	0.08	70	-	74	38.0	36.3	2.09
6	1	250	4	0.08	70	-	95	4.3	5.8	1.67
7	1	500	4	0.08	70	-	79	10.7	9.7	1.79
8	1	750	4	0.25	70	-	85	12.4	15.6	1.76
9	1	1000	4	30	70	-	85	17.1	20.8	1.70
10	1	500	10	0.08	70	-	90	5.2	4.4	1.77

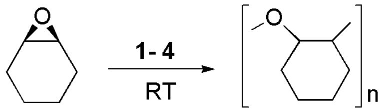
^{a} Reactions were performed at room temperature in an inert atmosphere workstation by using 9.0 µmol of catalyst and 4.5 mmol of CHO. ^{b}Conversions determined by ^1H NMR spectroscopy. ^{c} Determined by GPC . ^{d} Calculated M_n of PCHO (in gmol^{-1}) =98.14 x ([CHO]/[cat]) x conversion of CHO hypothesizing the formation of a single chain for catalyst unit (runs 4-8), for runs 9-11 M_n =98.14 x ([CHO]/[cat+^{i}PrOH]) x conversion of CHO.

When the same experiment was performed with complex **3** at higher temperatures (100 °C) in the presence of four equivalents of isopropyl alcohol no induction time was observed and the catalytic activity improved significantly (fig S8 of ESI†).

Homopolymerization of Cyclohexene Oxide (CHO).

The previously discussed data strongly support the hypothesis of a cooperation between the two reactive centers of the dinuclear complex **1** favoured by the architecture of the salen ligand that forces the two coordinative pockets in proximal positions. Considering that the cooperation between two metal centers is often invocated as an important requisite to have highly active catalysts for the ring-opening polymerization[30] and copolymerization of epoxides,[31] we started to investigate the behaviour of these complexes in the ROP of several epoxides (Table 2).

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.



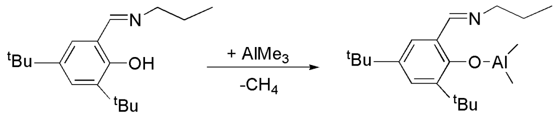
Scheme 4 Ring-opening polymerization of CHO.

The reactivity of complexes **1**-**3** toward cyclohexene oxide (CHO) was first examined in CH_2Cl_2, as solvent (Scheme 4). After 48 h at room temperature, a conversion of 22 % of the monomer was achieved when complex **1** was used (run 1, Table 2). As expected, under the same polymerization conditions, no activity was observed with binuclear complexes **2** and **3**.

These observations are coherent with the hypothesis that the cooperation between the proximal two reactive centers is a fundamental prerequisite to have catalytic activity in this kind of reaction. Thus, for complexes **2** and **3**, where a longer alkyl bridge connect the imine functionalities, the distance between the coordinative pockets does not allow interaction between the two aluminum atoms.

When the reaction was carried out in the absence of a solvent, the polymerization occurred much more rapidly, leading to a conversion of 40% of monomer within 20 min with complexes **1** and **2** (runs 2 and 3, Table 2), while still no conversion was achieved with complex **3**. The different behavior showed by complex **2** in the polymerization performed in neat conditions with respect to that done in the presence of solvent can be a consequence of the different polarity of the reaction medium that can influence the fluxionality of the binuclear complex and, consequently, the interaction between the reactive centers.

To confirm definitively the responsibility of the cooperation between the two metal centers in the ROP of CHO, we synthesized the phenoxy-imine aluminum complex **4** whose structure reproduces the coordinative environment of each aluminum center in the dinuclear complexes (Scheme 5).



Scheme 5 Synthesis of complex **4**.

This hemi-salen complex did not show polymerization activity, not only when it was used in the same concentration of aluminum centers used for bimetallic complexes but even when this concentration was ten times higher. These results unequivocally confirm that, for these systems, the polymerization proceeds *via* a bimetallic process that is favored by the closeness of two metallic centers. The same observation is reported in a recent work in which the ROP of CHO is promoted by $[UO_2Cl_2(THF)_3]$ as a catalyst.[32]

In all cases, polyethers with high molecular masses and molecular weight distributions less than 2.0 (Table 2) were obtained. The examples of catalysts able to produce high molecular weight polyethers are limited,[33] they include group 4[34] and rare earth catalysts[35] and, more recently, aluminum amine-phenolate complexes reported by Kerton.[36]

