PAPER

Check for updates

A pinch of silver salt to enable *rac*-lactide ring-opening polymerisation at room temperature using Ti-salen complexes†

Justin Koh, (ID) Chloe A. Baker, Marianna N. Diamantakis, (ID) Nicholas J. Long (ID) *
and Charles Romain (ID) *

Exploiting non-covalent interactions (NCIs) has become a powerful tool in catalyst design, including those for polymerisation reactions. Herein we report a simple strategy relying on the addition of silver salt to Ti-salen complexes, leading to Ti/Ag cooperativity *via* cation-π interactions. Three different Ti-salen complexes were investigated alongside several silver salts. In all cases, these Ti/Ag systems led to good or high activity at room temperature for *rac*-lactide ROP, a rare feature for Ti-based catalysts. Interestingly, the weakly coordinating anion (WCA) of the silver salt was found not only to affect activity but also stereo-control in the polymerisation. Heterotactic PLA with P_r up to 0.7 was obtained.

Introduction

Exploiting non-covalent interactions (NCIs) has become a powerful tool in designing catalysts for various organic reactions. Different attractive interactions (*e.g.* hydrogen bonds, π interactions) and strategies (*e.g.* inter-ligand, substrate-ligand) have been investigated to control the formation of "supramolecular" catalytic species.[1] Such approaches exploiting NCIs have also been applied in polymerisation catalysis, especially for olefin polymerisation using late-transition metal catalysts.[2] For example, $C_{Ar}F\cdots H$ interactions between fluorinated ligands and polymeric chains have been demonstrated to reduce β-H elimination and to lead to high molar mass polymers.[3] Regarding Lewis acid metal-catalysed polymerisations such as ring-opening polymerisation (ROP) and ring-opening copolymerisation (ROCOP), similar strategies have been investigated but remain underexplored compared to organo-catalysed polymerisations where hydrogen bonding is ubiquitous.[4]

In epoxide/CO_2 ROCOP, ionic interactions between the carbonate chain-end of the polymeric chain and cationic species (either exogeneous or ligand-tagged) were found to enhance selectivity towards the formation of carbonate linkages (leading to the development of bifunctional catalysts).[5] In ROP, since the pioneering work of Rzepa and co-workers drawing attention to the role of weak attractive C–H···π interactions in lactide polymerisation,[6] few other studies have highlighted the role of NCIs in metal-catalysed ROP. Comprehensive investigations from Carpentier, Guillaume and co-workers demonstrated that CH···π or CH···Cl interactions between the ligand and growing polymeric chains were responsible for the stereoselective polymerisation of some functionalised β-lactones using yttrium-bisphenolate complexes.[7] Other strategies relying on hydrogen bonding from the NH moieties in reduced Schiff base ligands and amino-phenolate ligands have been proposed to explain high activity or selectivity both in ROP and ROCOP.[8] Along these lines, some of us highlighted the role of hydrogen bonds in the catalytic pocket of *catam* aluminium complexes to orientate and activate monomers.[9] More recently, our group exploited cation-π interactions to form *in-situ* highly active heterobimetallic Ag–Ti species for lactide ROP,[10] thus taking advantage of metal cooperativity in lactone ROP.[11] The addition of silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $[Ag][B(Ar^{CF_3})_4]$ to a simple Ti-salen complex was found to enable fast and controlled lactide polymerisation at room temperature. Under similar conditions, both components were independently inactive and only the combination of both "switched on" the polymerisation.[10] This was attributed to cation-π interactions positioning the silver cation near the Ti-metal centre which allowed for monomer activation and stabilisation of key intermediates during the polymerisation. Similarly, Waymouth and co-workers recently reported the key role of counter-ions in anionic ROP mediated by organocatalysts were two alkali–metal cations where differently positioned through cation-π interactions and showed contrasting roles.[12] Herein we report a series of bicomponent catalytic systems for *rac*-lactide ROP comprising different Ti-salen complexes and various silver salts containing weakly coordinating

Department of Chemistry, Imperial College London, MSRH, W12 0BZ London, UK.
E-mail: n.long@imperial.ac.uk, c.romain@imperial.ac.uk

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4py01319k

anions (WCA). Among others, the effect of the WCA on polymerisation activity and stereoselectivity was investigated. Following condition optimisations, the Ti/Ag cooperativity led to a highly active system at room temperature, enabling access to heterotatic PLA with P_r up to 0.7.[13]

