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Aminopiperidine based complexes for lactide polymerisation

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Herein we report the synthesis and characterisation of a series of salalen and salan ligands derived from 2-(aminomethyl)piperidine. Depending on the choice of starting salicylaldehyde, a bicyclic salan type ligand (**1**-**3**H$_2$) or imino salalen type ligand (**4**-**6**H, **7**-**9**H$_2$) were prepared. The ligands were successfully complexed to group 4 metals and aluminium; with hafnium and zirconium octahedral complexes, M(**1**-**3**)$_2$, were realized; whilst with aluminium tetrahedral and trigonal bipyramidal complexes, Al(**1-9**)Me$_x$ (x = 1,2), were isolated. The complexes have been characterised in solution *via* ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and in the solid state by X-ray crystallography. The group 4 complexes were observed to have a *fac-fac* arrangement of ligands and there were two isomers present when **3**H$_2$ was ligated. The imino aluminium complexes Al(**7**-**9**)Me were isolated as a mixture of diastereoisomers. The resultant complexes were trialed in the ring opening polymerisation of *rac*-lactide with both heterotactic and isotactic PLA being demonstrated. Tacticity was found to be dependent on the nature of the ligand and metal used; the M(**1**-**3**)$_2$ complexes were generally found to have a heterotactic preference (P_r = 0.67-0.76) and the aluminium polymerisation outcome was dictated more by the steric influence of the ligand, particularly for Al(**4**-**6**)Me$_2$/Al(**7**-**9**)Me.

Introduction

Sustainable plastics are receiving increased interest due to dwindling petrochemical resources and a desire for more biodegradable materials. At the forefront of such research are polylactic acid (PLA) based materials, which can have similar properties to petrochemical derived polymers and a broad range of applications.[1] There are a range of polymer microstructures that can be accessed and this can be tuned by varying the stereochemistry of the monomer and judicious choice of initiator; in particular, there is great emphasis placed on controlling the chain stereoregularity in the polymerisation of *rac*-lactide (*rac*-LA) to achieve improved polymer properties.[2] For this, an initiator capable of polymerizing *rac*-LA with strong isoselectivity and fast kinetics is urgently being sought.[3] This is related to the desired properties (higher T_m) of the resulting polymer. There are a range of initiators in the literature with metals such as Sn(II)[4], Zn(II)[5], Al(III)[2g,6], In(III)[7], Group II[5b,8], rare-earth[3,9] and Group IV[6a,10] being widely reported.

Common themes previously seen in successful ring opening initiators for lactide polymerisation include a cyclic backbone and a stereocentre, allowing for enantiomorphic control over the propagating chain.[2b,2g,5a,5e,6b,6g,6j,7a,7e,10c,11] The metal centre employed can also have a profound effect on the polymerisation outcome.[6a,9b] Early work by Spassky and co-workers demonstrated this approach by using *R*-binapthyldiamine ligands with an Al(III) centre.[2g,6j] These salen complexes showed a distinct preference for the polymerisation of *D*-lactide leading to isotactic stereocomplexed PLA. Feijen *et al* have utilized Jacobsen's ligand containing a *trans*-1,2-diaminocyclohexyl backbone for *rac*-LA polymerisation.[6g,11c] Once again, aluminium was used and isotactic PLA was realized on application of the racemic complex. A series of unsymmetrical Al(III) salalens based around this diaminocyclohexyl structure were prepared by Jones *et al*.[6b] Moderate stereocontrol was observed for all complexes with greatest heterotacticity being related to chloro-substituted phenyl moieties. More recently, work by Kol has demonstrated the use of chiral aminomethylpyrrolidine salalen ligands with aluminium giving heterotactic or gradient isotactic PLA depending on aryl substituents.[6c]

Chiral bipyrrolidine based complexes feature in recent investigations by Jones *et al.*[6a,10c] These reports highlight the use of Zr(IV) and Hf(IV) initiators to afford PLA exhibiting moderate isotactic bias in the melt, although P_m values up to 0.86 can be achieved in solution. Interestingly, replacing the group 4 metal with Al(III) caused a shift in selectivity towards heterotactic PLA.[6a] Other metals have also been demonstrated for the ROP of lactide. Abbina and Du have recently described a novel amido-oxazolinate ligand as a tuneable alternate to the β-diketiminate motif.[5a] The corresponding chiral zinc complexes were shown to polymerise *rac*-lactide with both a fast rate and strong isotactic preference with evidence of