The discrepancy between the experimental molecular weights and the theoretical ones calculated presuming the formation of a single chain for catalysts unit, suggests a partial activation of the catalysts, reasonably because of the poor nucleophilicity of the alkyl ligands as initiating groups. To obtain a more strict control over the molecular weights, the alkoxide derivative of complex **1** was formed *in situ* by addition of four equivalents of hexogen alcohol, according to the procedure followed in the ring-opening polymerization of *rac*-lactide. The addiction of alcohol had no effect on the catalytic activity (27 % of conversion in 48 hours) but the molar masses of the obtained polyethers became close to the theoretical values (cfs runs 1 and 4, Table 2). When the polymerization reaction was performed at 70 °C the catalytic activity improved dramatically and, even in the absence of alcohol, a very good control of the molecular weights was achieved. These results suggest that both the increase of the reaction temperature or the addition of a hexogen alcohol as co-initiator at room temperature have beneficial effects on the initiation rate. Thus, performing the reactions at 70°C and in the presence of several equivalents of alcohol, complex **1** appears to be well suited for achieving immortal polymerization of CHO enabling the production of many polymeric chains per metal initiator (runs 6-9, Table 2).

The linear relationship between the M_n and monomer/ initiator ratio (see runs 6-9 of Table 2 and Fig. S9 in the ESI†) confirms the ability of the catalytic system **1**/iPrOH to promote an efficient control of the molecular masses.

The MALDI-TOF spectrum of the PCHO sample obtained in run 6 of Table 2 (Fig. S10 in the ESI†) showed a single series of peaks with a mass difference between them of 98 Da. The data are consistent with the formation of sodium adducts of PCHO chains bearing hydroxyl and isopropoxide end groups ($^iPrO-\{CHO\}_n-H\cdot Na^+$).

The microstructure of the obtained poly(1,2-cyclohexeneoxide) was investigated by ^1H NMR and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum, three peaks (δ 3.52, 3.39, and 3.36), attributable to syndiotactic (*rr*), heterotactic (*mr* and *rm*), and isotactic (*mm*) triads, were observed for the methine protons. Correspondently, three main signals were found in the ^{13}C NMR spectrum for the methine carbons at δ 80.0, 78.7, and 75.6, confirming the stereoirregularity of the polymer.

Various other epoxides (PO, styrene oxide and epichlorohydrin) were tested as monomers in the ROP by using complex **1**. In all cases, including reactions conducted at 70 °C no polymers were detected by ^1H NMR. These results, although uncommon, find a precedent in the behavior of the aluminum catalysts reported by Kerton.[36]

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

Cationic polymerization of cyclohexene oxide (CHO) and propylene oxide (PO)

Cationic aluminum species are generally expected to have very high Lewis acidity and, therefore, are interesting catalysts for the ROP of epoxides.[38]

The catalytic system formed by **1** activated by two equivalents of $B(C_6F_6)_3$ was found to be very active in the ROP of cyclohexene oxide under mild reaction conditions (2 mL of CH_2Cl_2, 25 °C). The instantaneous conversion of 500 equivalents of monomer was observed to produce an oily atactic poly(cyclohexeneoxide), as confirmed by $^{13}C\{^1H\}$ NMR. The molecular mass of the obtained PCHO was 13.4 10^3 g mol^{-1} with a PDI of 2.24.

The same catalytic systems were tested toward a less reactive monomer such as PO (see Table 3). While the neutral aluminum complexes **1** and **4** were inactive in PO polymerization at room temperature, the corresponding cationic species, obtained by addition of $B(C_6F_6)_3$, revealed to be highly active. When complex **1** was activated by a single equiv. of $B(C_6F_6)_3$, a conversion of 47% of monomer was achieved after 30 seconds (run 1, Table 3), by doubling the amount of cationizing agent the conversion reached 80% (run 2 , Table 3). The same results were obtained when complex **4,** activated by $B(C_6F_6)_3$, was used in the same molar concentration of aluminum centers (cf runs 1 and 3 with runs 2 and 4 in Table 3, respectively).

This is coherent with the hypothesis that the present PO polymerization catalysis proceeds *via* a Lewis acid-assisted cationic mechanism, therefore the yield is depending only by the concentration of the cationic initiators and, in this case, no cooperation between the adjacent aluminum centers is observed.