Results and discussion

Bis(iso-propoxide) Ti-salen complexes **1–3** with various Schiff-base ligands (and thus different geometry and flexibility) were synthesised (Fig. 1) *via* standard procedures using the corresponding ligand precursor and Ti(O^{i}Pr)$_4$.[14,15] Complex **2** was prepared using a racemic mixture of the *trans* ligand precursor, whereas the complex referred to as **(S,S)-2** was prepared using the (*S*,*S*)-*trans* ligand precursor as depicted in Fig. 1. All complexes were obtained in moderate to good yields (~50%–70%). ^{1}H NMR spectroscopy analyses in C$_6$D$_6$ confirmed that **1** adopts a *trans* configuration whereas **2** and **3** adopt a *cis*-β configuration in solution, consistent with previous reports.[14,15] Indeed, the ^{1}H NMR spectrum of **1** is in line with a C$_2$-symmetric structure in C$_6$D$_6$ with only two ^{t}Bu signals, two aromatic proton signals, one imine signal and one isopropyl [*i.e.* heptet for C*H*(CH$_3$)] signal. On the contrary, the ^{1}H NMR spectra of **2** and **3** show four ^{t}Bu signals, four aromatic proton signals, two imine signals and two isopropyl signals [*i.e.* heptet for C*H*(CH$_3$)] (see ESI†).

In order to develop a straightforward method to gauge the potential cooperativity between silver salts and Ti-salen complexes for *rac*-LA ROP, we turned our attention toward silver salts [Ag][X] which: (i) were soluble in DCM at room temperature, as is *rac*-LA, (ii) have a stable or inert counter-anion [X]$^-$; (iii) provide a source of a "naked" silver cation by possessing a weakly coordinating anion (WCA), and (iv) are ideally commercially available. Thus, the following silver salts [Ag][X] were found to be suitable candidates, with [X]$^-$ = [OTf]$^-$ (triflate),‡ [SbF$_6$]$^-$ (hexafluoroantimonate), [B(Ar^{CF_3})$_4$]$^-$ (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), and [Al(OR^F)$_4$]$^-$ (tetrakis[perfluoro *tert*-butoxy]aluminate, *i.e.* R^F = C(CF$_3$)$_3$).
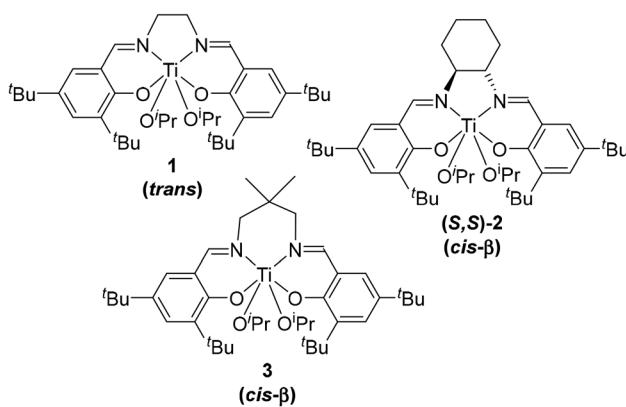
The combination of **1** with any of the selected silver salts (Table 1) led to efficient *rac*-LA ROP at room temperature to afford atactic PLA with controlled molar masses and low dispersity (~1.2), in line with a controlled living polymerisation. For example, about 87% of *rac*-LA was converted in 20 minutes at room temperature in DCM (Table 1, entry 5) whereas in the absence of the silver salt, only 73% conversion was reached in 24 h at 90 °C in toluene (Fig. 2). Plots of ln([*rac*-LA]$_0$/[*rac*-LA]$_t$) against time show linear trends as generally observed for such reactions.[10,14]

Reactions rates were calculated assuming a first order in monomer and using a temporal least squares fit (see ESI†). The molar masses increase linearly *versus rac*-LA conversion and the polymers feature relatively low dispersity, consistent with a controlled living polymerisation. In all cases (except Table 1, entry 1), the molar masses are in accordance with each isopropoxide group being able to initiate one chain, as confirmed by MALDI-ToF analysis showing O^{i}Pr terminated PLA and no evidence of transesterification as peaks are spaced by 144 (see ESI†). In the case of AgOTf as a co-catalyst, only one chain is initiated by the catalyst (only one isopropoxide). This could be attributed to the OTf anion being the most coordinating anion of the series, and thus hampering initiation of the second chain by the other isopropoxide group due to potential interaction between the OTf anion and the O^{i}Pr group. It should be noted that in the absence of any silver salt, no activity is observed in the same conditions (*i.e.* room temperature), and any of the silver salts alone (*i.e.* without **1**) do not initiate ROP of lactide, even in the presence of one equivalent of alcohol as initiator. These results confirm the cooperativity between **1** and Ag$^+$ for *rac*-LA ROP at room temperature and demonstrate how the simple addition of a silver salt can significantly increase catalyst activity in mild conditions.