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Electronic Supplementary Information (ESI) available: Full analysis of ^{1}H and ^{13}C{^{1}H} NMR spectra and data are provided as well as examples of polymer characterisation and the crystal data in the .cif format. The crystal data have been deposited with the CCDC numbers 1432292-1432306. See DOI: 10.1039/x0xx00000x

stereocomplexation. Mehrkhodavandi *et al*. have reported a series of dinuclear In(III) initiators involving chiral, cyclic backbones.[7a,7e] In the first instance enantiomerically pure $[(NNO)InI(\mu\text{-}OEt)]_2$ complexes were prepared and applied to the room temperature polymerisation of lactide. The highest stereocontrol was achieved using a ^{t}Bu/Me substituted aryl ring with slight isotactic preference being reported. Further work saw the employment of Jacobsen ligand to yield $[(ONNO)InOEt]_2$ complexes. In solution, high activity is observed as well as a more pronounced isotactic bias. The analogous phosphasalen incorporating a cyclohexyl backbone has been reported by Williams *et* al.[9a] These yttrium alkoxide based initiators demonstrated high activity towards *rac*-LA polymerisation and induced a strong heterotactic bias in the resulting PLA.

In this paper, the synthesis of salalen and salan type ligands based on a 2-(aminomethyl)piperidine backbone is reported and discussed. These have been complexed to a range of metals {Al(III), Zr(IV), Hf(IV) and Ti(IV)} and trialed for the ring opening polymerisation of *rac*-LA.

Results and discussion

The condensation between 2-(aminomethyl)-piperidine and various 3,5-substituted salicylaldehydes yielded two distinct products; for salicylaldehydes bearing alkyl moieties the expected imine product was formed as the major species. However, for the 3,5-di-halosalicyaldehyde starting materials the imine appears as the minor species with a bicyclic tautomer being the major isolated product. Such compounds have been previously been prepared by Beim and Day who also observed a dynamic equilibrium between the two tautomeric forms.[12] However, herein is the first systematic synthesis and application of these bicyclic species in catalysis.

For these sets of precursor ligands, the distribution of products can be related to the electron donation of the substituents of the aryl group; inductive donors such as ^{t}Bu, Me and Ad disfavour the cyclization due to increased electron density on the benzyl carbon. Conversely, electron withdrawing halo groups facilitate intramolecular attack. As in the work of Beim and Day, interchange between the cyclic and acyclic structures is observed *via* variable temperature (VT)-NMR spectroscopy.[12] This chemical exchange is further shown through EXSY NMR in which there are clear cross peaks between the two forms (see ESI, Figure SI2)

The corresponding bisphenol ligands were realized by an S_N2 reaction with 3,5-di-tert-butyl-2-hydroxybenyzlbromide affording the salalen or salan moiety depending on the on the aryl substituents (Scheme 1). Characterisation of all ligands, **1**-**9**H_x (x = 1,2), included $^1H/^{13}C\{^1H\}$ NMR spectroscopy, high resolution ESI-MS and the bicyclic salan structure of **1**H_2 was further characterised by X-ray crystallography (see ESI, Figure SI5). Ligands based on this fused ring system are rare and this is the first reported synthesis of a phenolate version of such a 2-azaindolizidine ring system and its use in catalysis. The bicyclic systems offer an interesting motif in which the rigid backbone confers a tighter tridentate coordination as the bridging nitrogen does not participate in bonding to the metal centre. This is contrasted by the tetradentate imine form in which both nitrogen atoms are well positioned to contribute to metal coordination.

The zirconium (IV), hafnium (IV) and aluminium (III) complexes were formed and characterised *via* single crystal X-ray diffraction (where appropriate), solution-state NMR spectroscopy and elemental analysis.

Reaction of the tridentate ligands **1**-**3**H_2 with zirconium exhibited a strong preference for the coordination of two ligands around one metal centre yielding a 6-coordinate species. In the solid state these bis-ligated zirconium complexes, Zr(**1**-**3**)$_2$, show a *pseudo* octahedral Zr(IV) centre with *fac-fac* binding of the two ligand sets. For the chloro- and bromo- complexes, Zr(**1**/**2**)$_2$, the ligands bind to the metal centre so that the halophenoxy groups approach in a *trans* configuration. For the iodo form, Zr(**3**)$_2$, other configurations were observed. Complexation of **3**H_2 under the same conditions as Zr(**1**/**2**)$_2$ (hexane, 70 °C, 24 hrs) afforded the *trans* relationship in solution as the major product; though no crystals were acquired the $^1H/^{13}C\{^1H\}$ spectra were directly comparable to that of Zr(**1**/**2**)$_2$ (See ESI, Figure SI16). A minor product (~20%) was also formed under these conditions and this is likely to be another unsymmetrical structural isomer similar to the *cis* form. When the complexation was carried out in CH_2Cl_2, the isolated product was still the *trans* isomer for Zr(**1**/**2**)$_2$; with **3**H_2, however, the *cis* form was observed in the solid state and in solution (Scheme 3.).

