

# Catalytic Synergy Using Al(III) and Group 1 Metals to Accelerate Epoxide and Anhydride Ring Opening Copolymerizations

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**ABSTRACT:** The controlled synthesis of polyesters *via* epoxide/anhydride ring-opening copolymerization (ROCOP) is a versatile and generally applicable method to make many sustainable polymers but catalyst activities are limited and required catalyst loadings are typically high. Here, novel heterodinuclear complexes, featuring Al(III)/M(I) (M = Na, K, Rb, Cs), show exceptional activities for phthalic anhydride (PA) and cyclohexene oxide (CHO) copolymerization (Catalyst = Al(III)/K(I), TOF = 1072 h<sup>-1</sup>, 0.25 mol% catalyst loading vs anhydride, 100 °C). The Al(III)/K(I) catalyst is also tolerant to low loadings, maintaining a good performance at 0.025 mol% catalyst vs. anhydride loading and 0.005 mol% vs. epoxide. It rapidly polymerizes other epoxide/anhydride combinations, as well as showing activity in carbon dioxide/epoxide copolymerization, yielding various semi-aromatic, rigid and/or functionalizable polyesters. The results of structure-activity, X-ray crystallography, polymerization kinetics and DFT investigations support a mechanism with chain growth alternation between the metals. The rate limiting step is proposed to involve epoxide coordination at Al(III) with K(I) carboxylate attack. Future exploitation of abundant and inexpensive Group 1 metals to deliver synergic polymerization catalysts is recommended.

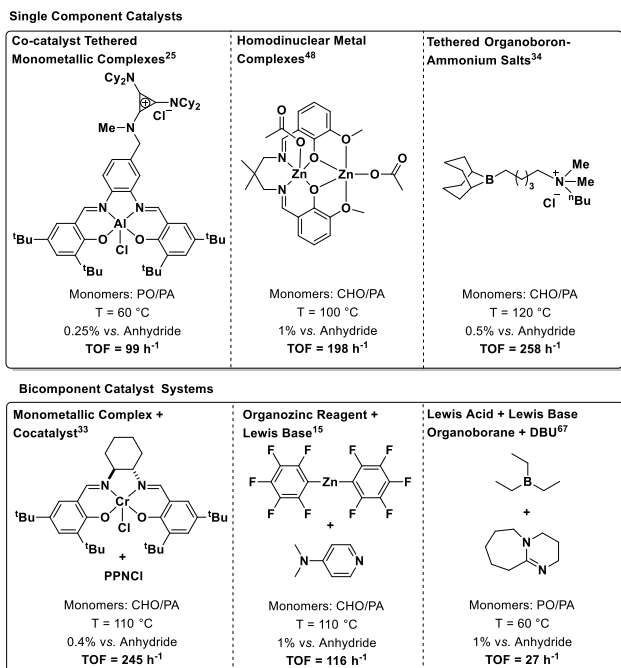
## Introduction

Polyesters are an important part of the solution to growing concerns around petrochemical polymer sustainability: many monomers are, or could be, bio-based and their polymer-monomer equilibria can be easily manipulated to facilitate chain degradation reactions relevant to both chemical recycling and biodegradation.<sup>1-4</sup> Scalable solvolyses or thermally catalysed depolymerizations allow for recycling to monomers and front-runner commercial chemical recycling processes have been validated using polyesters.<sup>5-7</sup> Some polyesters are also fully biodegradable and compostable which is attractive for short-term applications or those where environmental retrieval is unfeasible.<sup>7</sup>

Despite their potential, technical barriers remain, including limited understanding of structure-property relationships, a narrow range of polymer properties and high energy demand production methods. Today most polyesters are manufactured by step-growth polymerizations, which show low atom economy, necessitate high temperatures to drive conversion and produce poorly controlled polymers; these features severely hamper structure-property fine-tuning and prevent formation of block, graft or copolymers. Chain growth polymerizations are feasible using either cyclic ester ring opening polymerization (ROP) or epoxide/anhydride ring opening copolymerization (ROCOP), both are highly atom efficient and well-controlled polymerizations.<sup>8</sup>

Cyclic ester ROP is best suited to aliphatic polyester production using 4-, 6- or 7-membered rings but other lactones, especially substituted heterocycles, can suffer from polymerization thermodynamic constraints, and many are not commercially available.<sup>9, 10</sup> In contrast ROCOP applies monomers which are already commercialised at scale (epoxides and anhydrides), is thermodynamically feasible and delivers semi-aromatic, rigid, functionalized and aliphatic polyesters.<sup>11, 12</sup>

Epoxide/anhydride ROCOP catalysis is at an earlier developmental stage than cyclic ester ROP and there is still a need for high activity, selectivity, tolerant and well-controlled catalysts.<sup>11, 12</sup> There is also a lack of mechanistic insight and of catalyst structural diversity. New homogeneous polymerization catalysts should apply easy-to-synthesise, scalable ligands and earth-abundant, inexpensive and light metals. Although some high activity organo-catalysts and acid/base catalyst systems are reported,<sup>13-23</sup> the highest performing catalysts remain metal complexes (Chart 1).<sup>24-32</sup> Leading examples are mononuclear metal complexes, some of which feature a tethered ionic co-catalyst, usually attached to the ancillary ligand.<sup>25, 26, 33</sup> For example, Coates and co-workers reported a highly active and selective cyclopropenium chloride tethered Al(III)-salen catalyst for propylene oxide (PO)/phthalic anhydride (PA) ROCOP (TOF = 99 h<sup>-1</sup>, 60 °C, 0.25 mol% catalyst).



**Chart 1.** Selection of high-performance epoxide/anhydride ROCOP catalysts.

Utilising the same design strategy, tethered organocatalyst complexes showed competitive activity and were stable at high operating temperatures (TOF = 258 h<sup>-1</sup>, 0.5% vs. anhydride, T = 120 °C).<sup>34</sup> Very recently, a trimetallic chromium salen-derivative has shown exceptional activities, albeit still requiring added cocatalyst (TOF = 10,620 h<sup>-1</sup>, 0.017% vs. anhydride, T = 100 °C).<sup>35</sup>

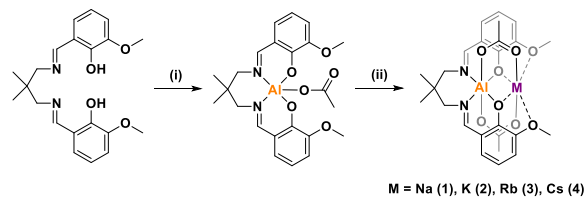
It would be desirable to obviate ionic co-catalyst usage without compromising rate; the most effective co-catalysts tend to be expensive, may be corrosive and require complex, multi-step procedures to install them onto ligands. We have previously investigated heterodinuclear epoxide/carbon dioxide ROCOP catalysts which operate without co-catalyst; some show metal cooperativity which improves activity compared with homodinuclear catalysts.<sup>36-40</sup> However, *a priori* understanding of which metal combinations are synergic is lacking with some heterodinuclear catalysts underperforming against homodinuclear analogues.<sup>41</sup> Recent reports of high activity homodinuclear epoxide/anhydride ROCOP catalysts raise the question as to whether activities can be driven yet higher by mixed metal combinations.<sup>27, 28, 42-47</sup>

Here, a series of new heterodinuclear Al(III)/M(I) (M(I) = Na, K, Rb, Cs) catalysts for epoxide/anhydride ROCOP are investigated. The dinucleating Schiff base ligand is selected since it is easily prepared in high yields from commercial reagents and provides two differentiated metal coordination environments (*N,N,O,O*- and *O,O,O,O*-).<sup>48</sup> The catalysts will be complexes of Al(III) and Group 1 metals, targeted as they are earth abundant, inexpensive, and expected to be low/non-toxic.<sup>49</sup> Each metal also has precedent for activity in epoxide/anhydride ROCOP catalysis, but in every case with clear room for improvements. For example, the known Al(III) catalysts are highly active but require tethered co-

catalysts,<sup>25, 26</sup> whilst Group 1 carboxylates are easy to use but show low rates (KOAc catalyst, TOF = 23 h<sup>-1</sup>, 1 mol% vs. anhydride, neat CHO, 110 °C).<sup>50, 51</sup> It is hypothesized that by combining these metals within the correct ancillary ligand framework, synergic catalysis could exploit the benefits of each metal without compromising on catalyst ease of synthesis, activity, selectivity and tolerance.

