*catalysts*

*Perspective*

# Use of Metal Catalysts Bearing Schiff Base Macrocycles for the Ring Opening Polymerization (ROP) of Cyclic Esters

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**Abstract:** Schiff base macrocycles are emerging as useful scaffolds for binding two or more catalytic metals in close proximity. Such coordination chemistry allows for the evaluation of potentially beneficial catalytic cooperative effects. In the field of ring opening polymerization (ROP) of cyclic esters, only a handful of metal systems bound by Schiff base [2 + 2] type macrocycles have been studied. Nevertheless, results to date have, for certain metals, identified some interesting structure activity relationships, whilst for other systems results have revealed particular combinations of metals and macrocycles to be virtually inactive. This perspective review takes a look at two types of recently-reported Schiff base macrocycles that have been employed as pro-ligands in the metal-catalyzed ROP of cyclic esters, specifically ε-caprolactone and *rac*-lactide.

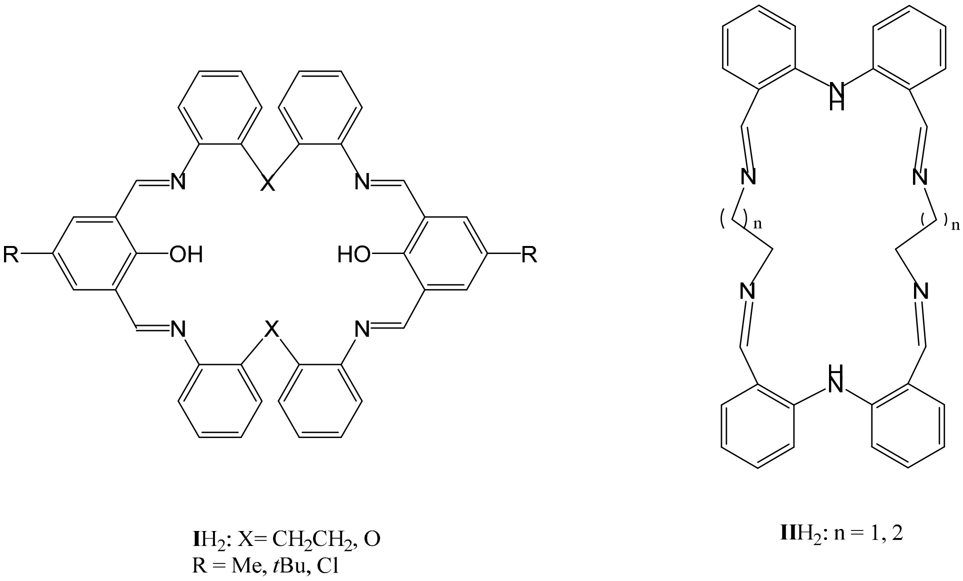
**Keywords:** Schiff base macrocycle; metal catalysts; ring opening polymerization; cyclic esters

## 1. Introduction

There remains immense interest in catalytic systems capable of producing poly(lactide) and poly(caprolactone) given that such biodegradable polymers have found widespread application, notably in the medical and packaging fields [1]. The catalysts of choice should be both cheap and non-toxic, whilst being highly active and are, hopefully, constructed in such a way that they can be readily modified and thereby allow for a high degree of control over the ring opening polymerization (ROP) process. It is now well established that the use of bimetallic catalysts versus their monometallic counterparts can impart improved activities and selectivities over the catalytic process, be it α-olefin polymerization [2] or for the ROP of lactides [3]. In order to synthesize such bimetallic catalysts, suitable pro-ligand frameworks need to be available, whose coordination chemistry is well suited to binding more than one metal simultaneously in close proximity. Macrocycles are ideal in this respect, and we and others have had some success with the use of calix[*n*]arenes in ROP [4–9].

A relatively untapped pro-ligand family are imine-based macrocycles, the frameworks of which can be readily manipulated to allow multiple metal centers to bind at specific distances apart. For a particular macrocyclic family, combining the catalytic studies with crystallographic work can give insight into the optimum degree of metallation, the preferred geometrical parameters at each metal, and favourable inter-metallic distances for enhanced catalysis. In-turn, this allows for control over possible synergistic cooperation between the metal centers. Imine-based macrocycles can vary greatly in composition, for example [2 + 2], [3 + 3], [4 + 4], and [6 + 6] condensation products have all been found to be readily accessible [10,11].