The polymerization activity and the TOF (valuated on the concentration of the aluminum centers) were similar for both complexes, and much higher than those reported for five-coordinated aluminum complexes[39,40] and comparable to those reported for related cationic aluminum complexes supported by bidentate monoanionic ligands.[41]

The GPC analysis of the obtained oily polymers exhibited the formation of a low-molecular-weight samples (M_n = 687-762) with a moderately narrow polydispersity (PDI = 1.17-1.38).

Table 3 Polymerization of PO using **1** and **4** / $B(C_6F_5)_3$[a]

[a]Run	Cat	$B(C_6F_5)_3$ (eq)	[b]Yield (%)	[c]M_{nGPC} (×10^3)	[c]PDI	TOF (s^{-1})
1	1	1	47	762	1.38	7.8
2	1	2	80	715	1.31	6.6
3 [d]	4	1	50	687	1.25	8.3
4 [d]	4	1	80	690	1.17	6.7

[a] Reactions were performed at room temperature in an inert atmosphere workstation by using 9.0 μmol of catalyst and 4.5 mmol of PO in 2 mL of CH_2Cl_2, reaction time= 30 sec. [b] Conversions determined by ^1H NMR spectroscopy. [C] Determined by GPC. [d] 18 μmol of catalyst and $B(C_6F_5)_3$.

Experimental

Materials and Methods.

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in the oven at 120 °C overnight and exposed three times to vacuum-nitrogen cycles.

Benzene, hexane and toluene (Sigma Aldrich) were distilled under nitrogen over sodium benzophenone. CH_2Cl_2 was distilled over CaH_2. The aluminum precursor $AlMe_3$ was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. *Rac*-Lactide was purchased from Aldrich and dried in vacuo over P_2O_5 for 72 h, and afterward stored at −20 °C in glovebox. CHO and PO were purchased from Aldrich and distilled over CaH_2. All other chemicals were commercially available and used as received unless otherwise stated.

The salen ligands were prepared according to the procedure described in the ESI . The phenoxy-imine ligand and complex **4** were synthesized as previously described.[42]

Instruments and measurements. The NMR spectra were recorded on Brucker Advance 250, 300, 400 and 600 MHz spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^1H NMR spectra are referenced using the residual solvent peak at $\delta = 7.16$ for C_6D_6 and $\delta = 7.27$ for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ = 128.06 for C_6D_6 and δ = 77.23 for $CDCl_3$.

Melting points (T_m) of polymers were measured by differential scanning calorimetry (DSC) using a DSC 2920 apparatus manufactured by TA Instruments under a nitrogen flux of 50 mL min^{-1} with a heating and cooling rate of 10 °C min^{-1} in the range -10 to 200 °C. All calorimetric data were reported for the second heating cycle.

Synthesis of complexes.

Complex **1**. To a stirred solution containing $AlMe_3$ (0.056 g, 0.78 mmol) in benzene (2 mL) was added dropwise a solution of the

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

ligand precursor L1 (0.200 g, 0.39 mmol) in benzene (2 mL). The solution was stirred for 2 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (92%).

^{1}H NMR (250 MHz, C_6D_6, 298 K): δ 7.70 (d, J = 2.5 Hz, 2H, ArH), 7.14 (s, 2H, CH=N), 6.79 (d, J = 2.5 Hz, 2H, ArH), 2.84 (t, J = 7.0 Hz, 4H, CH_2), 1.72 (t, J = 7.0 Hz, 2H, CH_2), 1.60 (s, 18H, t-Bu), 1.32 (s, 18H, t-Bu), -0.29 (s, 12H, Al-CH_3).

^{13}C NMR (250 MHz, C_6D_6, 298 K): δ 172.3, 162.0, 141.0, 139.3, 132.2, 128.9, 118.8 (Ar or ArCHN), 54.7 (C=NH), 35.6 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), -8.8 (Al-CH_3).

Complex **2**. To a stirred solution containing $AlMe_3$ (0.047 g, 0.68 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor L2 (0.180 g, 0.34 mmol) in benzene (2 mL). The solution was stirred for 2 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (95%).

^{1}H NMR (250 MHz, C_6D_6, 298 K): δ 7.69 (d, J = 2.5 Hz, 2H, ArH), 7.26 (s, 2H, CH=N), 6.84 (d, J = 2.5 Hz, 2H, ArH), 2.87 (t, J = 7.2 Hz, 4H, N-CH2), 1.60 (s, 18H, t-Bu), 1.32 (s, 18H, t-Bu), 1.23-1.29 (m, 4H, C-CH_2-CH_2-N), 0.77 (m, 2H, C-CH_2-C), -0.24 (s, 12H, Al-CH_3).