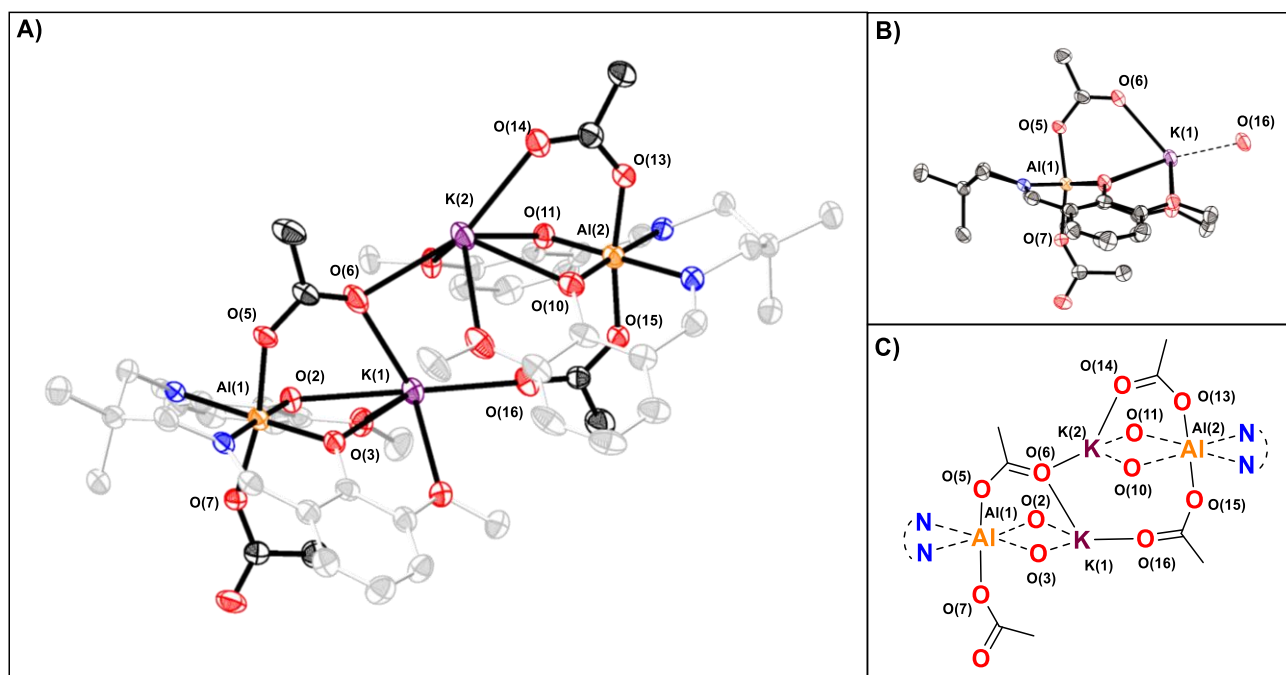
## Results and Discussion

The dinucleating Schiff base ligand, L<sub>van</sub>H<sub>2</sub>, was targeted to coordinate to Al(III) through the Schiff base binding 'pocket' and to Group 1 metals through the adjacent ortho-ether groups (Scheme 1, see ESI for experimental details).<sup>41, 48</sup> It was synthesised in high yield and in a single step from commercial starting materials; the procedure is also successful on a multigram scale.<sup>48</sup>



**Scheme 1.** Synthesis of complexes 1 - 4. (i) 1.05 equiv. AlEt<sub>3</sub>, 2 h, RT then 1.0 equiv. AcOH, 16, RT, 74%. (ii) 1.0 equiv. MOAc, CHCl<sub>3</sub>, 16 h, RT, Yields = 64% (1), 98% (2), 86% (3), 99% (4).

First, the monometallic, Al(III) complex [L<sub>van</sub>Al(OAc)] was prepared in good yield (74%) by reaction of the pro-ligand with triethylaluminium, followed by the addition of acetic acid.<sup>52</sup> To make heterodinuclear complexes 1 - 4, the Al(III) intermediate was reacted with an equivalent of the desired Group 1 metal acetate, in chloroform. All the heterodinuclear complexes were characterized using <sup>1</sup>H, <sup>13</sup>C, and <sup>27</sup>Al NMR spectroscopy, which confirmed coordination of both the Al(III) and the Group 1 metal acetates (Fig. S1 - S30). For example, complex 2, in comparison to [L<sub>van</sub>Al(OAc)], shows shifts in the *o*-methoxy (3.80 to 3.39 ppm) and imine (8.10 to 7.90 ppm) proton resonances. Furthermore, the methylene and methyl protons of the propylene diamine ligand backbone are diastereotopic in the monometallic [L<sub>van</sub>Al(OAc)], but become equivalent after Group 1 metal coordination which results in a single peak for these protons in complexes 1 - 4. The heterodinuclear solution NMR data suggests that the Group 1 metal coordination renders both complex faces equivalent and is consistent with the acetate ligands adopting bridging coordination modes. The <sup>27</sup>Al NMR spectra of 1 - 4 each show a single resonance at *ca.* -1 ppm, values which are shifted compared to that for [L<sub>van</sub>Al(OAc)] at 14.8 ppm.<sup>52</sup> The spectra are characterized by sharp peaks consistent with octahedral Al(III) coordination geometries. The catalysts' temperature stability was confirmed by heating samples at 100 °C for 16 hours without any significant change to mass balance or signals as assessed by NMR spectroscopy using internal standards, indicating there are no monomer-dimer equilibria and a single speciation under catalysis conditions (Fig S36).



**Figure 1.** Molecular structure of complex **2** obtained from X-ray diffraction experiments, with thermal ellipsoids presented at 50% probability and H atoms omitted for clarity (Atom colour scheme: Al (orange), K (purple), O (red), N (blue), C (greyscale/black)). A) Structure of the dimer, showing acetate co-ligands bridging between two molecules of the complex. B) Structure of one half of the dimer, showing the ligand, and aluminate centre (Al(1)-O(5) = 1.905(2) Å, Al(1)-O(7) = 1.869(2) Å. C) Schematic showing key binding of both metals and acetate groups.

