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Ring opening polymerisation of lactide with uranium(IV) and cerium(IV) phosphinoaryloxide complexes†

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The C_3-symmetric uranium(IV) and cerium(IV) complexes $Me_3SiOM(OAr^P)_3$, M = U (1), Ce (2), $OAr^P = OC_6H_2$-6-^{t}Bu-4-Me-2-PPh_2, have been prepared and the difference between these 4f and 5f congeners as initiators for the ring opening polymerisation (ROP) of L-lactide is compared. The poorly controlled reactivity of the homoleptic analogue $U(OAr^P)_4$ (3) demonstrates the importance of the M-$OSiMe_3$ initiating group. The incorporation of a nickel atom in 1 to form the U–Ni heterobimetallic complex $Me_3SiOU(OAr^P)_3Ni$ (4) may be the first example of the use of the *inverse trans influence* to switch the reactivity of a complex. This would imply the formation of the U–Ni bond strengthens the U–$OSiMe_3$ bond to such an extent that the ROP catalysis is switched off. Changing the conditions to immortal polymerisation dramatically increases polymerisation rates, and switches the order, with the Ce complex now faster than the U analogue, suggesting ligand protonolysis to afford a more open coordination sphere. For the ROP of *rac*-lactide, uranium complex 1 promotes heterotacticity at the highest levels of stereocontrol yet reported for an actinide complex.

Introduction

Poly(lactic acid), PLA, is a now common-place biodegradable polyester built from the renewable cyclic diester lactide. With a monomer feedstock readily derived from resources such as corn and sugarbeets, PLA is playing an increasingly important role as a sustainable alternative in plastic packaging and modern biomaterials.[1–3] While the thermal and mechanical properties of PLA can be dramatically changed by tuning molecular weights, blending with other polymers, or building more complicated macrostructures, the stereochemical control over the opening of D, L, or meso monomers has perhaps the most dramatic impact. Thus, catalyst design to control this tacticity in ring-opening polymerisations (ROP) of lactide and other cyclic esters is at the forefront of research at the inorganic/polymer interface.

While industrial PLA production is dominated by an unselective tin-mediated reaction,[1] a wide range of Lewis acidic metal complexes can facilitate either isotactic or heterotactic ROP (*vide infra*). Importantly, the design principles that guide how a ligand will govern tacticity are still not clear.[4] One ligand family of particular interest are the C_3 tris(phenolate) trianions; stereoselective initiators based on Zr^{IV} have generated highly heterotactic polymers,[5] while we have previously shown that a chiral, racemic heterobidentate alkoxide can selectively assemble to form homochiral, C_3 symmetric complexes that are active initiators for the formation of isotactic PLA (P_i = 0.75, 298 K).[6]

Although often overlooked due to misconceptions of scarcity and excessive oxophilicity, the f-block cations possess a unique capability to tune the ROP performance due to the available range of size and Lewis acidity.[7–10] This variability is difficult for other metals; the propensity of In^{III} to adopt a coordination number of 5 limited the scope in our system.[11] While rare, both Ce^{III} and Ce^{IV} are known to initiate ROP reactions, and judicious choice of ligands can dramatically alter activity. For instance, the Ce^{III} initiator Ce(O^{t}Bu)(phosfen) (phosfen = 1,1′-di(2-*t*-butyl-6-diphenyl-phosphiniminophenoxy) ferrocene) is a fast initiator for polymerisation, exhibiting good control of $Đ$.[12]

We recently demonstrated how the simple heterobidentate O–P aryloxide anion $[OC_6H_2$-6-^{t}Bu-4-Me-2-$PPh_2]^-$ (OAr^P) is an excellent hemilabile ligand for U^{IV}, with only weak P-coordination to the U centre in $UI(OAr^P)_3$ **A** (Chart 1).[13]

The strongly bound, sterically protected U–OAr groups help enforce a C_3-symmetry on the complexes when a second, softer metal cation is added to bind the three P donors, forming $XU^{IV}(OAr^P)_3M^O$ **B**, for which the U–Ni bond is the strongest. We reasoned that the C_3-symmetry available to the U^{IV} complex, and the tunability provided by formation of a

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†Electronic supplementary information (ESI) available: Full details of synthesis, characterisation and lactide polymerisation studies. CCDC 1543395 and 1543396. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02167d

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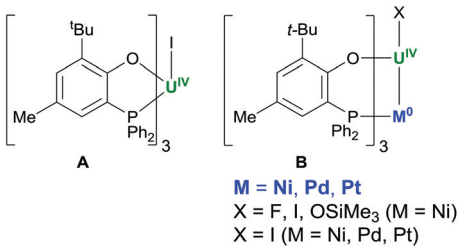


Chart 1 Uranium(IV) mono and heterobimetallic U–M bonded derivatives.