^{13}C NMR (250 MHz, C_6D_6, 298 K): δ 171.8, 161.9, 140.9, 139.0, 131.8, 128.9, 128.5, 128.2, 128.1, 118.8 (Ar or ArCHN), 57.3 (C=NH), 35.6 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), -8.9 (Al-CH_3).

Complex **3**. To a stirred solution containing $AlMe_3$ (0.034 g, 0.47 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor L3 (0.150 g, 0.23 mmol) in benzene (2 mL). The solution was stirred for 2 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (94%).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.69 (d, J = 2.5 Hz, 2H, ArH), 7.26 (s, 2H, CH=N), 6.84 (d, J = 2.5 Hz, 2H, ArH), 2.87 (t, J = 7.6 Hz, 4H, N-CH_2), 1.60 (s, 18H, t-Bu), 1.32 (s, 18H, t-Bu), 1.23-1.29 (m, 4H, C-CH_2-CH_2-N), 0.77 (m, 2H, C-CH_2-C), -0.24 (s, 12H, Al-CH_3).

^{13}C NMR (400 MHz, C_6D_6, 298 K): δ 171.5, 162.0, 140.9, 138.8, 131.6, 128.8, 118.9 (Ar or ArCNH), 57.9 (C=NH), 35.6 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 30.4 (CH_2), 29.6 ($C(CH_3)_3$), 27.0 (CH_2), -8.9 (Al-CH_3).

rac-Lactide polymerization.

The polymerization was carried out in inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a solution of *rac*-lactide in toluene. Subsequently, a toluene solution of metal-complex and ^{i}PrOH (0.1 M) was added. The reaction mixture was stirred at 70 °C. At desired times; small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization the product was precipitated in MeOH then filtered and dried under vacuum oven.

CHO polymerization.

Bulk: The polymerization was carried out in inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a solution of metal-complex (and ^{i}PrOH) in CHO. The reaction mixture was stirred at RT or at 70 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization the product was dissolved in hexane and then precipitated in HCl:Ethanol 1:3.

Solution: The polymerization was carried out in inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with a CH_2Cl_2 solution (2 mL) of metal-complex (and ^{i}PrOH) and CHO. The reaction mixture was stirred at RT. At desired times, small aliquots of the reaction mixture were sampled, dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. At the end of the polymerization the product was dissolved in hexane and then precipitated in HCl:Ethanol 1:3.

Conclusions

Dinuclear aluminum complexes ligated by salen-type frameworks, selected to feature two metal sites at varying distances from one another, were synthesized and tested as initiators in the ring-opening polymerization of *rac*-LA and epoxides. All complexes, activated by isopropyl alcohol, promoted controlled homopolymerization of *rac*-LA showing different activities depending on the distance between the two metal centers as consequence of the possibility of synergic interaction between the metal centers. Dinuclear complex in which the aluminum centers are proximal has been found to be 5 times more active than complexes in which longer alkyl bridges prevent the interaction between the reactive aluminum centers. The NMR studies of the structure of the active species showed that when the two reactive centers are proximal the growth of the polymer chain occurs on a single aluminum center. Otherwise, the independent grow of two polymer chains, one for each metal center, is supposed when the two reactive centers are distant.

Kinetic studies indicated that no induction period is present in the ROP of lactide promoted by a dinuclear complex, activated with an exogenous alcohol, in which the two reactive centers are proximal while an induction period of two hours is necessary for complexes in which the distance between the aluminum centers prohibits any cooperation. All these data support the hypothesis of a synergic action between the two metal centers that has a role both in the alcoholysis reaction and in propagation steps. This supposition was confirmed by the results obtained in the ROP of cyclohexene oxide where the complex bearing the shortest distance between the two aluminum centers was the only active. These results highlight that the cooperation between metal reactive centers in a

Pre-print version DOI:10.1039/c6dt02592g. ISSN:1477-9226 DALTON TRANSACTIONS 2016 vol. 45 pp.16001-16010.

multinuclear species can be induced by an opportune ligand design.