Single crystals, suitable for X-ray diffraction experiments were grown by layering hexane onto saturated solutions of the complexes in dichloromethane (**1**) or chloroform (**2** – **4**). Complexes **1** – **3** display dimeric structures in the solid state, whilst complex **4** shows an extended polymeric structure (Fig 1 and S32-S34, Tables S1-S5). In all cases the Al(III) centre is hexacoordinate, with a distorted octahedral coordination geometry, and is speciated as an aluminate. For example, complex **2** (Al(III)/K(I)) shows similar bond lengths for the two  $O_{\text{phenolate}}\text{-Al(III)}$  and  $O_{\text{phenolate}}\text{-K(I)}$  bonds and the values are consistent with the phenoxide being anionically coordinated to Al(III) and with a dative covalent bond to K(I) [Al(1)-O(2) = 1.842(2) Å; Al(1)-O(3) = 1.854(2) Å, K(1)-O(2) = 2.7220(19) Å; K(1)-O(3) = 2.738(2) Å]. Further, the two oxygen atoms from the acetate ligands are also coordinated as anions to Al(III) and show very similar bond lengths [Al(1)-O(5) = 1.905(2) Å; Al(1)-O(7) = 1.869(2) Å]. The clear identification of the Al(III) centres as anions, with the potassium cation balancing overall complex charge is important since there remains a lack of clarity in the field regarding the true catalyst metal charge and speciation especially during use.<sup>25, 26, 53</sup> Recently, Coates and Tolman and co-workers conducted elegant kinetic investigations of [Al(Salen)(X)]/PPNX epoxide/anhydride ROCOP catalyst systems and proposed that propagating intermediates are octahedral aluminate complexes, but until now structural support for such species was lacking.<sup>25, 26, 53</sup>

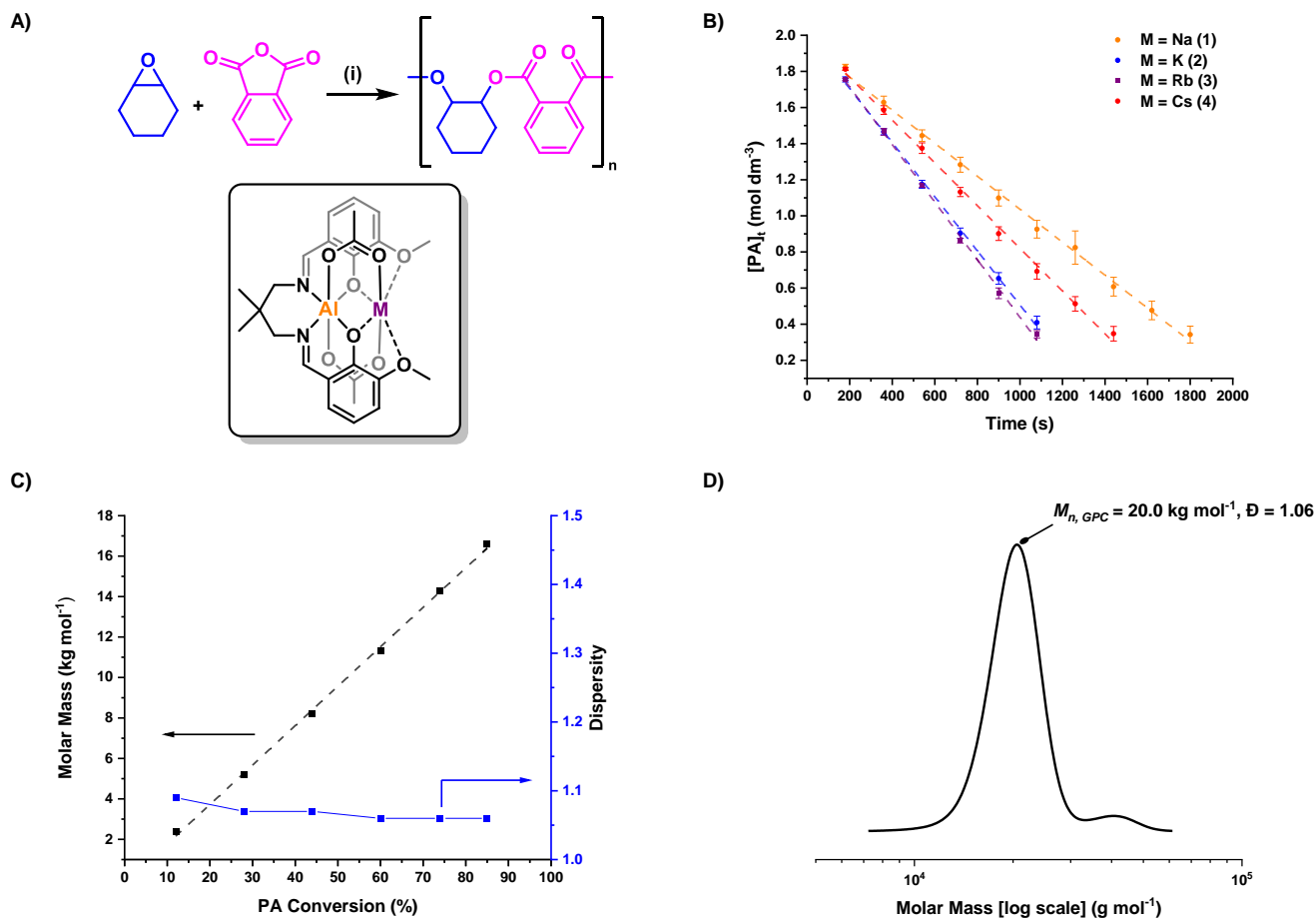
Catalyst solution nuclearity was investigated using DOSY NMR spectroscopy for complex **2** since it showed the best

catalytic performances (*vide infra*). In non-coordinating chloroform, **2** maintains its dimeric structure and shows similar solid state and solution hydrodynamic radii ( $r_{\text{solv}} = 7.4$  Å,  $r_{\text{crystal}} = 6.0$  Å, Fig S37). Adding an equivalent of a strong Lewis base, DMAP, did not change the diffusion coefficient. Under catalysis conditions, there are >2000 equivalents of epoxide present and, as such, it is proposed complexes are speciated as discrete heterodinuclear complexes (i.e. monomers).

### Epoxide and Anhydride ROCOP Catalysis

The four new heterodinuclear Al(III)/M(I) catalysts were tested in polymerizations using phthalic anhydride (PA) and cyclohexene oxide (CHO), as these monomers are commonly applied and allow for catalyst calibration and comparison (Fig 2, A and B, Table S7). Polymerizations were conducted at 100 °C, using 0.25 mol% catalyst loading and neat epoxide (i.e. 1:400:2000, [Catalyst]<sub>0</sub>: [PA]<sub>0</sub>: [CHO]<sub>0</sub>).

Complexes **2** (M = K) and **3** (M = Rb) were the most active, displaying very high turnover frequencies (TOFs) of  $1072 \pm 6$  and  $1136 \pm 6$  h<sup>-1</sup> ( $k_{\text{obs}} = 1.50 \pm 0.03 \times 10^{-3}$  s<sup>-1</sup> and  $1.59 \pm 0.03 \times 10^{-3}$  s<sup>-1</sup>), respectively. Complexes **1** and **4** show slightly lower activities compared to the K(I) and Rb(I) congeners but values are still at the upper end for the field as a whole (**1**(AlNa), TOF =  $712 \pm 9$  h<sup>-1</sup>,  $k_{\text{obs}} = 9.1 \pm 0.2 \times 10^{-4}$  s<sup>-1</sup>; **4**(AlCs), TOF =  $875 \pm 8$  h<sup>-1</sup>,  $k_{\text{obs}} = 1.18 \pm 0.03 \times 10^{-3}$  s<sup>-1</sup>). The same activity trends are observed using either point kinetics (TOF values) or rate coefficients ( $k_{\text{obs}}$ ) which gives confidence in the use of TOF values to infer propagation rates.



**Figure 2.** Data for ROCOP of CHO and PA. A) CHO/PA ROCOP with complexes 1 – 4. (i) Polymerization conditions:  $[\text{Cat}]_0:[\text{PA}]_0:[\text{CHO}]_0 = 1:400:2000$ ,  $T = 100 \text{ }^\circ\text{C}$ . B) Plot of  $[\text{PA}]_t$  vs. time for complexes 1 – 4. Reactions repeated in triplicate, average values of  $[\text{PA}]_t$  plotted, with error  $\pm\sigma/\sqrt{n}$ . C) Plot of change in polymer molar mass and dispersity with increasing PA conversion for complex 2. D) GPC Trace of PCHPE obtained with complex 2 at full PA conversion.