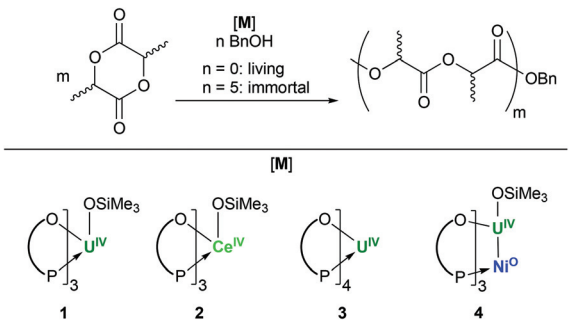


Fig. 1 Summary of ROP of L-lactide studied for the new U^{IV} and Ce^{IV} initiators **1** to **4**. The O–P arc is used to represent the OAr^P ligand (OAr^P = OC_6H_2-6-^{t}Bu-4-Me-2-PPh_2-κ^2*O,P*).

bonding interaction with the added M in the lower pocket, might afford good control over the ROP of lactide, while the hemilabile ligand framework would allow us to probe the important coordination chemistry factors that shape both polymerisation activity and tacticity control.

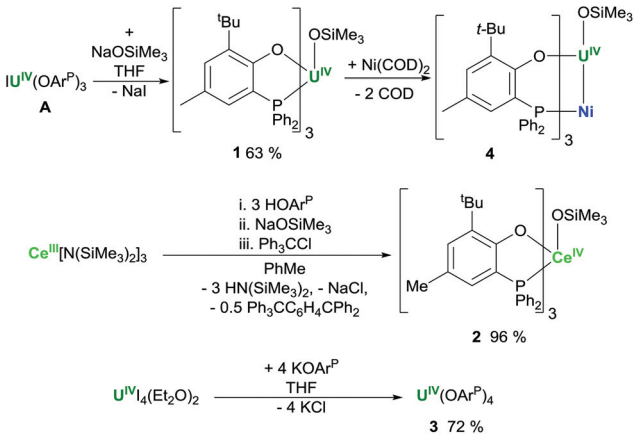
Herein we describe the preparation and comparison of new C_3-symmetric U^{IV} and Ce^{IV} initiators which offer surprising reactivity differences under living and immortal polymerisation conditions, and additionally explore the effect of the incorporation of a transition metal on this reactivity (Fig. 1).

Results and discussion

Synthesis

The uranium complex $Me_3SiOU(OAr^P)_3$ **1** is prepared by treatment of $IU(OAr^P)_3$ with equimolar $NaOSiMe_3$ in THF solution (Scheme 1). The methodology is analogous to that we used to prepare **B** for M = Ni, X = $OSiMe_3$ (Chart 1), which is referred to here as $Me_3SiOU(OAr^P)_3Ni$ **4**.[13] The homoleptic uranium complex $U(OAr^P)_4$ **3** is prepared from the reaction of $UI_4(Et_2O)_2$ with four molar equivalents of $KOAr^P$ in THF.

The cerium $Me_3SiOCe(OAr^P)_3$ **2** complex is not conveniently made by salt metathesis routes, but in a one-pot procedure the cerium(III) tris(amide) $Ce[N(SiMe_3)_2]_3$ reacts with three equivalents of $HOAr^P$ to form $Ce(OAr^P)_3$ which is further functionalised and then oxidised *in situ* by sequential addition of $NaOSiMe_3$ and trityl chloride, yielding **2** as dark brown crystals



Scheme 1 Syntheses of the U^{IV} and Ce^{IV} complexes **1–3** and the previously reported **4**.

in 96% (relative to the cerium amide), and the group 1 halide and Gomberg's dimer as by-products, Scheme 1.[14,15]