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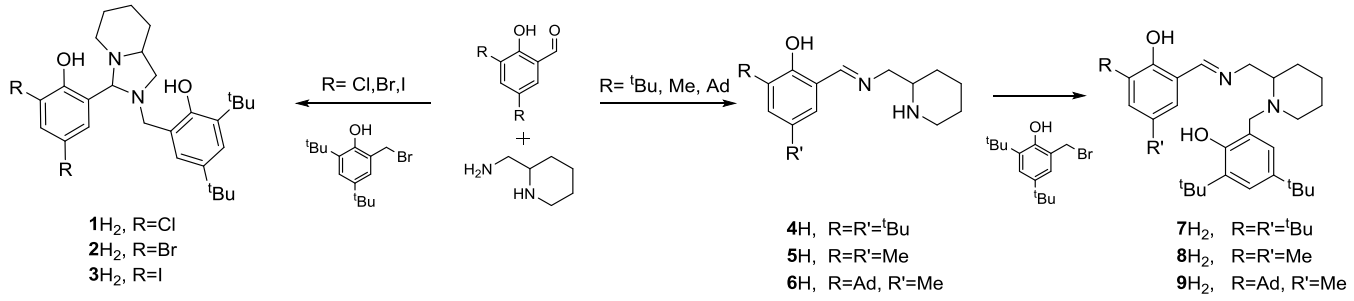
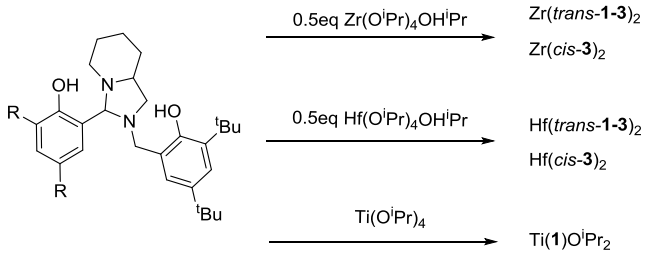


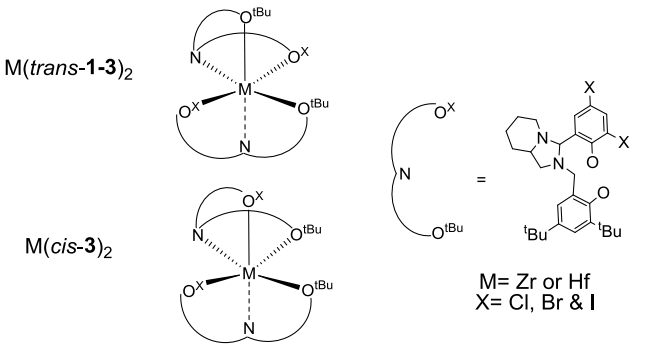
Scheme 1: Preparation of **1**-**3**H_2 salans, **4**-**6**H half salalen and **7**-**9**H_2 salalen ligands used in this study.



Scheme 2: Zr, Hf and Ti(IV) complexes of **1-3**H_2

These bonding motifs observed in the solid state structures are also corroborated in solution by ^{1}H NMR spectroscopic analysis; Zr(*trans*-**1-3**)$_2$ has four discrete aromatic resonances indicating the respective phenolate groups of both ligands are chemically identical. However, for Zr(*cis*-**3**)$_2$ there are 8 such resonances which is in line with the solid state structure whereby each phenolate group sits *trans* to a different group.

Hafnium complexes of **1-3**H_2 were also prepared and similar to the Zr(IV) complexes, the bis ligand octahedral complexes were preferentially formed with a *fac-fac* arrangement being observed. The iodo form, Hf(**3**)$_2$ was again observed to adopt more coordination isomers relative to Hf(**1/2**)$_2$. In this case, both the *cis* and *trans* arrangements were formed in hexane and separated through sequential recrystallisations. The *cis* form was supported by X-ray crystallography and the *trans* form was comparable to Hf(**1/2**)$_2$ by ^{1}H/^{13}C{^{1}H} NMR spectroscopy. Hf(*trans*-**3**)$_2$ was isolated with a small amount (~12%) of another unsymmetrical isomer in an analogous fashion to Zr(*trans*-**3**)$_2$ and Hf(*cis*-**3**)$_2$ contained Hf(*trans*-**3**)$_2$ (~20%) and this second unsymmetrical isomer (~10%). DOSY NMR spectroscopy was carried out on Hf(*cis*-**3**)$_2$ revealing a similar diffusion rate for the *trans* and *cis* form (See ESI, Figure SI23).



Scheme 3: Octahedral isomers observed for M(**1-3**)$_2$ (M= Zr/Hf)

Addition of Ti(IV) to the chloro ligand, **1**H_2, afforded the mono ligand-isopropoxide complex with five coordination around the smaller metal centre.