All catalysts were highly selective, forming only ester linkages and yielding poly(cyclohexene oxide-*alt*-phthalate) (PCHPE) (Fig S38 and S39). Given the similarity in rates between complexes 2 and 3, but potassium's lower cost, weight, and earth-abundance ( $K = 18,400 \text{ ppm}$  vs.  $\text{Rb} = 78 \text{ ppm}$ ), complex 2 was selected for more detailed investigations.<sup>54</sup> Polymerizations using complex 2 were monitored *via* aliquot analysis and showed good polymerization control, with polyester molar mass values increasing linearly with PA conversion and yielding polyester with narrow dispersity throughout the reaction ( $< 1.10$ ) (Fig 2, C and D). MALDI-ToF spectrometry confirmed that the acetate co-ligands were the principal initiating species (Fig S40).

So far, many epoxide/anhydride ROCOP catalysts are ineffective at loadings below 1 mol% vs. anhydride (*vide infra*). With this in mind, complex 2 was tested at 0.025 mol% vs. anhydride and 0.005 mol% loading vs. epoxide (i.e.  $[\text{2}]_0:[\text{PA}]_0:[\text{CHO}]_0 = 1:4000:20,000$ ). Its TOF remained at  $1010 \text{ h}^{-1}$  which is equivalent to reactions conducted at higher catalyst loading and demonstrates its high tolerance. To better understand whether there was any beneficial placement of the metals in catalyst 2, each of the metallic

precursor complexes were also tested under equivalent conditions. The mono-Al(III) complex,  $[\text{L}_{\text{van}}\text{Al}(\text{OAc})]$ , shows very much lower activity ( $\text{TOF}_{\text{polyester}} = 168 \text{ h}^{-1}$ ) and a very low selectivity for ester linkages in the resulting polymer (22%) (Table 1, Entry 1). The potassium carboxylate salt, KOAc, shows even lower activity ( $\text{TOF}_{\text{polyester}} = 23 \text{ h}^{-1}$ ) but retains good ester linkage selectivity (Table 1, Entry 2). In comparison, the Al(III)/K(I) catalyst 2 shows 50 times higher rate than the K(I) precursor and 6 times higher activity than the Al(III) precursor, it is also 5 times more selective than the Al(III) complex. These experiments indicate metallic synergy within complex 2. We have recently reported heterodinuclear Zn(II), Cd(II), Mg(II)/Group 1 metal (I) complexes, coordinated by the same ancillary ligand; unfortunately none of these metal combinations were synergic and all under-performed compared with the di-zinc catalyst.<sup>41</sup> In this work, the clear benefits of changing the metals to Al(III)/M(I) are apparent. For example, catalyst 2 shows 5-times higher activity than the equivalent di-Zn(II) catalyst. These results underscore both the need for insight into how the synergic catalysts function.

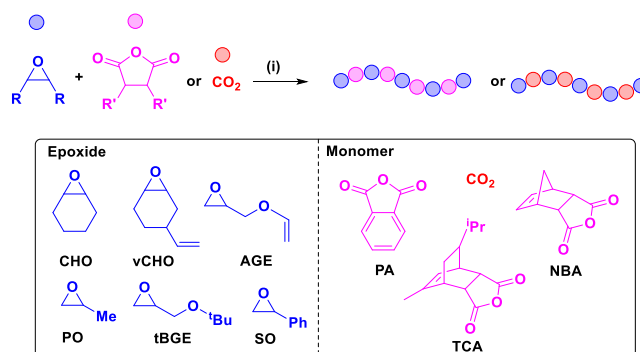
**Table 1. Data for CHO and PA ROCOP using comparative complexes to complex 2<sup>a</sup>.**

Entry	Catalyst	Time (m)	TON <sub>Polyester</sub> <sup>b</sup>	TOF <sub>Polyester</sub> <sup>c</sup> (h <sup>-1</sup> )	Selectivity <sup>d</sup> (%)	M <sub>n, GPC</sub> [Đ] <sup>e</sup> (kg mol <sup>-1</sup> )
1	[L <sub>van</sub> Al(OAc)]	30	83	168	22	3.7 [1.86]
2	KOAc <sup>f</sup>	60	23	23	>99	4.0 [1.27]
3	[L <sub>van</sub> Al(OAc)]/KOAc	5	89	1068	>99	7.4 [1.07]
4	[L <sub>sal</sub> Al(OAc)]	60	8	8	4	N.d.
5	[L <sub>sal</sub> Al(OAc)]/KOAc	60	32	32	>99	N.d.

<sup>a</sup> Conditions: [Cat]<sub>0</sub>: [PA]<sub>0</sub>: [CHO]<sub>0</sub> = 1:100:500, T = 100 °C. <sup>b</sup> Turnover number (TON) for polyester formation = number of moles of PA consumed/number of moles of catalyst. Determined by <sup>1</sup>H NMR through comparison of resonances associated with PA (8.10 – 7.85 ppm) and PCHPE (7.65 – 7.30 ppm). <sup>c</sup> Turnover Frequency for polyester formation, TOF = TON/time(h). <sup>d</sup> Selectivity for polyester over polyether, determined by comparison of <sup>1</sup>H NMR integrals corresponding to PCHPE (5.22-5.06 ppm) and PCHO (3.60 – 3.20 ppm). <sup>e</sup> Determined by GPC in THF, at 30 °C, using narrow dispersity polystyrene standards. <sup>f</sup> Conditions: [KOAc]:[PA]:[CHO] = 1:100:500, T = 110 °C in reference [51].