In terms of the ROP of cyclic esters, the use of [2 + 2] tetraimine Schiff bases has found favour as of late. Of these, two types that have attracted increased attention are the bis(imino)phenoxide-derived macrocycles $\mathbf{I}H_2$ (see Scheme 1, left) and the bis(anilido)tetraimine macrocycles $\mathbf{II}H_2$ (see Scheme 1, right) [12–16]. The ROP behaviour of complexes derived from $\mathbf{I}H_2$ and $\mathbf{II}H_2$ is discussed herein.



$\mathbf{I}H_2$: X= $CH_2CH_2$, O
R = Me, *t*Bu, Cl

$\mathbf{II}H_2$: n = 1, 2

**Scheme 1.** Macrocycles $\mathbf{I}H_2$ and $\mathbf{II}H_2$ discussed herein.

## 2. Discussion

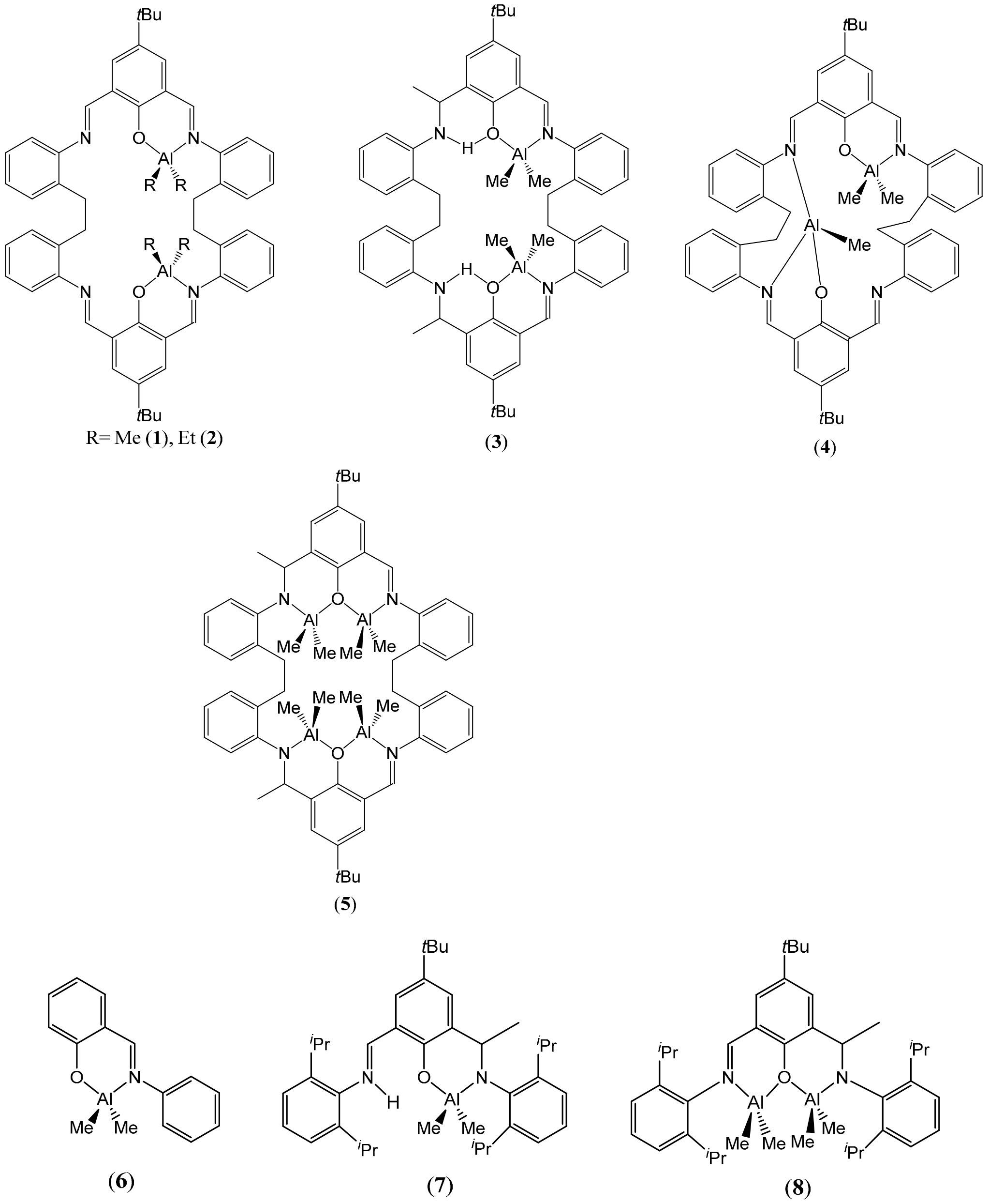
### 2.1. The Use of $\mathbf{I}H_2$ (X = $CH_2CH_2$)