Crystallography

A sample of **2** suitable for X-ray diffraction was grown from a concentrated hexane solution (Fig. 2). The seven-coordinate cerium centre is tethered to the ligands with Ce–O distances from 2.190(2) to 2.162(2) Å for the aryloxides down to 2.067(2) Å for the trimethylsiloxide. The diversity in the Ce–P distances of 3.1575(7), 3.190(1), and 3.307(1) Å may be attributed to the minimisation of steric interactions between the large ligands at the expense of the weaker, more labile Ce–P interaction.[16] A single crystal of **3** was isolated directly from a reaction mixture and the structure shows that, in comparison with the structure of the parent $IU(OAr^P)_3$, the introduction of a fourth aryloxide results in elongation of the U–P interactions to 3.276 Å to com-

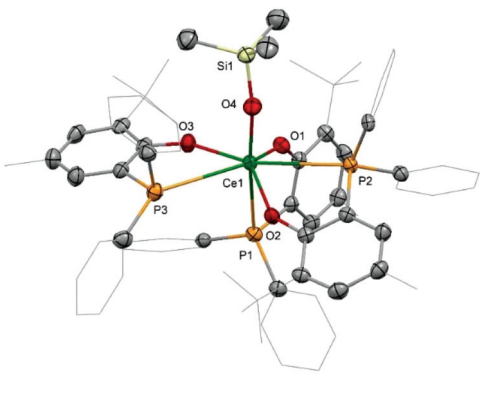


Fig. 2 Molecular structure of **2**. Hydrogen atoms are omitted, and peripheral carbon atom are depicted as wireframe, for clarity. Thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Ce1–O1: 2.174(2), Ce1–O2: 2.190(2), Ce1–O3: 2.162(2), Ce1–O4: 2.067(2), Ce1–P1: 3.1575(7), Ce1–P2: 3.190(1), Ce1–P3: 3.307(1), O1–Ce1–P1: 61.83(5), O2–Ce1–P2: 61.50(5), O3–Ce1–P3: 58.20(5), Ce1–O4–Si1: 159.4(1).

pensate for the steric encumbrance around the uranium centre (see ESI†). The U–O distances, 2.193 Å, are similar to those previously reported for the other complexes featuring this phosphinoaryloxide ligand.[13,17] Unfortunately, despite repeated attempts, we have been unable to grow single crystals of **1**.

NMR spectroscopy

The NMR spectroscopic analysis of the uranium complex **1** shows highly fluxional behaviour, similarly to the parent compound $IU(OAr^P)_3$ with no resonances being observable in ^1H, ^{29}Si, and ^{31}P NMR at ambient temperature. Variable temperature ^1H NMR experiments reveal paramagnetically shifted signals at elevated temperatures (see ESI†). In contrast, the homoleptic uranium compound **3** exhibits sharp, paramagnetically-shifted resonances in ^1H NMR spectrum in the range 1.38 to 11.73 ppm (see Fig. S7†). No ^{31}P NMR signal is observed again here suggesting that the uranium–phosphine interaction is retained in solution and giving rise to a resonance which is too shifted and/or broadened to observe. The spectroscopic data for the diamagnetic Ce^{IV} complex **2** shows fluxional behaviour as ^1H NMR resonances for the aromatic protons and the *tert*-butyl groups are strongly broadened at R.T. and sharper when measured at elevated temperatures (see Fig. S8†). In agreement, the ^{31}P NMR spectrum contains three broadened and overlapping shifts at 23.6, 16.4, and 12.2, which coalesce to a single resonance at 16.23 at elevated temperatures (see Fig. S9†). The trimethylsiloxide ^{29}Si NMR chemical shift is at 6.1 ppm.

Lactide polymerisation

Initial studies on the ROP of L-lactide indicate that both **1** and **2** are active catalysts (Fig. 1 and Table S1†). These screening reactions were run under "living" conditions, in the absence of any added BnOH, initiating from the bulky siloxide ligand. Molecular weights obtained from GPC are in good agreement to the theoretical molecular weights, evidenced by monodisperse dispersities (*Đ*). Less control is observed with **2** (entry 10, Table S1†) compared to the U^{IV} complex **1** (entry 1, Table S1†), as shown by broader *Đ*s. While control is maintained for **1** in toluene, benzene and dichloroethane (DCE), polymerisation in DCE with **2** gives lower conversions and a loss of control (entry 12, Table S1†). The harder Ce(IV) ion in the active species derived from **2** may permit solvent interference or catalyst decomposition. The use of the homoleptic **3** confirms the importance of the siloxide ligand as a reactive initiator. Insertion into the aryloxide of the ligand is sluggish (entry 6, Table S1†), as polymerisation is slow and poorly controlled, and forms polymers with molecular weights twice that expected from conversion.