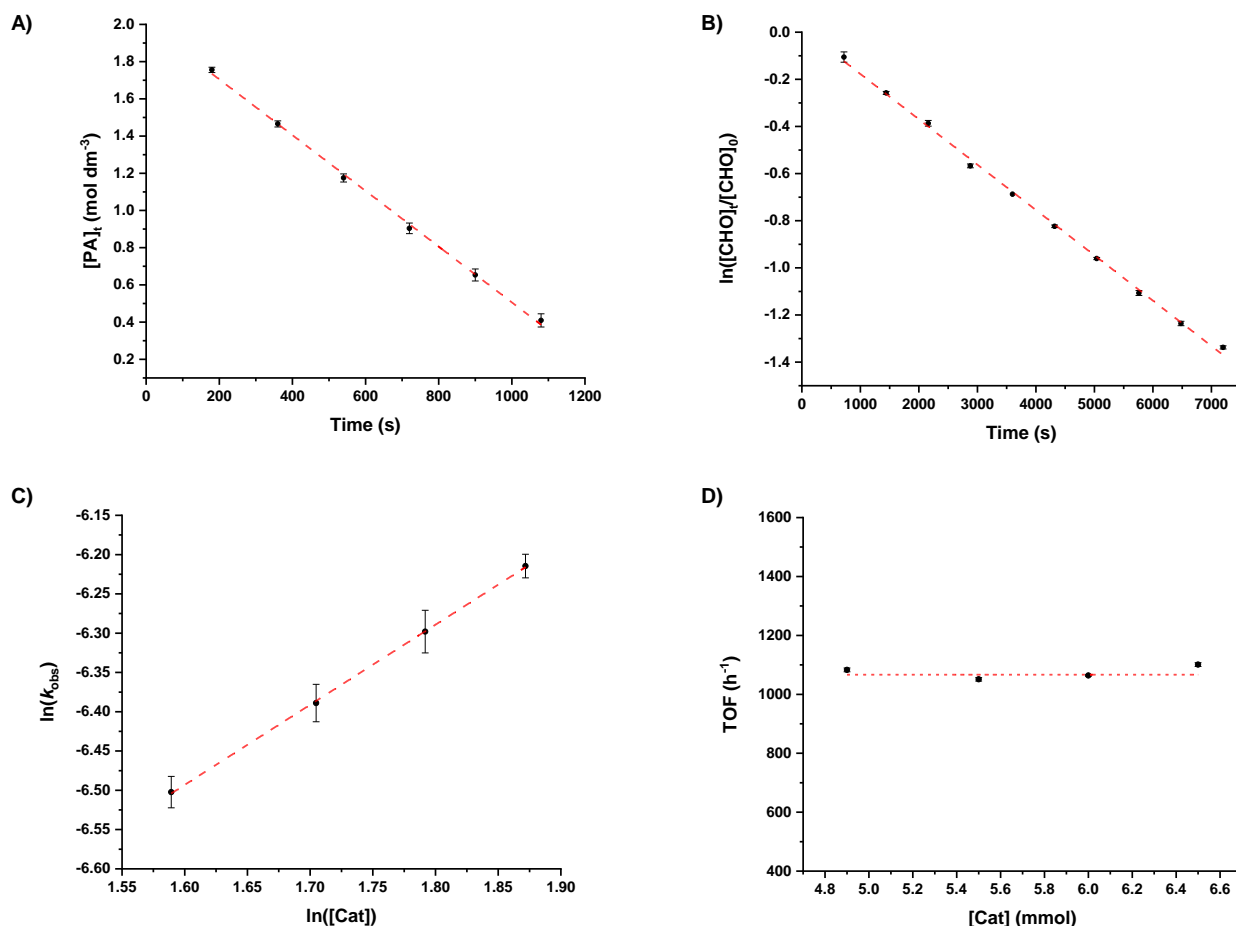
To investigate whether **2** needs to be isolated or can be prepared *in situ* through reaction of the two precursors, a mixture of [L<sub>van</sub>Al(OAc)] and KOAc was tested and results in nearly equivalent activity and selectivity compared to using isolated complex **2** (Table 1, Entry 3). These findings suggest that the same active species is present in both cases and that the mixture likely forms **2** *in situ* during the polymerization. In comparison, when a simple aluminium salen ([L<sub>sal</sub>Al(OAc), see ESI for structure and experimental details) is utilised, both with and without KOAc, no equivalent increase in activity is observed but selectivity does improve with added potassium (4% to >99%). The suppression of ether linkage formation when KOAc is utilised may be due to the formation of an aluminate species *in situ* which reduces the Al(III) Lewis acidity and suppresses sequential epoxide enchainment. Unfortunately, the simple Al(III)salen species lack coordination sites for the K(I) and so fail to deliver the desirable activity increments. Thus, intermetallic synergy is only feasible using the right ancillary ligand which can coordinate both the Al(III) and K(I) centres, not merely by having both components present in generic mixtures. Using the correct coordination environment, the activity of the Al(III) centre can be markedly improved, as demonstrated by the 33 x increase in activity for **2** compared to the [Al(salen)(OAc)]/KOAc system (Table 1, Entries 3 *cf.* 5).

Given the excellent performance of catalyst **2**, it was tested using other anhydrides and epoxides, allowing access to semi-aromatic, rigid and/or functionalizable polyesters (Table 2). It remains highly active using other epoxides and anhydrides, including the sterically hindered tricyclic anhydride (TCA, TOF = 288 h<sup>-1</sup>) and norbornene anhydride (NBA, TOF = 266 h<sup>-1</sup>) (Table 2, Entries 2 and 3, respectively). It is also successful using 'challenging' epoxides such as styrene oxide (SO), *tert*-butylglycidyl ether (tBGE) and propylene oxide (PO), with TOFs of 152, 320 and 20 h<sup>-1</sup>, respectively (Table 2, Entries 4 - 6). For such terminal epoxides, regiorandom polyesters are obtained.

**Table 2. Data for the ROCOP of a range of epoxides with comonomers utilising complex 2.<sup>a</sup>**

Entry	Monomers	Time (min)	TON <sup>a</sup>	TOF <sup>b</sup> (h <sup>-1</sup> )	M <sub>n, GPC</sub> [Đ] <sup>c</sup> (kg mol <sup>-1</sup> )
1	CHO/PA	15	268	1072	14.3 [1.06]
2	CHO/TCA	30	144	288	4.7 [1.22]
3	CHO/NBA	30	133	266	4.5 [1.10]
4	tBGE/PA	30	160	320	7.9 [1.24]
5	SO/PA	30	76	152	3.2 [1.24]
6	PO/PA <sup>f</sup>	1200	400	20	33.2 [1.13]
7	vCHO/PA	30	296	592	42.9 [1.06]
8	AGE/PA	30	136	272	8.2 [1.20]
9	CHO/CO <sub>2</sub> <sup>g</sup>	60	58	58	3.5 [1.18]
10	CHO/CO <sub>2</sub> <sup>h</sup>	120	1010	505	23.4 [1.21]

<sup>a</sup> Conditions for anhydride: [2]:[Anhydride] = 1:400, 1 mL epoxide, [2] = 4.9 mmol, 100 °C. Conditions for CO<sub>2</sub>: [2]:[CHO] = 1:2000, 100 °C. <sup>b</sup> Turnover number = moles of epoxide consumed (=moles of anhydride consumed, when present)/ moles of catalyst. Determined by <sup>1</sup>H NMR spectroscopy (See Fig S41 - S49). For entries 9 and 10, TON is for polycarbonate formation. <sup>c</sup> Turnover frequency = TON/time (hours). <sup>d</sup> Determined by GPC in THF, at 30 °C, using narrow dispersity polystyrene standards (See Fig S50). <sup>f</sup> Reaction run at 60 °C. <sup>g</sup> p(CO<sub>2</sub>) = 1 bar. <sup>h</sup> p(CO<sub>2</sub>) = 20 bar.



**Figure 3.** A) Plot of  $[PA]_t$  vs. Time, revealing a linear relationship and hence zero order dependence of rate on  $[PA]$ . Conditions:  $[2]_0:[PA]_0:[CHO]_0 = 1:400:2000$ ,  $T = 100\text{ }^\circ\text{C}$ ,  $[2]_0 = 4.9\text{ mmol}$ . B) Plot of  $\ln([CHO]_t/[CHO]_0)$  vs. Time, revealing a linear relationship and hence a first order dependence of rate on  $[CHO]$ . Conditions:  $[2]_0:[PA]_0:[CHO]_0 = 1:400:500$ ,  $0.75\text{ mL Toluene}$ ,  $T = 100\text{ }^\circ\text{C}$ ,  $[2] = 4.9\text{ mmol}$ . C) Plot of  $\ln(k_{obs})$  vs.  $\ln([Cat])$  at various concentration of complex **2**. A gradient of  $1.02 \pm 0.01$  is found for a linear fit of the data, revealing a first order dependence of rate on  $[2]$ .  $k_{obs}$  extracted from plots of  $[PA]_t$  vs. Time for different catalyst concentrations (Fig S49). D) Plot of TOF ( $=TON/time$ ) vs.  $[2]_0$  showing that TOF is not affected by catalyst concentration. For plots A and D error represented as  $\pm\Delta x = \sigma/\sqrt{n}$ , where  $n = 3$ . For plots B and C, error represented as  $\pm\Delta x/x$ , where  $\Delta x = \sigma/\sqrt{n}$ , and  $n = 3$  and  $2$ , respectively.