Initial ROP work focused on macrocycles of type $\mathbf{I}H_2$ derived from the dianiline $[(CH_2CH_2)(2\text{-}C_6H_4NH_2)_2]$ and organoaluminium complexes [12]. The macrocycles $\mathbf{I}H_2$ were readily accessible via standard condensation procedures.

### 2.1.1. Organoaluminium Complexes

A number of complexes **1**–**5** were prepared by employing either two or four equivalents of $R_3Al$ (R = Me, Et)—see Scheme 2. For the type **2** complexes, a '*trans*' structure rather than the '*cis*' structure shown in Scheme 2 was subsequently characterized by X-ray crystallography [13]. Complex **4** was also isolated in which a methylaluminium centre was bound by the macrocycle in a tridentate *N*,*N*,*O*-fashion. The tetranuclear complexes have undergone a double alkyl transfer to one side of the macrocycles. Screening of **1**–**5** (compared to **6**–**8**) for the ROP of ε-caprolactone revealed how the pro-catalyst structure can influence the observed catalytic behaviour. The use of alkylaluminium complexes for the ROP of cyclic esters has recently been reviewed [17], as has the use of aluminium alkyl complexes bearing salicylaldiminato ligands [18].

Using the ratio 500:1:1 (ε-CL:Cat:BnOH) over 24 h at 25 °C, the activities of **1** and **2** are similar and are better than that of the acyclic complex **6**, whilst acyclic complexes **7** and **8** perform poorer than type **3** and **5** macrocyclic complexes. Interestingly, complexes of type **3** outperform type **5**, which suggests that although there is a cooperative effect observed, this only operates in the absence of aluminoxane-type bonding. It should be noted that MAO, with its Al-O-Al bonds, has been reported to exhibit poor activity [19]. Looking at the geometrical parameters for **3** and **5**, a favourable distance between Al centres appears to be ca. 5.78 Å (as in **3**), whilst the closer Al centres in **5** (ca. 3.22 Å) appears to hinder the polymerization process. However, such correlations are system-specific; for example, we have noted that in the case of acyclic systems derived from *o*-, *m*-, or *p*-anisidines, the highest activity is exhibited by the *ortho* system for which the Al-Al distance is ca. 3.11 Å [20].



R= Me (**1**), Et (**2**) (**3**) (**4**)

(**5**)

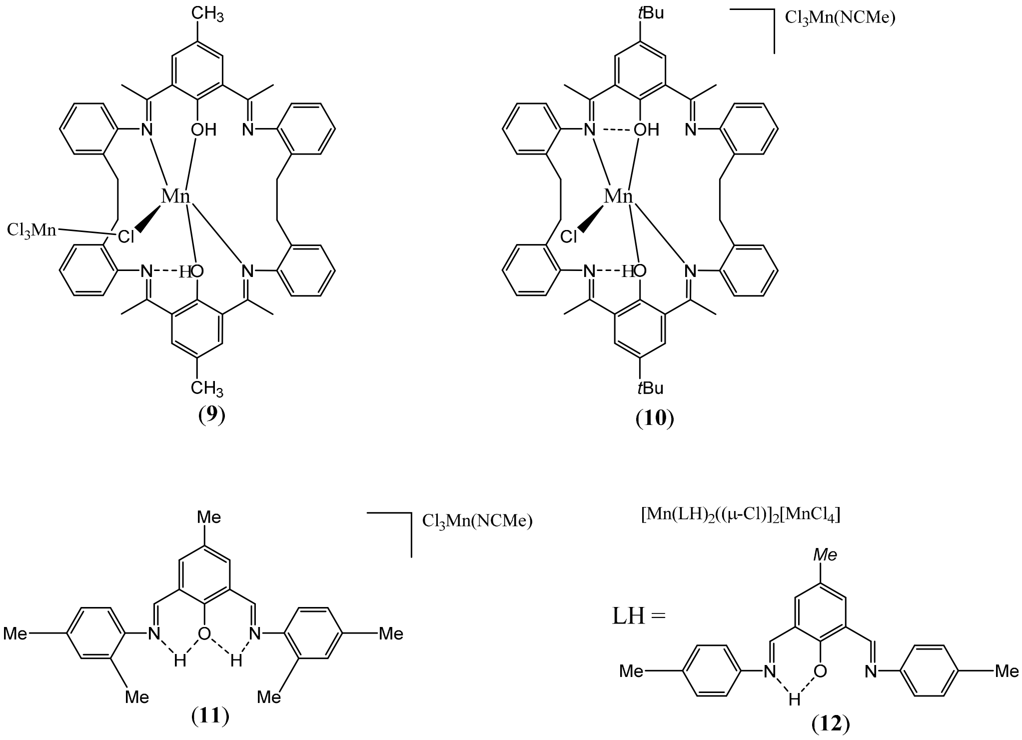
(**6**) (**7**) (**8**)