The addition of Ni^0 to **1** to form a U–Ni metal–metal bond dramatically alters the polymerisation behaviour. When preformed heterobimetallic complex **4** is tested under living or immortal conditions, essentially no polymerisation activity is observed (entries 8 and 9, Table S1†). Our previously reported experimental and computational analyses of **4** show a particularly short, but relatively weak U–Ni bond.[13]

It may be possible to ascribe this 'switching off' by *trans*-Ni coordination to the *Inverse Trans Influence* (ITI), the mutual strengthening of two *trans*-coordinated ligands that occurs in f-block complexes, and is opposite to the weakening effect for the d-block. It is receiving increasing attention in f-block bonding because of its effect on uranyl $[UO_2]^{2+}$ behaviour, and is now attributed primarily to the ligands interacting with pseudocore-like 6p orbitals and inducing a quadrupolar polarisation of the metal core electrons.[18] Thus, here the *trans*-bound Ni strengthens the U–$OSiMe_3$ bond sufficiently to prevent protonolysis or esterification. We should also note that the Ni–P bond in **4** is stronger than the parent U–P bonding in **1**. Even though the formal coordination number for U^{IV} is lower than in **1**, the loss of hemilability in the OAr^P ligands upon formation of **4** may hamper monomer access in the subsequent reactivity studies. Calculations of the percent buried volume for the set of U^{IV} complexes $UI(OAr^P)_3$ **A** and $IU(OAr^P)_3Ni$ (the iodide analogue of **4**), and $Me_3SiOU(OAr^P)_3$ (a model made by replacement of Ce^{IV} by U^{IV} in the X-ray structure of **2**) show almost no difference in accessible space at the initiating ligand (Table S3†).[19]

Polymerisations of **1** and **2** were also investigated under immortal conditions with a monomer : catalyst : BnOH ratio of 200 : 1 : 5, where the excess of BnOH as a chain transfer agent permits a decrease in catalyst loading. While both catalysts maintain the exceptional polymerisation control under immortal conditions (entries 5 and 14, Table S1†), remarkable differences were observed in reaction rates. Kinetic studies of both catalyst **1** and **2** were conducted by monitoring the reaction *in situ* with ^1H NMR spectroscopy (Fig. 3 and ESI†). In the absence of BnOH, polymerisation of L-lactide reaches completion in 160 and 600 min for **1** and **2** respectively. The relatively higher affinity of the P donor for U will result in a fixed coordination geometry, with monomer coordination to the productive siloxide face assured. Conversely, a more labile Ce–P bond creates a more open and flexible coordination geo-

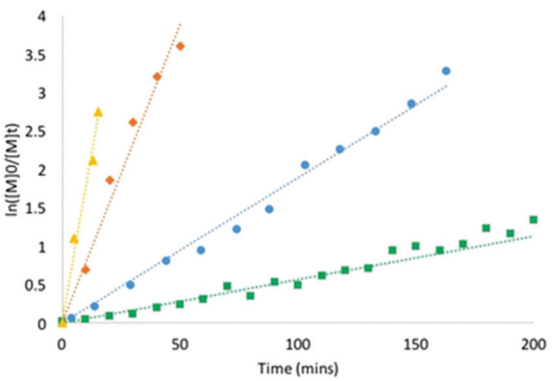


Fig. 3 Kinetic plot of the ROP of L-lactide in toluene-d_8 at 333 K. Blue circles and green squares: catalyst **1** and catalyst **2** respectively with a monomer : catalyst ratio of 200 : 1. Orange diamonds and yellow triangles: catalyst **1** and catalyst **2** respectively under immortal conditions with a monomer : catalyst : BnOH ratio of 200 : 1 : 5. Graph cut off at 200 minutes for comparative purposes.

metry around **2**, enabling non-productive monomer coordination (*i.e. trans* to the growing chain after phosphine dissociation). However, both U and Ce catalysts are exceptionally faster under immortal conditions: polymerisations are complete in 50 and 15 minutes for **1** and **2**, respectively. Intriguingly, the reactivity switches, with the Ce complex now faster. This suggests that the added BnOH may participate in chain exchange reactions with both siloxide and ligand phenoxide groups, alleviating steric congestion and easing monomer access to the more Lewis acidic Ce^{IV} centre.