High activities were also obtained using vinyl-cyclohexene oxide (vCHO, TOF =  $592\text{ h}^{-1}$ ) or allyl glycidyl ether (AGE, TOF =  $272\text{ h}^{-1}$ ) (Table 2, Entries 7 and 8, respectively). In all cases perfect selectivity for polyester formation is observed and molar mass distributions show narrow dispersity. In order to compare different monomer combinations, fixed time point experiments were conducted but complete anhydride conversions can be obtained in all cases, allowing access to polymers showing molar masses from  $15 - 55\text{ kg mol}^{-1}$  (Table S8). Catalyst **2** is effective in producing rigid polyesters, e.g. CHO/PA or CHO/TCA, which show promise as hard, high  $T_g$ , blocks in thermoplastic elastomers.<sup>55-58</sup> It is also effective for PO/PA or tBGE/PA ROCOP producing elastomeric polyesters.<sup>22</sup> Finally, it is successful for AGE/PA or vCHO/PA ROCOP yielding polyesters that can be post-functionalised to change solubility, hydrophilicity, ion or metal binding, amongst other properties.<sup>59-61</sup>

Complex **2** was also trialled for CHO/ $\text{CO}_2$  ROCOP at both 1 and 20 bar (Table 2, Entries 9 and 10). At 1 bar pressure, it showed moderate activity forming both poly(cyclohexene carbonate) and cyclic carbonate (TOF<sub>PCHC</sub> =  $58\text{ h}^{-1}$ , Selectivity<sub>PCHC</sub> = 50%). At 20 bar pressure activity and selectivity for polycarbonate both increased (TOF<sub>PCHC</sub> =  $505\text{ h}^{-1}$ , Selectivity<sub>PCHC</sub> = 88%). No polyether was formed in either case. These promising results should inspire further research into Al(III) carbon dioxide copolymerization catalysts since there remain only limited examples to date but the advantages of using earth-abundant and colourless metal centres are clear.<sup>62-65</sup> Through further optimization it may be possible to challenge the current leading Al(III) catalyst system, featuring a tethered co-catalyst, reported by Nozaki and co-workers.<sup>62</sup>

## Polymerization Kinetics and Mechanism

To better understand the behaviour of catalyst **2** in epoxide/anhydride ROCOP, its kinetics were investigated. Polymerizations show a zeroth order dependence on PA concentration, as established by linear fits to conversion vs. time data (Fig. 3, A). First order dependence in epoxide concentration is indicated by linear fits to  $\ln([\text{CHO}]_t/[\text{CHO}]_0)$  vs. time data (Fig. 3, B). Conducting polymerizations using a range of different catalyst concentrations and plotting each rate coefficient,  $k_{\text{obs}}$ , against the concentration of catalyst **2** also showed a linear fit. These results are indicative of a first order dependence in catalyst concentration and are consistent with catalyst speciation as discrete monomers (Fig. 3, C and D). The overall rate law is proposed to be:

$$v = k[\mathbf{2}]^1[\text{CHO}]^1[\text{PA}]^0$$

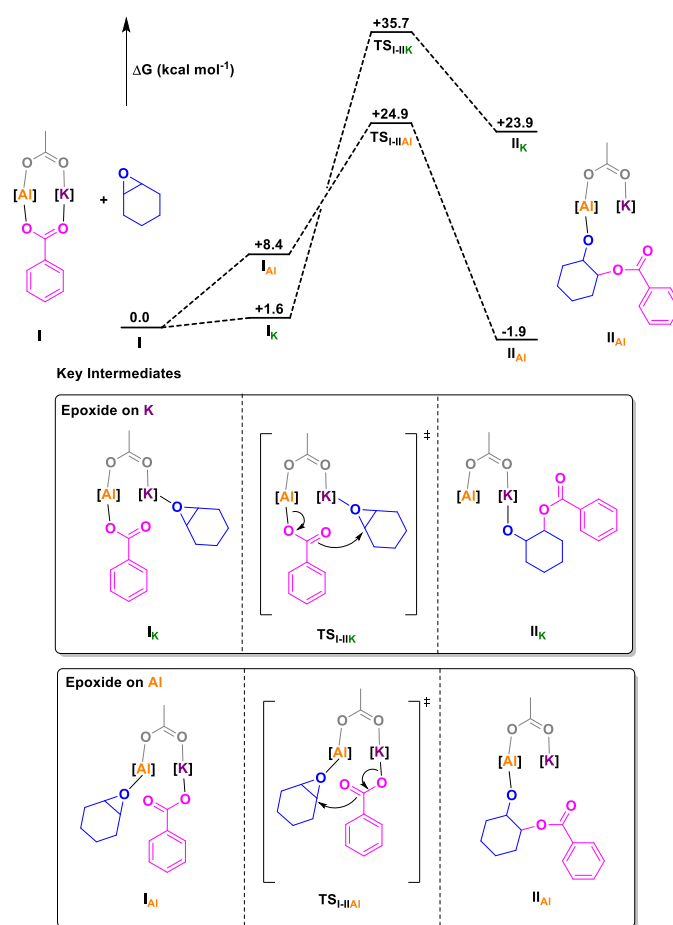
The rate law suggests that the rate determining step likely involves metal-carboxylate attack upon (second) metal coordinated epoxide. Further, the first order catalyst dependence confirms there is no monomer  $\rightleftharpoons$  dimer equilibrium occurring. It should also be considered that, were the alkali metal to dissociate from the ligand framework, a first order catalyst dependence would also result. However, we note that we demonstrated that without the KOAc present an unselective system with low activity results, implying that this dissociation does not occur.

To investigate the roles for Al(III) and K(I) centres during catalysis, density functional theory calculations were carried out for the epoxide ring opening step (*i.e.* the rate determining step). Species **I**, a monomeric catalyst model built from the solid-state structure of complex **2**, but featuring a benzoate coligand to mimic the propagating carboxylate species, was used as a starting point for calculations (Fig. 4, for computational details see ESI). Two propagation routes are possible from species **I**. Epoxide binding and activation can occur either at K ( $I_{\text{K}}$ ) or Al ( $I_{\text{Al}}$ ), with the carboxylate propagating species being coordinated at the other metal in either case. Accordingly, the metal-carboxylate attacks the coordinated epoxide *via* one of two different transition states,  $\text{TS}_{\text{I-IIK}}$  or  $\text{TS}_{\text{I-IIAl}}$ , resulting in epoxide ring-opening to form a metal bound alkoxide product ( $\text{II}_{\text{K}}$  or  $\text{II}_{\text{Al}}$ ).

Comparing the relative energies of the different intermediates, reveals that epoxide binding is thermodynamically more stable at the K(I) centre ( $\Delta G(\text{I}-\text{I}_{\text{K}}) = +1.6 \text{ kcal mol}^{-1}$  vs.  $\Delta G(\text{I}-\text{I}_{\text{Al}}) = +8.4 \text{ kcal mol}^{-1}$ ). To test this experimentally,  $[\text{L}_{\text{vanAlK}}(\text{OBz})_2]$  was synthesised (**5**, see ESI for details) and single crystals (from THF solution) confirmed THF coordination at the K(I) centre (Fig S35). Despite the results for most stable epoxide coordination site, in the DFT model of the catalytic cycle the subsequent propagation transition state is significantly lower energy when the epoxide is bound to Al(III) ( $\Delta G(\text{I}-\text{TS}_{\text{I-IIK}}) = +35.7 \text{ kcal mol}^{-1}$  vs.  $\Delta G(\text{I}-\text{TS}_{\text{I-IIAl}}) = +24.9 \text{ kcal mol}^{-1}$ ). Furthermore, the most stable alkoxide intermediate features the chain coordinated at aluminium ( $\Delta G(\text{II}_{\text{Al}}) = -1.9 \text{ kcal mol}^{-1}$  vs.  $\Delta G(\text{II}_{\text{K}}) = +23.9 \text{ kcal mol}^{-1}$ ).

Thus, considering the overall barrier and linkage stability suggests that a pathway involving Al(III)-epoxide coordination and K(I)-carboxylate attack is both kinetically and thermodynamically favoured.