Acknowledgements

The authors acknowledge Dr. Patrizia Oliva for NMR assistance, Dr. Patrizia Iannece for MALDI-TOF analysis and Maria Chiara Cozzolino for some synthetic work.

Notes and references

1 K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420.

2 C. Baleiza, H. Garcia, *Chem. Rev.*, 2006, **106**, 3987.

3 (*a*) C. M. Thomas, *Chem. Rev.* 2010, **39**, 165. (*b*) R. H. Platel, L. M. Hodgson, C. K. Williams, *Polym. Chem.* 2008, **48**, 11. (*c*) P. J. Dijkstra, H. Z. Du and J. Feijen, *Polym. Chem.*, 2011, **2**, 520. (d) Y.Wei, S. Wang, S. Zhou, *Dalton Trans.*, 2016, **45**, 4471.

4 N. Spassky, M. Wisniewski, C. Pluta, A. Le Borgne, *Macromol. Chem. Phys.*, 1996, **197**, 2627.

5 (*a*) Z. Zhong, P. J. Dijkstra, J. Feijen, , *Angew. Chem., Int. Ed.*, 2002, **41**, 4510; (*b*) Z. Y. Zhong, P. J. Dijkstra, J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291.

6 T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316.

7 (*a*) N. Nomura, R. Ishii, M. Akakura and K. Aoi, *J. Am. Chem. Soc.*, 2002, **124**, 5938. (*b*) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem.–Eur. J.*, 2007, **13**, 4433;

8 P. Hormniru, E. L. Marshall, V. C. Gibson, R. I. Pugh, A. J. P. White, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15343.

9 (*a*) Z. H. Tang, X. S. Chen, X. Pang, Y. K. Yang, X. F. Zhang and X. B. Jing, *Biomacromolecules*, 2004, **5**, 965; (*b*) H. Du, X. Pang, H. Yu, X. Zhuang, X. Chen, D. Cui, X. Wangand, X. Jing, *Macromolecules*, 2007, **40**, 1904; (*c*) X. Pang, H. Du, X. Chen, X. Wang and X. Jing, *Chem.–Eur. J.*, 2008, **14**, 3126.

10 (*a*) P. Hormniru, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688. (*b*) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen, J. Feijen, *Chem. Eur. J.*, 2009, **15**, 9836. (c) N. Ikpo, S. M. Barbon, M. W. Drover, L. N. Dawe, F. M. Kerton, *Organometallics*, **2012**, *31*, 8145

11 (*a*) E. L. Whitelaw, G. Loraine, M. F. Mahon, M. D. Jones, *Dalton Trans.*, 2011, **40**, 11469; (*b*) S. L. Hancock, M. F. Mahon, M. D. Jones, *Dalton Trans.*, 2013, **42**, 9279. (*c*) A. Pilone, N. De Maio, K. Press, V. Venditto, D. Pappalardo, M. Mazzeo, C. Pellecchia, M. Kol, M. Lamberti, *Dalton Trans.*, 2015, **44**, 2157.

12 (*a*) M. Bouyahyi, E. Grunova, N. Marquet, E. Kirillov, C. M. Thomas, T. Roisnel, J.-F. Carpentier, *Organometallics*, 2008, **27**, 5815; (*b*) A. Alaaeddine, C. M. Thomas, T. Roisnel, J.-F. Carpentier, *Organometallics,* 2009, **28**, 1469; (c) M. Bouyahyi, T. Roisnel, J. F. Carpentier *Organometallics*, 2010, **29**, 491.

13 K. Press, I. Goldberg, M. Kol, *Angew. Chem., Int. Ed.*, 2015, **54**, 14858.

14 A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo, M. Lamberti, *J. Am. Chem.Soc.*, 2014, **136**, 2940.

15 (a) X. Pang, R. Duan, X. Li and X. Chen, *Polym. Chem.*, 2014, **5**, 3894. (b) Z. Qu, R. Duan, X. Wang, X. Pang, X. Chen, B. Gao, X. Li and Z. Tang, *J. Polym. Sci. Part A: Polym. Chem.*, 2014, **52**, 1344. (c) D. J. Darensbourg, O. Karroonnirun, *Organometallics* 2010, **29**, 5627. (d) W. Li, W. Wu, Y. Wang, Y. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2011, **40**, 11378. (e) Z. Sun, R. Duan, J. Yang, H. Zhang, S. Li, X. Pang, W. Chen, X. Chen, *RSC Adv*. 2016, **6**, 17531.