Looking at the effect of the counter anion of the different silver salts (Table 1, entries 1–5), reactions using the most weakly coordinating anion such as [B(Ar^{CF_3})$_4$]$^-$ and [Al(OR^F)$_4$]$^-$ showed the highest activities, whereas the most coordinating anions such as [OTf]$^-$ and [SbF$_6$]$^-$ showed the lowest activities, as per Fig. 3. Interestingly, the acetonitrile adduct of [Ag][B(Ar^{CF_3})$_4$] (Table 1, entry 4) displayed low activity as compared to the Et$_2$O adduct (Table 1, entry 3). This was attributed to the strong coordination of CH$_3$CN to the silver cation, and thus hindering the interaction of Ag$^+$ with **1** and the resulting cooperativity.[10] Overall, these results show that the counter-anion influences the formation of a suitable supramolecular entity between Ag$^+$ and the Ti-salen complex **1** which in turn impacts the subsequent *rac*-LA polymerization.

In consideration of any potential deactivation of the catalytic system (*i.e.* **1** in the presence of a silver salt) and to investigate the difference in reactivity between the silver salts, "*same excess*" experiments were carried out on two catalytic systems (*i.e.* the most active and least active), *i.e.* **1** + [Ag][SbF$_6$]

**Fig. 1** Ti-salen complexes tested for *rac*-LA ROP in the presence of various silver salts.

‡ It should be noted that AgOTf has a limited solubility in DCM and a mixture DCM/toluene as solvent was used instead (see ESI†).

Table 1 *rac*-LA polymerisation initiated by **1** in the presence of different silver salts [Ag][X]

Entry	Cat./[Ag][X]/*rac*-LA (equiv.)	[X]$^-$	Time (min)	Conversion^a (%)	M_n ($Đ$)^b (kg mol^{-1})	M_n (calc.)^c (kg mol^{-1})
1	**1/1/100**	[OTf]$^-$	240	88.0	11.5 (1.2)	12.7^d
2	**1/1/100**	[SbF$_6$]$^-$	180	56.4	3.2 (1.2)	4.1
3	**1/1/100**	[B(Ar^{CF_3})$_4$]$^-$	60	81.9	6.2 (1.2)	5.9
4	**1/1/100**	[B(Ar^{CF_3})$_4$]$^-$·CH$_3$CN	80	7.3	—^{e}	0.5
5	**1/1/100**	[Al(OR^F)$_4$]$^-$	20	86.9	6.5 (1.3)	6.3
6[10]	**1/0/100**	—	240	0	—	—
7[14f]	**1/0/100**	—	1440	73	6.6 (1.3)	5.3
8	**0/1/100**	[B(Ar^{CF_3})$_4$]$^-$	180	0	—	—
9	**0/1/100**	[Al(OR^F)$_4$]$^-$	180	0	—	—
10	**0/1/100**	[SbF$_6$]$^-$	180	0	—	—