Overall, the proposed mechanism requires both metals, with Al(III) coordinating the epoxide whilst K(I) provides the nucleophilic polymer carboxylate group to attack it. There may be mechanistic parallels with the M(III)-tethered co-catalyst systems which are also proposed to operate by aluminate intermediates and where the growing polymer chain is 'coordinated' proximal to the metal by the cationic group.<sup>25</sup> One advantage of these dinuclear metallic complexes is that the polymer carboxylate and activated epoxide are spatially close ( $d(\text{Al}_{\text{III}} - \text{M}_{\text{I}}) \approx 3.5 \text{ \AA}$ ). In contrast, the co-catalyst tethered catalyst species can be located quite far from the metallate active site.



**Figure 4.** Density Functional Theory calculations for two different propagation pathways, depending upon the site for epoxide coordination. Ancillary ligand omitted for clarity.

**Table 3. Comparisons between complex 2 and other epoxide/anhydride ROCOP catalysts.**

	Entry	Catalyst	Monomers	Loading <sup>a</sup> (%)	Temp. (°C)	Time (h)	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )	<i>M<sub>n,GPC</sub></i> [Đ] <sup>d</sup> (kg mol <sup>-1</sup> )
Monocomponent Catalysts	1	<b>2</b> [L <sub>van</sub> AlK(OAc) <sub>2</sub> ]	CHO/PA	0.25	100	0.25	268	1072	14.3 [1.06]
	2	[L <sub>van</sub> Zn <sub>2</sub> (OAc) <sub>2</sub> ] (Chart 1) <sup>48</sup>	CHO/PA	1	100	0.5	99	198	5.3 [1.23]
	3	KOAc <sup>51</sup>	CHO/PA	1	110	1	23	23	4.0 [1.27]
	4	Cs(O <sub>2</sub> C(CF <sub>3</sub> )) <sup>51</sup>	CHO/PA	1	110	1	92	92	6.0 [1.20]
	5	tBuP <sub>1</sub> <sup>22</sup>	CHO/PA	1	100	2	96	48	18.4 [1.06]
	6	[L'AlCl] (Chart 1) <sup>25</sup>	CHO/NBA	0.25	60	6	51	34	8.2 [1.24]
	7	[L'AlCl] (Chart 1) <sup>25</sup>	PO/PA	0.25	60	4	>99	>99	22.1 [1.14]
	8	Organoboron tethered ammonium chloride (Chart 1) <sup>34</sup>	CHO/PA	0.5	120	0.66	172	258	24.5 [1.18]
Bicomponent Catalysts	9	[LFe <sub>2</sub> ] +2 equiv. PPNCI <sup>e 27</sup> (Chart S1)	CHO/PA	0.1	100	0.5	290	588	5.7 [1.30]
	10	[SalcyCrCl] +1 equiv. PPNCI <sup>52</sup> (Chart 1)	CHO/PA	1	100	0.083	97	1164	5.1 [1.17]
	11	[LAl <sub>2</sub> ] + 2 equiv. PPNCI <sup>66</sup> (Chart S1)	CHO/PA	0.4	50	0.3	225	750	9.8 [1.14]
	12	[LCr <sub>3</sub> ] + 3 eq. PPNCI <sup>35</sup> (Chart S1)	CHO/PA	0.017	100	0.33	3540	10620	12.3 [1.21]
	13	DBU + 1 equiv. BEt <sub>3</sub> <sup>67</sup>	PO/PA	1	60	3	80	27	13.2 [1.14]
	14	Ph <sub>4</sub> PBr + 1 equiv. BEt <sub>3</sub> <sup>21</sup>	PO/PA	1	80	0.3	91	303	20.0 [1.12]
	15	Zn(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> +2 equiv. DMAP <sup>15</sup>	CHO/PA	1	110	0.8	92	116	5.6 [1.20]

<sup>a</sup> Catalyst loading is with respect to anhydride. (1% = [Cat]:[Anhydride] = 1:100). L/L' represent ancillary ligands. See Charts 1 and S1 for structures. <sup>b</sup> Turnover number (TON) = Moles of anhydride/ moles of catalyst, as reported in respective literature. <sup>c</sup> TOF = TON/time (hours), as reported in respective literature. <sup>d</sup> As reported under conditions described in respective literature. <sup>e</sup> All values reported per metal centre, as analogous monometallic complex was shown to have an equivalent TOF when number of metal centres was accounted for.

Comparing the relative reactivity within the series of heterodinuclear catalysts also yields more information on the proposed mechanism. It seems likely that the spatial separation between the growing polymer chain and the activated, Al(III)-bound epoxide is important in reducing the relative energies of the transition states. For this series of complexes, the internuclear separation increases in the expected order Al(III)-Na(I) < Al(III)-K(I) < Al(III)-Rb(I) < Al(III)-Cs(I) (Tables S1 - S4). But relative Lewis acidity of the M(I) ions must also be considered in rationalising activity trends.

More acidic M(I) should form stronger M(I)-O<sub>carboxylate</sub> bonds, which must be broken in order for propagation to occur. As such, the reactivity would be expected to fall in the order Cs > Rb > K > Na. Considering the intermetallic distance trend, complex 1 should be most active, whilst the Lewis acidity trends suggest complex 4 should be most active. It is proposed that the two demands are counter-balanced in the middle of the series, namely for complexes 2 and 3.

## Discussion

Comparing the new heterodinuclear catalysts against the best literature catalysts is essential to appreciate the performance benefits but somewhat complex since this field does not have standardized conditions and each catalyst tends to be tested under different conditions (Table 3). Here, benchmarking is conducted using CHO/PA ROCOP where possible at temperatures  $\sim 100$  °C, [Cat]:[Anhydride] loadings at or below 1:100 and in neat epoxide. Such conditions are selected since typical polymerization rate laws are first order dependent in catalyst and epoxide concentrations. It's also appropriate to divide the literature catalysts into two classes: those that function without cocatalysts which are termed monocomponent catalyst systems (note that many of these include covalently attached co-catalyst), or those which require cocatalysts to either function, or significantly improve performance which are termed bicomponent catalyst systems.

Bicomponent catalyst systems can be optimized to show high activity and selectivity but only function at higher catalyst loadings and often show significantly decreased activities at lower loadings.<sup>25</sup> Amongst these, a homodinuclear Fe(III) trisphenolate complex, used with PPNCI, shows a high TOF of  $1180\text{ h}^{-1}$  at a loading of 0.2% but with activity reducing to  $588\text{ h}^{-1}$  at 0.1% loading (Table 3, Entry 9).<sup>27</sup> Likewise, Coates *et al.* demonstrated that bicomponent aluminium salen/PPNCI catalyst system showed a significant drop in activity at low catalyst loadings.<sup>25</sup>

Another effective bicomponent catalyst system is [SalcyCrCl]/PPNCI, initially reported by Duchateau *et al.*, showing a TOF of  $250\text{ h}^{-1}$  (0.4% vs. anhydride, T = 110 °C).<sup>33</sup> We have recently tested this complex and achieved much higher TOFs of ca.  $1150\text{ h}^{-1}$ , when using bulk epoxide conditions (Table 3, Entry 10).<sup>52</sup> It should be noted that the need for cocatalyst again renders it sensitive to catalyst loading, and other detractors are the cost of Cr(III), its potential toxicity and difficulty of catalyst residue removal (the catalyst is highly coloured). The di-Al(III) catalysts, reported by Lu *et al.*, also show very high activities at the lower temperature of 50 °C (TOF =  $750\text{ h}^{-1}$ , 0.4% vs. anhydride, Table 3, Entry 11).<sup>66</sup> When these are used without PPNCI, the reaction yields only polyether. Very recently, a trimetallic Cr(III) salen complex has shown exceptional activities, and loading tolerance (TOF =  $10,620\text{ h}^{-1}$ , 0.017% vs. anhydride, T = 100 °C), but still requires the use of cocatalytic PPNCI (Table 3, Entry 12). This catalyst shows extremely promising performances and highlights the benefits of the 'correct' placement of several metal centres, with the authors attributing it's outstanding rates to optimized intermetallic distances. One interesting future direction would be to combine the findings of this study using heterodinuclear catalysts with the multi-catalyst framework to benefit from both optimized catalyst distances and heterodinuclear synergy. Bicomponent organo-catalyst systems generally show lower activities than metallic complexes but may be easy to use and some are commercial products. One of the most effective for the ROCOP of CHO and PA is a mixture of organozinc reagent and DMAP which achieved a TOF of  $116\text{ h}^{-1}$  (1% vs. anhydride, 110 °C), whilst the use of DBU or phosphonium salts with triethyl borane results in effective systems for PO/PA ROCOP (DBU: TOF =  $27\text{ h}^{-1}$ , 1% vs. anhydride, 60