Complexation of the salan and salalen ligands to aluminium gives rise to two distinct coordination geometries (Scheme 4, Figure 2); Al(**1-3**)Me exhibit a tetrahedral Al(III) centre as the piperidine nitrogen is too far removed from the metal to bind. Conversely, the position of the imine backbone allows for interaction of the nitrogen with the metal centre in Al(**7-9**)Me giving rise to a trigonal bipyramidal arrangement as indicated by the angles N(1)-Al(1)-O(2) and O(1)-Al(1)-N(2) of 167.7(2)° and 120.6(2)° respectively. Al(**7**)Me was found to be in a monoclinic $P2_1/n$ space group whereas Al(**1**)Me and Al(**8**)Me were found to be triclinic *P*-1.

Table 1: Selected bond lengths (Å) and angles (°) for group 4 complexes Zr/Hf(**1-3**)$_2$

	Zr(1)$_2$	**Zr(2$_2$)**	**Zr(*cis*-3)$_2$**	**Hf(1)$_2$**	**Hf(*cis*-3)$_2$**
M-OAr$_x$	2.026(3)	2.026(3)	2.026(4)	2.024(2)	2.037(3)
M-OAr$_{tBu}$	1.976(4)	1.972(3)	1.960(4)	1.988(2)	1.956(3)
M-N	2.467(4)	2.469(4)	2.445(4)	2.455(2)	2.435(3)
Ar$_x$ -Ar$_{tBu}$	4.08/4.06	4.08	4.07/3.81	4.23 /3.99	4.00/3.83
Ar$_{tBu}$O-M-OAr$_{tBu}$	91.62(13)	92.78(14)	104.25(16)	89.47(7)	103.94(11)
Ar$_x$O-M-OAr$_x$	137.54(14)	137.51(14)	107.46(15)	137.84(8)	104.19(10)
Ar$_x$O-M- OAr$_{tBu}$	108.76(14)	108.54(14)	144.93(16)	107.69(8)	147.98(11)
Ar$_x$O-M- OAr$_{tBu}$	109.25(14)	108.72(14)	94.50(15)	108.52(8)	96.35(11)
Ar$_x$O -M-N	77.05(14)	77.19(14)	171.43(15)	77.55(7)	175.12(10)
Ar$_x$O -M-N'	77.18(14)	76.99(14)	78.77(15)	76.73(7)	77.58(10)
Ar$_{tBu}$O -M-N	168.60(14)	169.87(15)	173.33(15)	168.39(7)	173.17(10)
Ar$_{tBu}$O -M-N'	168.88(14)	170.00(14)	79.30(15)	166.81(8)	80.00(10)

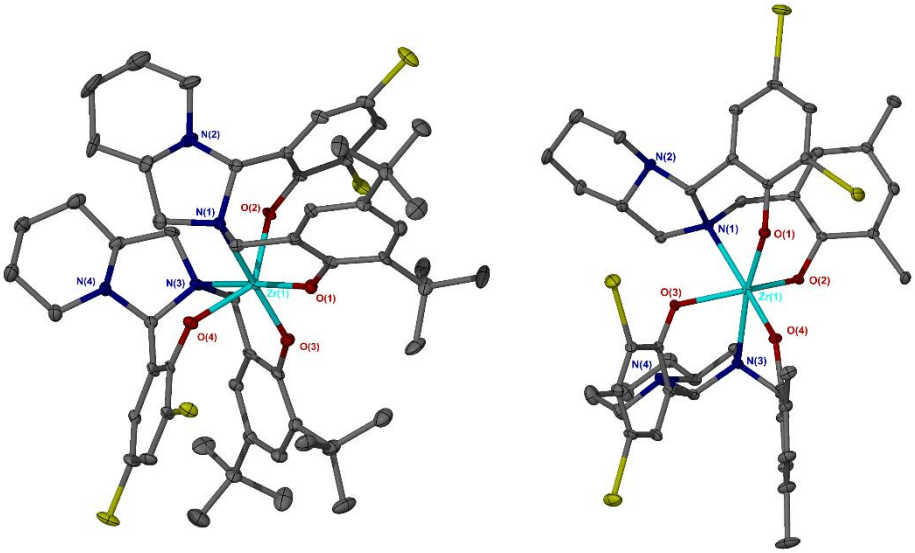


Figure 1: The solid state structures of Zr(*trans*-**1**)$_2$ (left) and Zr(*cis*-**3**)$_2$ (right). Ellipsoids are shown at the 30 % probability level, hydrogen atoms removed for clarity

Solution state NMR investigation of Al(**7-9**)Me revealed two distinct aluminium methyl species in solution for each complex; DOSY NMR of Al(**7**)Me indicated that these two species have analogous diffusion coefficients (5.69×10^{-10} m^2 s^{-1}) and VT-NMR (298K-353K, d_8-tol) of Al(**7**)Me suggested there was no interchange between species (see ESI, Figure SI33), this was similar for Al(**8**)Me. Crude NMR spectra of the complexation showed that these two species are formed in almost equal quantities during the course of the reaction. Purification with hexane (recrystallisation or washing) allowed for selective isolation or enrichment of one form over the other based on their solubility (Figure 3). Elemental analysis of these complexes conforms to the expected formula.