Reaction conditions: cat. = **1**, [*rac*-LA]$_0$ = 1 M, DCM, 25 °C. ^{a} Calculated using ^{1}H NMR spectroscopy. ^{b} Calculated using SEC calibrated with polystyrene standards and corrected by 0.58. ^{c} Calculated considering, two chains per Ti-salen complex (one chain per isopropoxide initiating). ^{d} Calculated considering one chain per Ti-salen complex (only one isopropoxide initiating). ^{e} Not isolated due to low conversion. ^{f} Reaction at 90 °C in toluene.
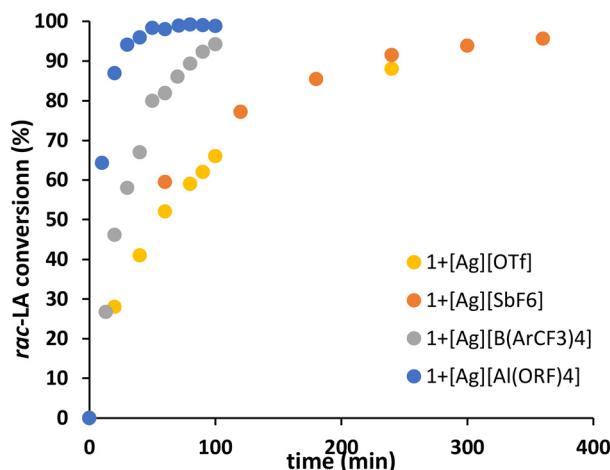
Fig. 2 *rac*-LA conversion *versus* time for polymerisation initiated by **1** in the presence of different silver salts AgX (conditions: [*rac*-LA]$_0$ = 1 M, DCM, [1]/[AgX]/[*rac*-LA]$_0$ = 1/1/100).
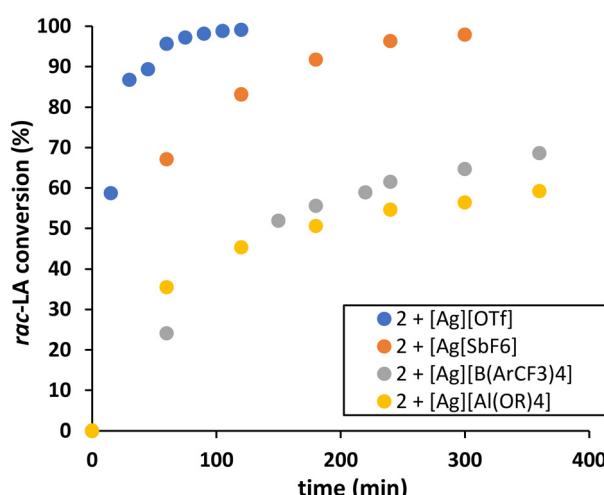
Fig. 3 *rac*-LA conversion *versus* time for polymerisation initiated by **2** in the presence of different silver salts AgX (conditions: [*rac*-LA]$_0$ = 1 M, DCM, [2]/[AgX]/[*rac*-LA]$_0$ = 1/1/100).

and **1** + [Ag][Al(OR^F)$_4$], with initial concentration of [*rac*-LA]$_0$ = 1.5 M and 1.0 M (see details in ESI†).[9b,16] In the case of [Ag][Al(OR^F)$_4$] as a co-catalyst, the time-shifted curve for the reaction at higher concentration superimposed onto the curve of the reaction at lower concentration with minimal deviation, indicating no deactivation of the catalytic system, in line with [Al(OR^F)$_4$] being an inert counter-anion. On the contrary, in the case of [Ag][SbF$_6$] as a co-catalyst, the time-shifted curve for the higher concentration reaction did not overlap with the curve for the reaction at lower concentration showing significantly lower activity, thus suggesting some deactivation. This could be attributed to the SbF$_6$ counter-anion which, while being a WCA, is known to decompose to SbF$_5$ + F$^-$ and then can further react with Ti.[17] These results highlight the importance of the counter anion, not only being weakly coordinating, but also inert to prevent undesired reactions with the Ti metal centre. MALDI-ToF analysis of complex **1** in the presence of [Ag][SbF$_6$] and [Ag][Al(OR^F)$_4$] was performed (Fig. S1 and S2†). In both cases, the adduct corresponding to m/z = [**1** + Ag]$^+$ was observed, likely due to cation π interactions. Interestingly, in the case of [Ag][SbF$_6$], a fluorinated cationic Ti–F salen complex has been observed, in line with potential decomposition of SbF$_6$ providing a source a fluoride.

As [Al(OR^F)$_4$]$^-$ was confirmed to be a suitable counter-anion (*i.e.* inert and weakly coordinating), further investigations were carried out to examine the influence of the stoichiometry of the silver salt co-catalyst on the ROP. Thus, *rac*-LA ROP was found to be successfully initiated by one equivalent of **1** in the presence of half, one and two equivalents of [Ag][Al(OR^F)$_4$]. While using one or two equivalents of Ag[Al(OR^F)$_4$]$^-$ led to comparable activities (86.9% and 92.2% *rac*-LA conversion in 20 minutes, respectively), using only 0.5 equivalents of [Ag][Al(OR^F)$_4$] led to a significantly slower reaction (62% conversion in 60 minutes), as per Fig. S37.† This is in line with the proposed formation of a 1 : 1 aggregate between **1** and Ag$^+$.[10]