°C; Ph<sub>4</sub>PBr: TOF =  $303\text{ h}^{-1}$ , 1% vs. anhydride, T = 80 °C) (Table 3, Entries 13 - 15).

The benefits of single component catalysts, particularly with respect to use at lower catalytic loading, are clear. Group 1 metal acetate catalysts are attractive as they are commercial and easy to use but their activities are low (Table 3, Entries 3 and 4). Under optimized conditions, caesium trifluoroacetate showed a TOF  $\sim 100\text{ h}^{-1}$  (1% vs. anhydride, 110 °C) but activity values using cheaper and more abundant KOAc were significantly lower (TOF =  $23\text{ h}^{-1}$ , 1% vs. anhydride, 110 °C). The organocatalyst <sup>t</sup>BuP<sub>1</sub> likewise shows low activity, with a TOF of  $48\text{ h}^{-1}$  (1% vs. anhydride, 100 °C) (Table 3, Entry 5). One successful strategy has been to make monometallic complexes featuring a tethered cocatalyst, as was clearly demonstrated by Coates *et al.* using the Al(III) catalyst that showed excellent activities and high tolerance for PO/NBA ROCOP (TOF =  $99\text{ h}^{-1}$ , 0.25 mol% vs. anhydride, Table 3, Entries 6 and 7). This same catalyst design strategy was also used to make an ammonium halide tethered organoboron catalyst (Table 3, Entry 8).<sup>34</sup> It outperforms previous bicomponent organocatalysts, but remains less active than metal catalysts under equivalent conditions (TOF =  $245\text{ h}^{-1}$ , 0.5% vs. anhydride, 120 °C). The boron-ammonium organocatalyst can be used at temperatures up to 180 °C, as expected increasing the TOF to  $945\text{ h}^{-1}$  (0.4% vs. anhydride).

Catalyst **2** shows strong performances compared with the best bicomponent metal catalysts. In making such comparisons its essential to recall that rate laws are almost always first (or higher order) in catalyst concentration, hence the optimal scenario is to maintain high rates at the lowest loading. To exemplify the strong performance, **2** shows equivalent activity but at 40 x lower loading than the [Cr(III)(salcy)(Cl)]/PPNCI catalyst systems for the ROCOP of CHO and PA. It also shows 2 x activity at 8 x lower loading than the [Fe(III)]/PPNCI catalyst systems. Catalyst **2** shows 8 x higher activity at equivalent loading to the leading cocatalyst tethered [L'Al(III)] catalyst (Chart 1, Table 3), albeit with **2** operating at higher temperature. Nonetheless, there is still room for improvement since for PO/PA ROCOP, the [L'Al(III)] catalyst system is more active than **2** (*N.b.* that the system was not reported for the ROCOP of PA and CHO, preventing direct comparison with many other complexes). Because catalyst **2** is straightforward to prepare future optimizations should be straightforward, in comparison the tethered Al(III) catalyst requires an 8-step synthesis with a 9% overall yield. Catalyst **2** is also 10 x faster, at 4 x lower loading, than the di-Zn(II) catalyst, coordinated by the same ancillary ligand, highlighting the potential for synergic metal combinations (Table 3, Entry 2).

## Conclusions

A series of heterodinuclear Al(III)/M(I) catalysts, coordinated by an easily synthesized Schiff base ligand, showed a step-change in catalytic activity and loading for epoxide/anhydride ring-opening polymerizations. The best catalysts feature Al(III)/K(I) and combine exceptionally high activity, quantitative alternating polyester selectivity and excellent polymerization control (TOF =  $1072\text{ h}^{-1}$ , 0.25 mol% catalyst, T = 100 °C). They are also successful using other epoxide/anhydride combinations, providing access to various semi-aromatic, rigid or functionalizable polyesters. The

polymerization rate law, underpinned by a DFT investigation, implicates a rate limiting step in which Al(III)-epoxide intermediate is attacked by a K(I)-carboxylate moiety. Overall, the benefits of synergic heterometallic combinations using inexpensive, colourless and abundant metals are clearly identified. Future investigations into other ligand scaffolds and metals is warranted. The use of chiral linker groups, in the Schiff base, should be explored as the research groups headed up by Coates and Lu have both pioneered stereoselective [M(III)(salen)] catalysts to make interesting new stereo-complex polyesters.<sup>29-32, 68-71</sup> These Al(III)/M(I) catalysts should also be prioritized for development in carbon dioxide/epoxide ring-opening copolymerizations,<sup>38-40, 72</sup> cyclic ester/carbonate ring-opening polymerizations, and for use in switchable polymerizations to access more complex multi-block structures.<sup>56, 60, 73-82</sup>

## ASSOCIATED CONTENT

Supporting information is available free of charge at <http://pubs.acs.org>.

Characterisation data of complexes (NMR, X-ray crystallography, elemental analysis); polymerization data (GPC chromatograms, MALDI-ToF Spectra); DFT calculation details:

Crystal Data:

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Author Contributions

The manuscript was written through contributions of all authors.

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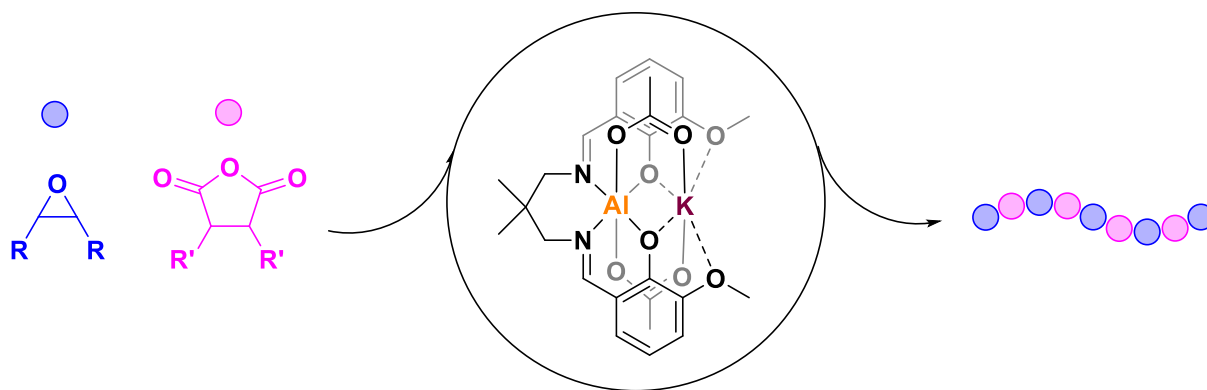
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TOF > 1000 h<sup>-1</sup> (up to 250 ppm vs. anhydride, 100 °C)  
>99% Polyester Selectivity  
Broad Monomer Scope  
Catalyst generated *in situ*  
Synergic Metal Combination

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