**Scheme 2.** Organoaluminium complexes (**1**–**8**).

The Al-Al distance in **3** may permit one metal centre to be used as a Lewis acid whilst the other can attack the carbonyl group of the monomer, akin to the situation postulated for the ROP of propylene oxide [21,22].

### 2.1.2. Manganese Complexes

As part of a programme aimed at exploring the use of earth abundant metal catalysts for ROP, [23–25] the manganese complexes **9** and **10** (Scheme 3) were screened for their ability to ROP ε-caprolactone in the presence of benzyl alcohol [14]. Results were compared against the acyclic salt compounds **11** and **12**. At temperatures above 60 °C, results for **10** were slightly better than observed for **9**, however both systems were poorly active with conversions <15%, and significant *trans*-esterification was present. The salts **11** and **12** were found to be inactive.



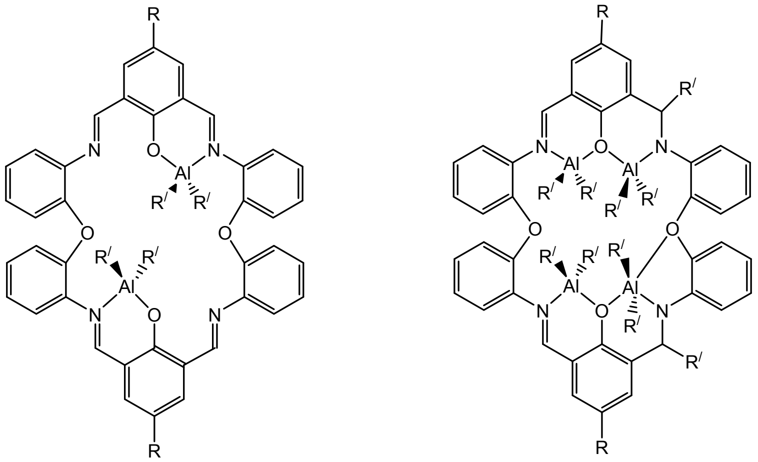
**Scheme 3.** Manganese complexes (**9**–**12**).

## 2.2. Use of $IH_2$ ($X = O$)

### 2.2.1. Organoaluminium Complexes

Similar use of the dianiline 2-(2-aminophenoxy)aniline $(2\text{-}NH_2C_6H_4)_2O$ in the condensation procedure afforded the Schiff base macrocycles $\mathbf{IH_2}$ ($X = O$) in good yield. Treatment with either two or four equivalents of $R_3Al$ afforded the complexes **13–18** and **19–22**, respectively (see Scheme 4) [13]. The structure of the compound **19** is shown in Figure 1, and reveals that, as for **5**, intramolecular regioselective methyl transfer to two imine moieties (originating from the same dianiline) of the macrocycle has occurred; such methyl transfers are well established in imine chemistry [26–30]. The bonding in **19** is asymmetrical in that one of the aluminium centres is five-coordinate, whilst the other three are distorted tetrahedral. This means that unlike the case of **5** (where the macrocycle has a $\text{-}CH_2CH_2\text{-}$ bridge), complex **19** does not possess approximate $C_2$ symmetry in the solid state.