It is suggested, therefore, that these two species are diastereoisomeric forms as a consequence of the inherent stereochemistry in the ligand backbone and the new chiral centre formed on complexation of the amine nitrogen to the aluminium centre. For polymerisations, these complexes were used as a mixture of these different species rather than isolated diastereomers.

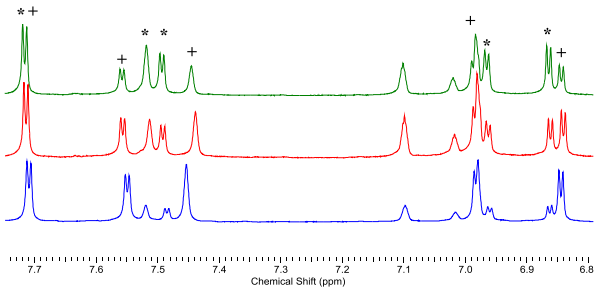
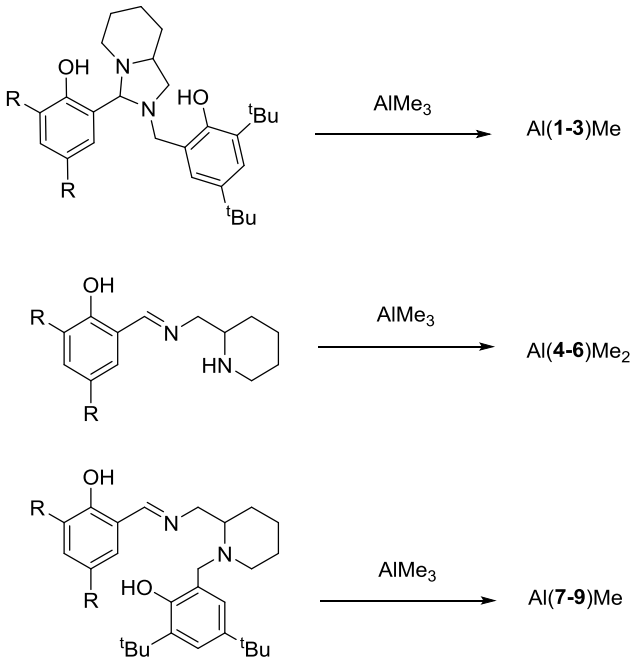


Figure 3: ^{1}H NMR of Al(**7**)Me (d_8-tol) showing two isomers (*,+) at differing compositions. The green spectra shows the * isomer to be the major form and the blue spectra has the + isomer as the main form. For the red spectra, both forms exist in equal quantities.

The monophenolate imine ligands **4-6**H were successfully complexed to aluminium to give well defined trigonal bipyramidal structures as demonstrated by a combination of NMR spectroscopy and X-ray crystallography. Complexation of the amine nitrogen is confirmed by the observation of sharp, discrete resonances for the piperidine CH_2 groups indicating the "*locking*" of this ring in solution.



Scheme 4: Al(III) complexes of **1-3**H$_2$, **4-6**H and **7-9**H$_2$

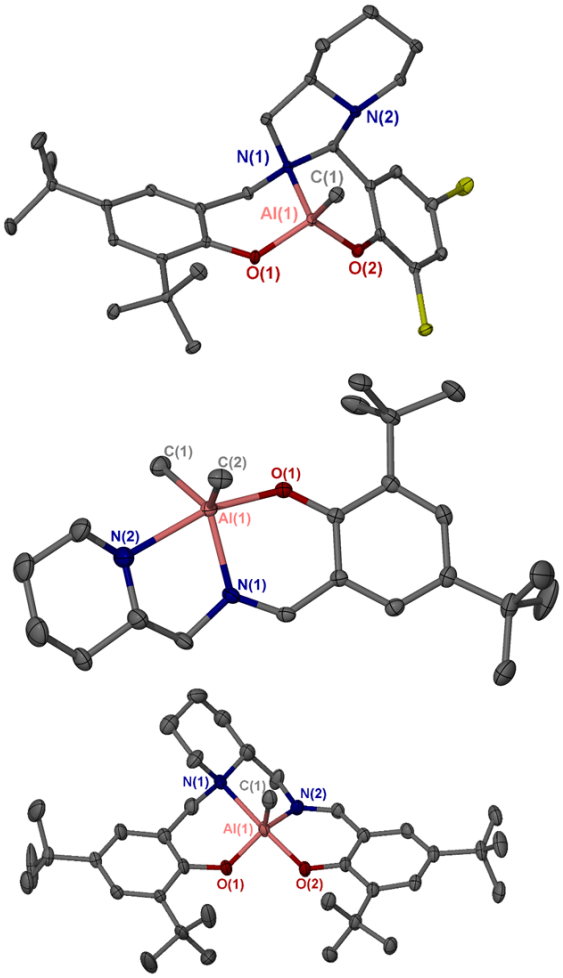


Figure 2: The solid state of Al(**1**)Me (top), Al(**4**)Me_2 (middle) and Al(**7**)Me (bottom) Ellipsoids are shown at the 30 % probability level, hydrogen atoms removed for clarity