Having established the best conditions for **1**, similar investigations were carried out with Ti-salen complex **2** bearing a more rigid ligand with a cyclohexyl moiety, and complex **3** bearing a more flexible ligand with a dimethyl

Table 2 *rac*-LA polymerisation initiated by **2–3** in the presence of different silver salts

Entry	Cat.	cat./Ag[X]/*rac*-LA (equiv.)	[X]$^-$ (1 equiv.)	Time (min)	Conversion^a (%)	M_n ($Đ$)^b (kg mol^{-1})	M_n (calc.)^c (kg mol^{-1})	P_r^{d}
1	**2**	1/1/100	[OTf]$^-$	30	86.7	11.2 (1.2)	12.5^e	0.71
2	**2**	1/1/100	[SbF$_6$]$^-$	180	91.7	6.2 (1.2)	6.6	0.49
3	**2**	1/1/100	[B(Ar^{CF_3})$_4$]$^-$	150	51.9	3.4 (1.2)	3.7	0.61
4	**2**	1/1/100	[Al(OR^F)$_4$]$^-$	180	50.6	4.3 (1.1)	3.7	0.60
5	**(*S,S*)-2**	1/1/100	[Al(OR^F)$_4$]$^-$	180	83.8	5.3 (1.2)	6.0	0.40
6^f	**2**	1/0/100	—	1440	57	5.3 (1.1)	8.2	0.54
7	**3**	1/1/100	[OTf]$^-$	90	50.8	12.0 (1.4)	7.3^e	0.71
8	**3**	1/1/100	[SbF$_6$]$^-$	20	84.8	22.4 (1.4)	6.1	0.44
9	**3**	1/1/100	[Al(OR^F)$_4$]$^-$	5	80.3	3.6 (1.6)	5.8	0.38
10^g	**3**	1/0/100	—	2880	10.9	2.7 (1.2)	1.6^e	0.67

Reaction conditions: [*rac*-LA]$_0$ = 1 M, DCM, 25 °C. ^{a} Calculated using ^{1}H NMR spectroscopy. ^{b} Calculated using SEC calibrated with polystyrene standards and corrected by 0.58. ^{c} Calculated considering two chains per Ti-salen complex (one chain per isopropoxide initiating). ^{d} Determined *via* ^{1}H{^{1}H} decoupled NMR spectrum of isolated PLA. ^{e} Calculated considering one chain per Ti-salen complex (only one isopropoxide initiating). ^{f} Reaction performed at 70 °C in toluene with [*rac*-LA]$_0$ = 1 M and [**2**]/[*rac*-LA] = 1/100, data from reference.[14] ^{g} Reaction performed at 100 °C in toluene with [*rac*-LA]$_0$ = 0.5M and [**3**]/[*rac*-LA] = 1/100, data from reference.[15]

propyl backbone. Both complexes **2** and **3** were previously reported to afford very slow polymerisation of *rac*-LA in toluene at 90 °C and 70 °C, respectively (Table 2, entry 6 and 10).[14,15] In the presence of any of the aforementioned silver salts, both catalysts **2** and **3** resulted in moderate to very high activity at room temperature for *rac*-LA ROP, as previously observed with **1**. This shows that this strategy could be applied to different Ti-salen complexes adopting either *trans* configurations (complex **1**) or *β-cis* conformations (complexes **2** and **3**), and that for these configurations, the binding of Ag$^+$ *via* cation-π interactions is possible, as supported by MALDI-ToF analysis (Fig. S3–S6†).

All the catalytic systems using **2** show controlled *rac*-LA ROP to afford polymers with predictable molar masses and low dispersity ($Đ \sim 1.2$). For all systems, one polymeric chain is initiated by each isopropoxide (*i.e.* two chains per complex **2**, see Table 2, entries 2–4, and Fig. S83†), except when [Ag][OTf] is used in which only one chain is initiated per Ti-salen complex (Table 2, entry 1), similar to what we observed when using **1** and [Ag][OTf].