These complexes were screened for the ability to act as pro-catalysts for the ROP of ε-caprolactone and of *rac*-lactide. Optimization of the screening conditions using complex **17** suggested that the ROP runs were best carried out using the ratio 250:1:1 (ε-CL:Cat:BnOH) over 30 min at 80 °C. Systems employing **13–18** all behaved similarly with Conversions in the range 93% (for **13**) to 98% (for **17**). For analogous compounds, the ethyl derivatives out-performed (higher activities and molecular weights) the methyl derivatives. All systems were relatively well behaved with PDIs in the range 1.22–1.49. Interestingly, when complexes **1** and **5** were screened under the same conditions as **13–18**, they were found to be far inferior exhibiting percent conversions of 25.6% and 38.5%, respectively. In the case of the tetranuclear complexes 19–22, screening for ROP of ε-CL was, again, conducted at 30 min at 80 °C, and it is thought that the enhanced solubility of the systems bearing a *para* methyl group at the phenolic group, i.e., **19** and **21**, leads to enhanced conversions (99% versus 80.9% (for 20) and 94.3% (for **22**)). Again, the ethyl derivatives outperformed the analogous methyl derivatives. There was little evidence of transesterification occurring, with close agreement between observed and calculated polymer molecular weights. When screened under the same conditions, the $\text{-}CH_2CH_2\text{-}$ bridged system **5** was far inferior, exhibiting only a percent conversion of 29.1%. It was postulated for these systems that the presence of the oxygen bridge in the macrocycle can help to stabilize the catalytically-active species, a situation reminiscent of the vanadium-based calixarene polymerization catalysis of ethylene [31].



R = R$^{/}$ = Me (**13**)
R = *t*Bu, R$^{/}$ = Me (**14**)
R = Cl, R$^{/}$ = Me (**15**
R = Me, R$^{/}$ = Et (**16**)
R = *t*Bu, R$^{/}$ = Et (**17**)
R = Cl, R$^{/}$ = Et (**18**)

R = *t*Bu, R$^{/}$ = Me (**19**)
R = Cl, R$^{/}$ = Me (**20**)
R = Me, R$^{/}$ = Et (**21**)
R = Cl, R$^{/}$ = Et (**22**)

**Scheme 4.** Organoaluminium complexes (**13**–**22**).

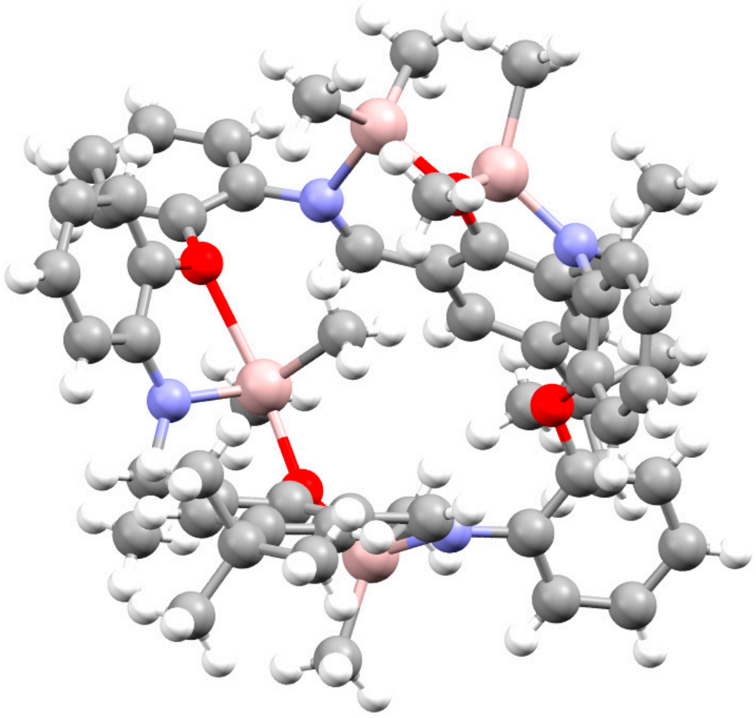
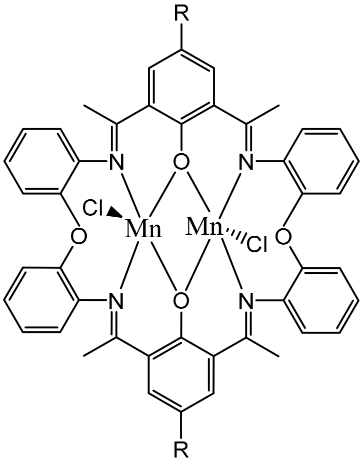