Polymerisation

The catalytic activity of these initiators was demonstrated in the ring opening polymerisation (ROP) of *rac*-LA. In most cases, recrystallised monomer was used to make the study more comparable to industrially relevant conditions. As the Zr(IV) and Hf(IV) complexes had no suitable initiating group, benzyl alcohol was added as the co-initiator. This requirement was demonstrated by a polymerisation without alcohol for Zr(**1**)$_2$ in which there was only trace amount of polymer formed. This approach was also taken for the aluminium methyl complexes to generate the active alkoxide *in situ*.

For the halo-zirconium complexes, Zr(**1-3**)$_2$, PLA of reasonable molecular weights and narrow molecular weight distributions were synthesized after 24 hours (Table 2, entries 1, 4,6-7). All initiators demonstrated moderate heterotactic bias, being most pronounced for the Zr(**1/2**)$_2$ complexes (P_r = 0.76). Interestingly, the iodo-complex, Zr(*trans*-**3**)$_2$, had reduced stereocontrol and this could be related to the shift in geometry that was observed in the solid and solution state.

Table 2: Polymerisation data for *rac*-lactide with Group 4 initiators.

Entry	Initiator	Time /h	Conv. %[f]	P_r[h]	M_n[i]	PDI[i]
1	Zr(**1**)$_2$[a]	24	93	0.76	16050	1.05
2	Zr(**1**)$_2$[b]	16	89	0.76	8850	1.05
3	Zr(**1**)$_2$[c]	3	96	0.42	29900	1.06
4	Zr(**1**)$_2$[a,d]	24	94	0.76	14400	1.07
5	Zr(**1**)$_2$[a,e]	8	29	-	2000	1.06
6	Zr(**2**)$_2$[a]	24	81	0.76	14900	1.04
7	Zr(*cis*-**3**)$_2$[a]	24	95	0.66	15400	1.11
8	Hf(**1**)$_2$[a]	24	55	0.76	13350	1.04
9	Hf(**1**)$_2$[a,d]	24	72	0.74	11750	1.04
10	Hf(**2**)$_2$[a]	24	35	0.74	6500	1.04
11	Hf(*trans*-**3**)$_2$ [a]	24	31	0.69	6850	1.05
12	Hf(*cis*-**3**)$_2$ [a]	24	28	0.67	7100	1.04
13	Hf(*cis*-**3**)$_2$ [a]	48	55	0.70	10200	1.04
14	Ti(**1**)(O^iPr)$_2$[f]	0.5	67	0.50	20800	1.04

[a] Conditions: [LA]:[I]:[BnOH]=100:1:1, 80 °C, toluene [b] Conditions: [LA]:[I]:[BnOH]=100:1:2, 80 °C, toluene. [c] Conditions: [LA]:[I]:[BnOH]=300:1:1, 130 °C, solvent free [d] Sublimed *rac*-LA. [e] L-LA. [f] Conditions: [LA]:[I]=300:1, 130 °C, solvent free. [g] Determined *via* ^{1}H NMR spectroscopy. [h] P_r is the probability of heterotactic enchainment, determined *via* homonuclear decoupled ^{1}H NMR spectroscopy. [i] Determined from GPC (in THF) referenced against polystyrene standards.

Further investigation into the solution polymerisation of Zr(**1**)$_2$ demonstrated the controlled character of the reaction with a linear increase of polymer molecular weight with conversion (Figure 4). Furthermore, the reaction also follows first order kinetics as shown by the linear relationship of $\ln([LA]_0/[LA]_t)$ against time (Tol, 80 °C, $[LA]_0$ = 0.694 moldm^{-3}, k_{app} = 0.11 hr^{-1}, see ESI Figure SI39). Similar kinetic experiments were carried out using Zr(**2**)$_2$, which revealed similar trends in the polymerisation as for Zr(**1**)$_2$ (See ESI, Figure SI40-41). The apparent rate constant for polymerisation was lower (k_{app} = 0.069 hr^{-1}).