Interestingly, the activity trend for catalytic systems using **2** is reciprocal to that for **1**. When using **2**, catalytic systems with weakly coordinating anions [B(Ar^{CF_3})$_4$]$^-$ and [Al(OR^F)$_4$]$^-$ show comparable activities (~50% *rac*-LA conversion in 3 hours) and were significantly slower than the most active system using [Ag][OTf] which show 87% conversion in 30 minutes. When using **1**, the reverse trend is observed with the [Ag][OTf] system affording 80% conversion in 4 hours as opposed to the system with [Ag][Al(OR^F)$_4$] which afforded 80% conversion in 20 minutes. This difference in reactivity could be due to the difference in the *trans* and *β-cis* configurations of **1** and **2** respectively. As the *β-cis* configuration of **2** offers a more open coordination sphere, an Ag$^+$ cation surrounded by a less dissociating counter-anion such as OTf$^-$ can thus be accommodated more easily. This is also supported by the kinetic analysis (Fig. S47 and S52†) showing a departure from the assumed first order in monomer when using the [Al(OR^F)$_4$]$^-$ and [B(Ar^{CF_3})$_4$]$^-$, suggesting catalyst saturation with lactide,[18]

in line with a more open coordination sphere. By extension, this would also suggest that the conformation and the flexibility of the salen ligand would also influence the nature of the supramolecular aggregate formed by the Ti-salen complex and silver salt.

In addition to enabling high activity at room temperature, the use of **2** in the presence of a silver salt as a co-catalyst was found to enable some stereocontrol, affording heterotactic PLA with P_r up to ~0.7. In the absence of silver salts, elevated temperatures are needed (>70 °C) for ROP and hence, stereocontrol is compromised ($P_r \sim 0.5$, Table 2, entry 6). The highest tacticity (Table 2, entry 1) was observed for AgOTf as a co-catalyst, in line with our previous observation that the triflate anion is the least weakly coordinating anion of the investigated series, thus congesting the coordination sphere, with potential interactions involving the OTf$^-$.[19] It is worthy to note that whereas zirconium and hafnium complexes were previously reported for stereocontrolled *rac*-lactide ROP,[13c,d,20] their titanium counterparts with the same ligand usually afforded atactic polymers.[21] Indeed, Ti complexes usually require higher temperature (usually > 70 °C) to exhibit significant activity for lactide ROP, and thus compromising stereocontrol. These results prompted us to investigate lactide ROP initiated by (*S,S*)-2 obtained from the corresponding (*S,S*)-*trans* ligand precursor (see ESI†). In similar conditions as per **2** (Table 2, entry 5), *rac*-LA ROP using (*S,S*)-2 in the presence of [Ag][Al(OR^F)$_4$] leads to a slightly isotactic PLA with P_r = 0.4, suggesting an enantiomorphic site control mechanism. This is confirmed by a slight difference in polymerisation rate when using D-lactide and L-lactide, one being the favoured isomer and the other the disfavoured one (Fig. S66, S67 and Table S3†).[22] The change from slightly heterotactic PLA (when using **2**) to slightly isotactic PLA (when using (*S,S*)-2) can be attributed to polymeryl chain exchanges which can occur when a racemic mixture of catalysts is used and their dimerization favoured.[9b,22b]

In the case of **3**, the addition of silver salt led to very fast conversion of *rac*-lactide, in particular using [Ag][Al(OR^F)$_4$], with up to 80% conversion in just 5 minutes (Table 2, entry 8).

In the absence of silver salts, only 11% conversion was observed in 48 h at 100 °C. However, while high activity was observed, polymerisation control was found to be poorer with significant discrepancy between theoretical and experimental molar masses. Molar masses tended to be higher than expected, suggesting partial or poorly controlled formation of active species. Interestingly, in some cases (Table 2, entries 7 and 8) the polymers show an isotactic bias ($P_r \sim 0.4$). Further investigations are ongoing to identify the nature of the active species.

Conclusions

Three bis(*iso*-propoxide) Ti-salen complexes were investigated for *rac*-lactide ROP in the presence of different silver salts. In all cases, these Ti/Ag bi-component systems afforded *rac*-lactide ROP at room temperature, a rather rare feature for Ti-based systems which usually require high temperatures (>70 °C) for significant activity. In the absence of any silver salt, Ti-salen complexes showed no activity at room temperature and only low to moderate activity at higher temperatures (>70 °C). These results highlight the ability of Ti/Ag cooperativity to enable polymerisation under mild conditions.[11] As we previously demonstrated with similar systems, this results from cation-π interactions positioning the silver cation near the Ti centre, allowing monomer activation and stabilisation of key intermediates.[10] More interestingly, the lower temperature afforded by addition of silver salts, allowed for stereocontrol which was observed with formation of heterotactic polymers with P_r up to 0.7. Finally, we observed that the nature of the counter anion in the silver salts influence both activity and polymer tacticity, depending on the Ti-salen complex. In line with our previous findings, this is likely related to the formation of different supramolecular catalytic species, for which further investigations are ongoing. Overall, this study has highlighted a simple strategy based on Ti/Ag cooperativity using several Ti-salen complexes to enable activity at room temperature for *rac*-LA ROP along with some stereocontrol. The findings in this work suggest that the same strategy could also be applied to other metal phenolate complexes to enable (stereocontrolled) ROP under mild conditions.