**Figure 1.** Molecular structure of tetranuclear complex (**19**).

When these systems were employed for the ROP of *rac*-lactide, best conversions were achieved at 110 °C with the ratio 100:1:1 (*rac*-LA:Al:BnOH) over 12 h. For organoaluminium systems, the ROP of lactide often requires more robust conditions than those employed for ε-CL [32]. However, there was no clear evidence of an enhanced performance for the tetranuclear versus the dinuclear systems. For the latter, the ethyl derivatives were slightly more active than the methyl derivatives; the same trend though was not evident for the tetranuclear systems. All of the systems appeared to be well behaved with PDIs in the range 1.07–1.38, and observed and calculated molecular weights did not differ greatly. The use of 2D J-resolved $^1$H NMR spectroscopy [33] revealed moderately isotactic PLA with $P_r$ values in the range 0.64–0.67.

### 2.2.2. Manganese Complexes

Under a variety of conditions, use of the compounds **23** and **24** (Scheme 5) for the ROP of ε-caprolactone failed to afford any polymer product [14].



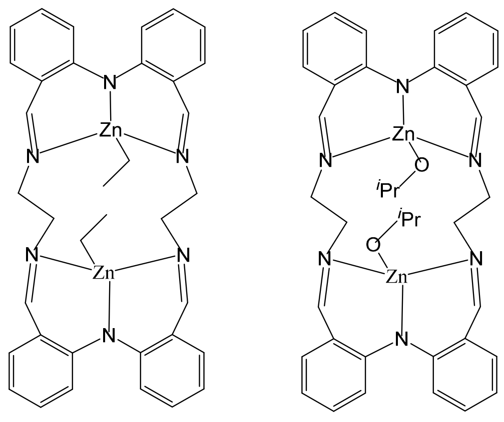
R =Me (**23**); R = *t*Bu (**24**)

**Scheme 5.** Manganese complexes (**23**) and (**24**).

### 2.3. *Use of* ***II****H*$_2$

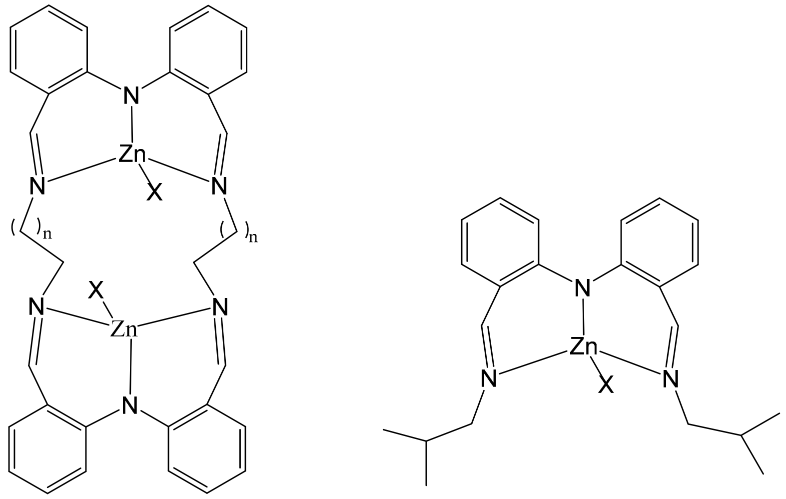
Condensation of 2,2′-iminobisbenzaldehyde with the likes of 1,2-diaminoethane or 1,2-diaminopropane in refluxing methanol affords macrocycles of type **II**H$_2$ [34]. Brooker et al. have shown that the reaction of **II**H$_2$ ($n$ = 1, a 22-membered macrocycle) with diethylzinc affords complex **25** which, on further treatment with isopropyl alcohol, affords **26** (see Scheme 6) [15]. This reaction needs to be heated to 60 °C over 2 h for complete conversion to **26** as evidenced by $^1$H NMR spectroscopy, whilst on scale-up the isolated yield is about 30%. The reaction is thought to proceed via two steps, namely protonation of the anilido function followed by an intramolecular deprotonation of the NH by a zinc-bound ethyl group. Using 25 (catalyst:*rac*-LA 1:200) in THF and adding two equivalents of isopropyl alcohol, 78% conversion is accomplished at 25 °C over 1 h. The system was well behaved with PDI of the atactic polymer <1.1 and with no evidence of transesterification observed.