Analysis by MALDI-ToF mass spectrometry of polymer obtained *via* Zr(**1**)$_2$ confirms the benzyl alcohol end group as well as revealing evidence of transesterification with the main series having a separation of 72 g mol^{-1} (See ESI Figure SI51), although the narrow dispersity is indicative of a well-controlled polymerisation.

To show further the heterotactic nature of the polymerisation with Zr(**1**)$_2$, an experiment was performed with *L*-LA (Table 2, Entry 5). As expected for a heterotactic initiator, the conversion is lower with the single enantiomer due to the preference to insert alternating *L*- and *D*- monomers (cf. an 8 hr polymerisation with *rac*-LA achieved 69 % conversion, Figure 4). A melt polymerisation was also carried out for Zr(**1**)$_2$, with BnOH, demonstrating good conversion and relatively higher molecular weights after 3 hours (Table 2, entry 3). The stereocontrol of this initiator under these conditions is switched to give very slight isotacticity.

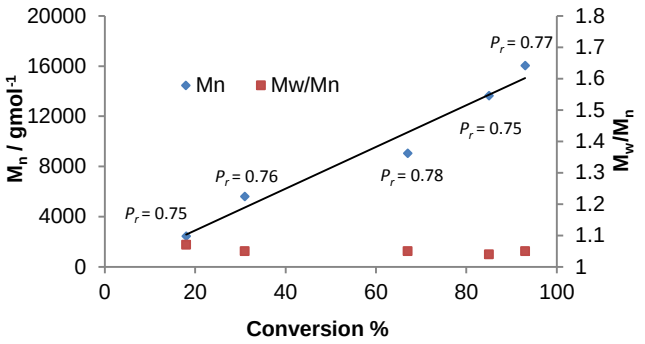


Figure 4: M_n and M_w/M_n against conversion for solution polymerisation of Zr(**1**)$_2$. Linear regression gave the equation of the line at y = 166× – 417 (R^2 = 0.96)

For these series of initiators, it is proposed that the ROP proceeds *via* an activated monomer mechanism;[13] coordination of the lactide carbonyl to the M(IV) centre facilitates attack from the free benzyl alcohol to give a zwitterionic intermediate which collapses into a dilactyl unit, (see ESI Figure SI56). This is not necessarily the case for the bulk polymerisation where yellow discolouration was observed. This could be an indication of increased ligand dissociation and a shift to a classical coordination-insertion mechanism, hence a different stereochemistry observed in the isolated PLA.

The polymerisations performed with the hafnium initiators, Hf(**1**-**3**)$_2$, generally showed poorer conversion compared to the analogous zirconium complexes (Table 2, entries 8, 10-13). Selectivity was, however, found to be almost identical with good control over molecular weight being maintained. These observations of reduced conversion were supported by kinetic data for Hf(**1**)$_2$; a plot of molecular weight against conversion shows slight deviation from linearity and the first order plot reveals a much reduced rate (k_{app} = 0.031 hr^{-1}, see ESI Figure SI42-43). Performing the same polymerisation with increased purity of lactide, i.e. sublimed, showed an increase in conversion with Hf(**1**)$_2$ suggesting this initiator is more susceptible to impurities in the monomer (Table 2, entries 8 vs 9) than Zr(**1**)$_2$ (Table 2, entries 1 vs 4) which maintained its high conversion and narrow dispersity.

Melt polymerisation of Ti(**1**)(O^{i}Pr)$_2$ at 130 °C showed relatively high conversion in a shorter time frame with good control over molecular weight however, there was no stereochemical preference exhibited by this initiator (Table 2, entry 14).

The polymerisation of *rac*-LA with the bicyclic complexes Al(**1**-**3**)Me revealed similar activity and control as the corresponding zirconium complexes with the absence of major stereochemical preference (Table 3, entries 1-3).

Table 3: Polymerisation data for *rac*-LA with Aluminium based initiators

Entry	Initiator	Time /h	Conv. %[a]	P_r[b]	M_n[c]	PDI[c]
1	Al(**1**)Me	24	72	0.51	15900	1.04
2	Al(**2**)Me	24	72	0.54	17700	1.04
3	Al(**3**)Me	24	85	0.56	21850	1.05
4	Al(**4**)Me$_2$	24	91	0.69	15300	1.07
5	Al(**5**)Me$_2$	24	96	0.68	20100	1.27
6	Al(**6**)Me$_2$	24	72	0.39	14550	1.05
7	Al(**7**)Me	240	88	0.37	22700	1.06
8	Al(**8**)Me	120	42	0.62	8000	1.07
9	Al(**8**)Me	240	88	0.56	20500	1.08
10	Al(**9**)Me	240	89	0.68	19350	1.05

Conditions: [LA]:[I]:[BnOH]=100:1:1, 80 °C, toluene [a] Determined *via* ^{1}H NMR spectroscopy. [b] P_r is the probability of heterotactic enchainment, determined *via* homonuclear decoupled ^{1}H NMR spectroscopy. [c] Determined from GPC (in THF) referenced against polystyrene standards.