Author contributions

Experimental investigations were performed by J. K., C. B. and M. N. D. All authors contributed to the project's conceptualisation. The manuscript was written and edited by all authors. C. R. and N. J. L. supervised the project and acquired the funding.

Data availability

The data supporting this article have been included as part of the ESI† and are also available on a data repository at **https://doi.org/10.14469/hpc/14821**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 (*a*) J. N. H. Reek, B. de Bruin, S. Pullen, T. J. Mooibroek, A. M. Kluwer and X. Caumes, *Chem. Rev.*, 2022, **122**, 12308–12369; (*b*) J. Trouvé and R. Gramage-Doria, *Chem. Soc. Rev.*, 2021, **50**, 3565–3584; (*c*) Y. Lou, J. Wei, M. Li and Y. Zhu, *J. Am. Chem. Soc.*, 2022, **144**, 123–129; (*d*) M. W. Drover, *Chem. Soc. Rev.*, 2022, **51**, 1861–1880; (*e*) M. Raynal, P. Ballester, A. Vidal-Ferran and P. W. N. M. van Leeuwen, *Chem. Soc. Rev.*, 2014, **43**, 1660–1733; (*f*) H. J. Davis and R. J. Phipps, *Chem. Sci.*, 2017, **8**, 864–877.

2 H. Zheng and H. Gao, *Macromolecules*, 2024, **57**, 6899–6913.

3 (*a*) C. Chen, *Nat. Rev. Chem.*, 2018, **2**, 6–14; (*b*) L. Falivene, L. Cavallo and G. Talarico, *Mol. Catal.*, 2020, **494**, 111118.

4 (*a*) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer and J. L. Hedrick, *Chem. Rev.*, 2007, **107**, 5813–5840; (*b*) A. P. Dove, *ACS Macro Lett.*, 2012, **1**, 1409–1412; (*c*) X. Geng, X. Liu, Q. Yu, C. Zhang and X. Zhang, *J. Am. Chem. Soc.*, 2024, **146**, 25852–25859; (*d*) J. Xu, X. Wang, J. Liu, X. Feng, Y. Gnanou and N. Hadjichristidis, *Prog. Polym. Sci.*, 2022, **125**, 101484.

5 (*a*) G. A. Bhat and D. J. Darensbourg, *Green Chem.*, 2022, **24**, 5007–5034; (*b*) C. A. L. Lidston, S. M. Severson, B. A. Abel and G. W. Coates, *ACS Catal.*, 2022, **12**, 11037–11070.

6 E. L. Marshall, V. C. Gibson and H. S. Rzepa, *J. Am. Chem. Soc.*, 2005, **127**, 6048–6051.

7 (*a*) R. Ligny, M. M. Hänninen, S. M. Guillaume and J.-F. Carpentier, *Chem. Commun.*, 2018, **54**, 8024–8031; (*b*) R. M. Shakaroun, A. Dhaini, R. Ligny, A. Alaaeddine, S. M. Guillaume and J.-F. Carpentier, *Polym. Chem.*, 2023, **14**, 720–727; (*c*) R. Ligny, M. M. Hänninen, S. M. Guillaume and J.-F. Carpentier, *Angew. Chem., Int. Ed.*, 2017, **56**, 10388–10393; (*d*) A. Dhaini, R. M. Shakaroun, A. Alaaeddine, J.-F. Carpentier and S. M. Guillaume, *Polym. Chem.*, 2024, **15**, 999–1014; (*e*) H. Li, R. M. Shakaroun, S. M. Guillaume and J.-F. Carpentier, *Chem. – Eur. J.*, 2020, **26**, 128–138.