When diaminopropane is employed as a precursor (i.e., $n$ = 2) in the condensation process, the result is a slightly larger 24-membered macrocycle, which is conformationally more flexible. This larger ligand, as well as **II**H$_2$ ($n$ = 1), have been reacted with {Zn[N(SiMe$_3$)$_2$]} and, subsequently, with two equivalents of isopropyl alcohol to afford the complexes **27** and **28** and **30** and **31**, respectively. For comparative catalytic studies, the monometallic complexes **29** and **32** were also prepared (Scheme 7) [16].



**25** **26**

**Scheme 6.** Zinc complexes (**25**) and (**26**).



X = N(SiMe$_3$)$_2$
n = 1 (**27**); n = 2 (**28**)

X= O*i*Pr
n = 1 (**30**); n = 2 (**31**)

X = N(SiMe$_3$)$_2$ (**29**)

X= O*i*Pr (**32**)

**Scheme 7.** Zinc complexes (**27**–**32**).

Screening for the ROP of *rac*-LA revealed that **27** and **28** could, in the absence of any additional alcohol, polymerize 1000 equivalents of monomer in 60 s with good control (PDIs $\leq$ 1.4). Evidence for a cooperative effect was provided by the observation that the activity of **28** was, per zinc centre, three times greater than that of **29**. The enhanced activity of these systems is best illustrated by the activity of **27**, which was found to be 600 times more active than the system employing **25**. Polymerization kinetics for these systems revealed a zero-order rate dependence on lactide concentration, which is thought to be associated with the pre-equilibrium constant of lactide binding at the metal. Furthermore, the systems **27** and **29** exhibit an induction period that, following a 15–20% conversion, a linear conversion versus time plot is adopted. Examination of the higher-than-expected molecular weights suggested that only a fraction of the catalyst was being utilized. This, in turn, suggests that complex **27** is 1.5 times quicker than **28** and six times more active than **29**. These results for **27** and **28** can be equated to the distance between the metal centres, which will be closer in **27**, enabling better 'communication'.

Somewhat surprisingly, the isopropoxide complexes **30** and **31** are much less active than the amide derivatives; for example, **30** is 400 times slower than **27**, but exhibited better control exhibiting first-order dependence on monomer concentration. Further, the mono- and bimetallic systems display comparable activities with one another. Molecular structure determinations (see Figure 2) shed some light on the reasons for the differing behaviour of these systems. In the case of the amide **27**, the complex was found to adopt a 'folded' $C_2$ symmetric structure with the amide on the same side of the complex. By contrast, the isopropoxide complex **30** possesses a more planar conformation, for which the flexibility is greatly reduced by the two bridging $k^2$ alkoxide ligands.