16 H.-L. Hang, Y. Lin, J.-Y. Lin, K. Nomura, Y. S. Li *Dalton Trans.*, 2013, **42**, 12346.

17 L. Li, B. Liu, D. Liu, C. Wu, S. Li, B. Liu and D. Cui, *Organometallics*, 2014, **33**, 6474.

18 N. Maudoux, T. Roisnel, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Chem. Eur. J.*, 2014, **20**, 6131.

19 C. Kan, J. Ge and H. Ma, *Dalton Trans.*, 2016, **45**, 6682.

20 Y. Wang and H. Ma, *Chem. Commun.*, 2012, **48**, 6729.

21 L. Chen, W. Li, D. Yuan, Y. Zhang, Q. Shen and Y. Yao, *Inorg. Chem.*, 2015, **54**, 4699.

22 M. A. van Aelstyn, T. S. Keizer, D. L. Klopotek, S. Liu, M.-A. Munoz Hernandez, P. Wie and D. A. Atwood, *Organometallics*, 2000, **19**, 1796.

23 M. Normand,V. Dorcet, E. Kirillov, J.-F. Carpentier, *Organometallics*, 2013, **32**, 1694.

24 W. Zhang, Y.Wang, W.-H. Sun, L. Wang, C. Redshaw, *Dalton Trans.*, 2012, **41**, 11587.

25 GPC values corrected according: J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.*, 1997, **18**, 325.

26 M. Normand, T. Roisnel, J. F. Carpentier, *Chem Commun.* 2013, **49**, 11692.

27 All bimetallic diphenylethylene –salen aluminum complexes reported by Carpentier (rif 18) only afforded atactic PLAs.

28 Y. Wang, H. Ma, *J. Organomet. Chem.*, 2013, **731**, 23.

29 (*a*) Ph. Dubois, C. Jacobs, R. Jerome and Ph. Teyssie, *Macromolecules*, 1991, **24**, 2266; (*b*) C. Jacobs, Ph. Dubois, R. Jerome and Ph. Teyssie, *Macromolecules*, 1991, **24**, 3027.

30 B. Wigand and J. Okuda, *Angew. Chem. Int. Ed.*, 2003, **42**, 64.

31 (*a*) A. Buchard, F. Jutz, M. R. Kember, A. J. P. White, H. S. Rzepa, C. K. Williams, *Macromolecules*, 2012, **45**, 6781. (*b*) S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott and B. Rieger, *J. Am. Chem. Soc.*, 2011, **133**, 13151. (*c*) F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen and C. K. Williams, *J. Am. Chem. Soc.*, 2011, **133**, 17395; (*d*) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738; (*e*) S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini and C. K. Williams, *Chem. Commun.*, 2015, **51**, 6459.

32 (*a*) R. J. Baker and A. Walshe, *Chem. Commun.*, 2012, **48**, 985; (*b*) J. Fang, A. Walshe, L. Maron and R. J. Baker, *Inorg. Chem.*, 2012, **51**, 9132.

33 Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296.

34 S. Pappuru, E. R. Chokkapu, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2013, **42**, 16412.

35 D. Cui, M. Nishiura and Z. Hou, *Macromolecules*, 2005, **38**, 4089.

36 H. Plommer, I. Reim and F. M. Kerton, *Dalton Trans.*, 2015, **44**, 12098.

37 G. Martinez, S. Pedrosa, V. Tabernero, M. E. G. Mosquera, T. Cuenca *Organometallics*, **27**, 2300.

38 Y. Sarazin and J.-F.Carpentier, *Chem. Rev.*, 2015, **115**, 3564.

39 N. Nakata, Y. Saito and A. Ishii, *Organometallics*, 2014, **33**, 1840.

40 D. A. Atwood, J. A. Jegier and D. Rutherford, *J. Am. Chem. Soc.*, 1995, **117**, 6778.

41 (*a*) S. Dagorne, L. Lavanant, R. Welter, C. Chassenieux, P. Haquette, Jaouen, G., *Organometallics*, 2003, **22**, 3732; (*b*) M. Haddad, M. Laghzaoui, R. Welter and S. Dagorne, *Organometallics*, 2009, **28**, 4584.

42 M. Cozzolino, K. Press, M. Mazzeo and M. Lamberti, *ChemCatChem*, 2016, **8**, 455.