8 (*a*) Y. Zhou, Z. Gao, C. Hu, S. Meng, R. Duan, Z. Sun and X. Pang, *Macromolecules*, 2022, **55**, 9951–9959; (*b*) J. Bruckmoser, S. Pongratz, L. Stieglitz and B. Rieger,

J. Am. Chem. Soc., 2023, **145**, 11494–11498; (*c*) T. Pongpanit, T. Saeteaw, P. Chumsaeng, P. Chasing and K. Phomphrai, *Inorg. Chem.*, 2021, **60**, 17114–17122; (*d*) K. M. Osten, D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Inorg. Chem.*, 2014, **53**, 9897–9906; (*e*) P. McKeown, M. G. Davidson, G. Kociok-Kohn and M. D. Jones, *Chem. Commun.*, 2016, **52**, 10431–10434; (*f*) B. Zhao, Z. Han and K. Ding, *Angew. Chem., Int. Ed.*, 2013, **52**, 4744–4788.

9 (*a*) S. Gesslbauer, H. Cheek, A. J. P. White and C. Romain, *Dalton Trans.*, 2018, **47**, 10410–10414; (*b*) S. Gesslbauer, G. Hutchinson, A. J. P. White, J. Burés and C. Romain, *ACS Catal.*, 2021, **11**, 4084–4093; (*c*) S. Gesslbauer, R. Salvela, Y. Chen, A. J. P. White and C. Romain, *ACS Catal.*, 2019, **9**, 7912–7920.

10 C. A. Baker, C. Romain and N. J. Long, *Chem. Commun.*, 2021, **57**, 12524–12527.

11 (*a*) W. Gruszka and J. A. Garden, *Nat. Commun.*, 2021, **12**, 3252; (*b*) L.-J. Wu, W. Lee, P. Kumar Ganta, Y.-L. Chang, Y.-C. Chang and H.-Y. Chen, *Coord. Chem. Rev.*, 2023, **475**, 214847; (*c*) W. Gruszka and J. A. Garden, *Chem. Commun.*, 2022, **58**, 1609–1612; (*d*) U. Yolsal, P. J. Shaw, P. A. Lowy, R. Chambenahalli and J. A. Garden, *ACS Catal.*, 2024, **14**, 1050–1074.

12 (*a*) J. Zhang, K. H. Lui, C. N. Jadrich, Y. Jia, P. L. Arrechea, J. L. Hedrick and R. M. Waymouth, *ACS Catal.*, 2023, **13**, 16097–16104; (*b*) C. N. Jadrich, V. E. Pane, B. Lin, G. O. Jones, J. L. Hedrick, N. H. Park and R. M. Waymouth, *J. Am. Chem. Soc.*, 2022, **144**, 8439–8443.

13 (*a*) Y. Jeong, M. Shin, M. Seo and H. Kim, *Organometallics*, 2022, **41**, 328–334; (*b*) W. Wang, *ACS Omega*, 2024, **9**,

29983–29993; (*c*) M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486–494; (*d*) A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007–9023.

14 C. K. Gregson, I. J. Blackmore, V. C. Gibson, N. J. Long, E. L. Marshall and A. J. White, *Dalton Trans.*, 2006, 3134–3140.

15 B. Gao, X. Li, R. L. Duan and X. Pang, *New J. Chem.*, 2015, **39**, 2404–2408.

16 C. D. T. Nielsen and J. Burés, *Chem. Sci.*, 2019, **10**, 348–353.

17 W. Beck and K. Suenkel, *Chem. Rev.*, 1988, **88**, 1405–1421.

18 M. O. Miranda, Y. DePorre, H. Vazquez-Lima, M. A. Johnson, D. J. Marell, C. J. Cramer and W. B. Tolman, *Inorg. Chem.*, 2013, **52**, 13692–13701.

19 I. M. Riddlestone, A. Kraft, J. Schaefer and I. Krossing, *Angew. Chem., Int. Ed.*, 2018, **57**, 13982–14024.

20 (*a*) A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2008, 1437–1443; (*b*) C. Romain, B. Heinrich, S. B. Laponnaz and S. Dagorne, *Chem. Commun.*, 2012, **48**, 2213–2215.

21 (*a*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257; (*b*) C. Romain, L. Brelot, S. Bellemin-Laponnaz and S. Dagorne, *Organometallics*, 2010, **29**, 1191–1198.

22 (*a*) Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291–11298; (*b*) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chemistry*, 2007, **13**, 4433–4451.