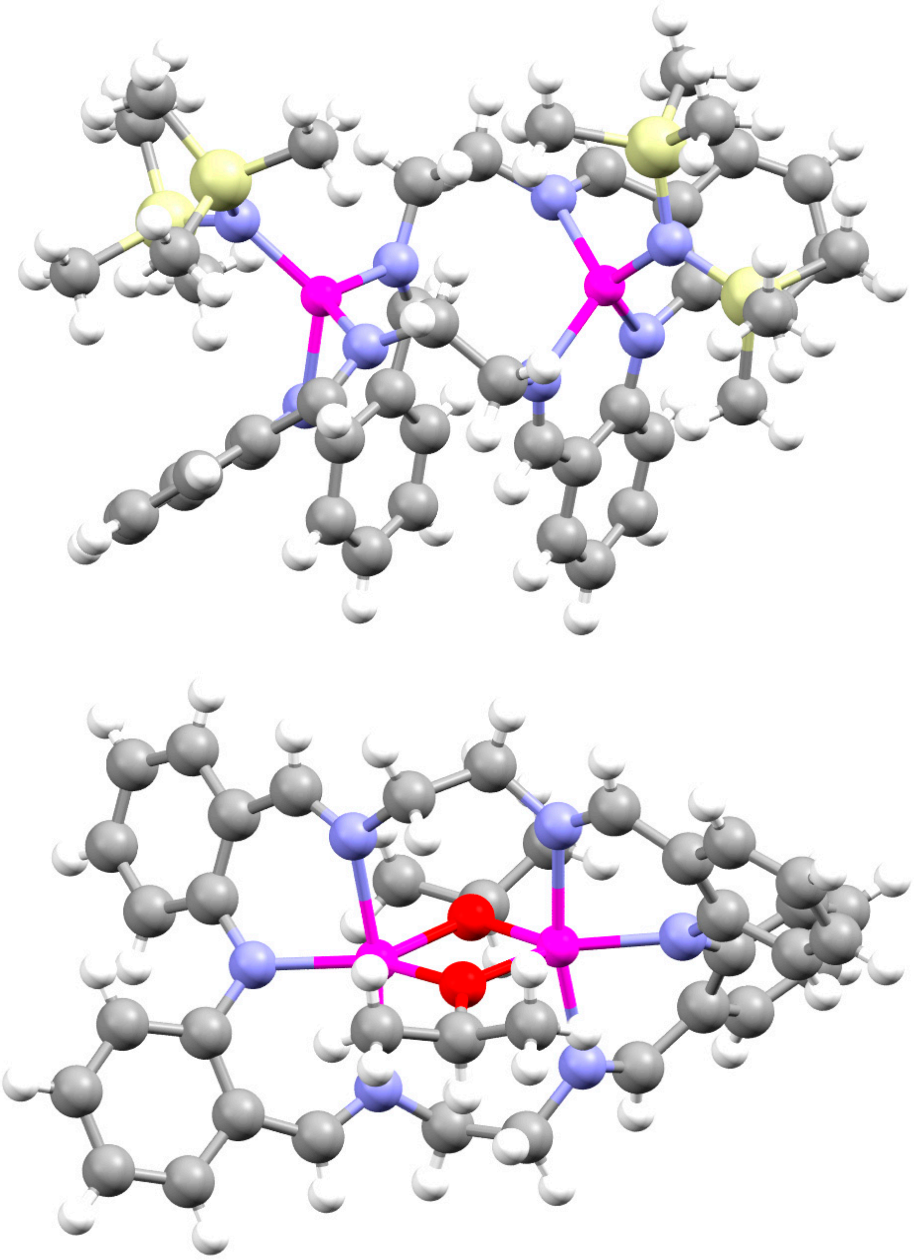


**Figure 2.** Molecular structures of complexes (**27**) (**top**) and (**30**) (**bottom**).

It proved possible to combine the catalytic advantages of both families of catalysts by use of **27**–**29** under immortal conditions (simultaneous addition of 10 equivs. of isopropanol and lactide monomer). The systems proved to be well behaved and extremely active under such conditions, achieving complete conversion in just 30 s; TOF values were three times greater than any other reported zinc-based systems. High activities were maintained even at very low catalyst loadings (0.02–0.002 mol %). It has been postulated that a new highly active alkoxide complex is present under these immortal conditions which possesses a 'folded' conformation. This can then rearrange over about one minute to **30** (thermodynamic stability) which, given that the ROP process is complete within 29 s, is not problematic and is consistent with the observations. End group analysis of the polymer (alkoxide and amide groups are present) and low temperature NMR measurements on the alcoholysis of **30** lends support to this theory.

## 3. Outlook

The handful of reports to-date involving the use of macrocycles as ancillary ligands for the metal-based ROP catalysis of cyclic esters clearly show there is much potential for developing systems of industrial relevance. Such systems have the advantage over acyclic systems, given that the ability to control the size of the macrocycle by judicious choice of starting materials allows for control over conformational flexibility and manipulation of metal-metal distances. They are also capable of supporting structural motifs not seen in acyclic systems. By combining catalytic studies with crystallographic work insight into the optimum degree of metallation, the preferred geometrical parameters at each metal and favoured inter-metallic distances can be gleaned. In turn, this allows for possible synergistic cooperation between the metal centres. Furthermore, the ability to incorporate pendant arms into the macrocycles has the potential to give a further dimension to the construction and coordinating ability of such macrocycles [35].

It is envisaged that many new macrocyclic catalysts will be reported in the coming years with controllable properties. Macrocycles also offer the opportunity to access mixed metal systems and this, in turn, will allow for new polymeric materials with desirable properties to be accessed.

**Conflicts of Interest:** The author declares no conflict of interest.

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