Indeed, ^{31}P NMR spectroscopy supports this idea of BnOH-promoted ligand displacement, as evidenced by growth of a 2-*tert*-butyl-4-methyl-6-(diphenylphosphino)phenol ($HOAr^P$) resonance upon addition of 5 equivalents of BnOH to **2** (Fig. S2†). Of course, siloxide protonolysis will be preferential and ^1H NMR spectroscopy supports replacement of $OSiMe_3$ with OBn (Fig. S3†). This ligand displacement even extends to the homoleptic complex **3** where immortal conditions improve control and polymerisation rates (entry 7, Table S1†), suggesting chain exchange creates the new active complex. Short polymer chains of L-lactide using **2** under immortal conditions in a 300 : 1 : 5 molar ratio were prepared for end-group analysis. ^1H and 2D (COSY, HSQC, HMBC) NMR spectroscopy revealed the resulting PLA chain was capped with an –OH group at one end and $PhCH_2O$– group at the other end (Fig. S4†). Moreover, MALDI mass spectrometry confirms BnOH end group incorporation (Fig. S5†). This is indicative of a coordination insertion mechanism.

Finally, to understand the influence these catalysts have on the stereoselectivity of polymerisations, the ROP of **1** and **2** were examined using *rac*-lactide; the results are summarised in Fig. 4.

Initiator **1** promotes the formation of heterotactic PLA, Pr = 0.79 (entry 2, Table S2†), whereas **2** displays no stereocontrol (entries 8–13, Table S2†). The more rigid coordination environment enforced by the strong U–P bonding induces chain end control stereoselectivity. The more labile bonding, and thus flexible coordination sphere, in Ce reduces any chain end influence, forming atactic PLA. Under immortal conditions, where we believe the coordination geometry opens up in both catalysts, a loss in heterotacticity is observed (Pr = 0.58, entry 7, Table S2†). Beyond chain exchange, reaction conditions also influence tacticity control. The best results are observed in dichloroethane (entry 2, Table S2†), likely due to the higher solubility of *rac*-lactide. Heterotacticity is also reduced at higher temperatures, with Pr = 0.62 at 90 °C (entry 4, Table S2†). It is noteworthy that, to our knowledge, **1** offers the greatest control over stereoselectivity for any U catalyst for lactide ROP.

While public opinion will likely not let industry make polymers from depleted uranium, the sharply contrasting behaviours of Ce and U, which have almost identical ionic radii, highlight the fundamental differences in 4f- *vs*. 5f- metal–ligand bonding, an area which is still poorly understood. We have demonstrated both uranium catalyst **1** and cerium catalyst **2** are active initiators in the ROP of lactide. The homoleptic uranium analogue **3** highlights the importance of the siloxide group for a controlled polymerisation and the addition of Ni(0) that forms a U–Ni bond *trans* to the $U–OSiMe_3$ initiating group in **4** switches off the polymerisation. This could be attributable to the *inverse trans influence* which would strengthen the $U–OSiR_3$ bond. Model volume calculations suggest the space available at the initiating site is barely changed, but the rigidity of the bound ligands is increased, which could reduce monomer access. However, in the absence of solid-state structures that would enable a detailed comparison of the two initiators, further evidence, such as computational bonding analyses would be required to unequivocally conclude this. We have further shown that under immortal conditions the rates of polymerisation using both **1** and **2** can be substantially increased while maintaining control over the dispersity. Finally, highly heterotactic PLA can be formed using catalyst **1** under living ROP of *rac*-lactide. Thus, through careful catalyst design and comparison we have made ROP catalysts capable of undergoing living and immortal polymerisations where reactivity can be shut down and tacticity can be switched off through manipulation off the catalyst coordination sphere.

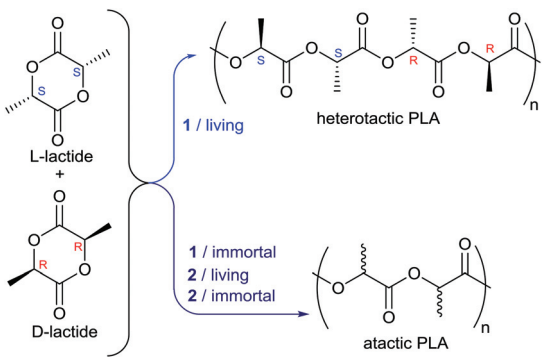


Fig. 4 Summary of the differences in reactivity and product tacticity between the U^{IV} and Ce^{IV} initiators **1** and **2** under different polymerisation conditions.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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