The half salalen complexes, Al(**4/5**)Me$_2$ showed an increased tendency to give heterotactic PLA with a P_r value of 0.69/0.68 with good conversion after 24 hours but the ortho-methyl complex had less control as evidenced by an increased PDI of 1.27. This is contrasted by the adamantyl half salalen complex Al(**6**)Me$_2$ which saw a switch to slight isotacticity (P_r = 0.39) with a reduced activity. These observations are undoubtedly related to the steric contribution at the ortho aryl position; the ortho methyl group of Al(**5**)Me$_2$ contributes less steric control over the metal centre whereas the bulkier adamantly group hinders the polymerisation but gives more control.

Representative kinetic data for this initiator series was recorded for the Al(**4**)Me$_2$ complex (See ESI, Figure SI44-45). A good correlation was observed between molecular weight and conversion and further information on initiator activity is provided by the apparent rate constant (k_{app} = 0.096 hr^{-1}).

The full salalen form of the ^{t}Bu ligand, Al(**7**)Me, also imparted some stereocontrol over the polymerisation (Table 3, entry 7). Isotactic preference was observed (P_r = 0.37) however the conversion was comparatively lower than the other initiators utilised in this study. For the ortho methyl and adamantly imino complexes, Al(**8-9**)Me, a similar reduced conversion is observed; stereochemically these complexes tend towards heterotactic PLA with the adamantyl complex yielding the greatest enchainment (P_r = 0.68).

The contrasting activity of these initiators compared to the previous entries is likely due to steric crowding of the aluminium centre. Unlike the halo complexes, Al(**1**-**3**)Me, which have lower tetrahedral Al coordination, Al(**7**-**9**)Me have a trigonal bipyramidal aluminium centre and generally bulkier groups in the ortho aryl position. The variation of stereocontrol for these initiators is also interesting; introduction of the second phenolate generally causes a switch in stereoselective bias and the ^{t}Bu and Ad groups always demonstrate the opposite stereocontrol (Table 3, entries 4/7 vs 6/10).

Analysis, by MALDI, of PLA derived from Al(**2/7**)Me and Al(**4**)Me_2 shows the expected benzyl alcohol end group (See ESI Figures SI52-54). Both the *tert*-butyl phenolate complexes, Al(**4**)Me_2 and Al(**7**)Me indicate a degree of transesterification having a minor series with a separation of 72 g mol^{-1}. These observations are likely related to the reduction in steric bulk around the metal and the extended reaction time for the mono- and bisphenolate respectively. Minimal transesterification is evidenced for the halo bicyclic complex Al(**2**)Me, with the main series having a peak separation of 144 g mol^{-1}.

It is noted that there is a similarity of the bicyclic ligand motif seen for **1**-**3**H_2 with the organocatalyst DBU. As DBU is known to be active for the ROP of *rac*-LA,[14] a brief study was carried out to ensure the activity observed is solely due to the metal initiator and there is no contribution due to ligand. Polymerisation with **1**H_2 and **7**H_2 in the melt (130 °C, [LA]:[I]:[BnOH]=100:1:1) afforded reasonable conversion after 24 hours with slight isotacticity (P_r = 0.4), however the polymers are brown in color. In both cases, the molecular weight, M_n, was around 10,000 Da, by GPC, with a relatively broad molecular weight distribution (M_w/M_n ~1.35). Analysis of the MALDI of this PLA showed a major series with a 144 g mol^{-1} separation (see ESI Figure SI55), the broad molecular weight in this case is most likely to arise from a slower rate of initiation compared to propagation. The solution polymerisation (toluene, 80 °C, [LA]:[I]:[BnOH]=100:1:1) of **1**H_2 did not produce polymer after 24 hours. Therefore it is highly unlikely that the activity of our metal complexes is related to ligand disassociation and can be assumed to arise from the metal complex.

Conclusions

A range of ligands have been prepared based on 2-(aminomethyl)piperidine and coordinated to a range of metals. From similar starting materials, two distinct ligand classes were realized offering diverse coordination chemistry when applied to zirconium, hafnium, titanium and aluminium; the bicyclic ligand form, **1**-**3**H_2, preferentially formed octahedral complexes M(**1**-**3**)$_2$ with hafnium and zirconium and tetrahedral mononuclear species were realised with aluminium. Monophenolate, **4**-**6**H, and bisphenolate, **7**-**9**H_2, imine based ligands yielded 5-coordinate aluminium complexes.

These complexes were tested for the ROP of *rac*-LA with good molecular weight control demonstrated by all initiators. The Zr(IV) and Hf(IV) initiators showed a heterotactic bias (P_r = 0.66-0.76) whereas Ti(**1**)(O^iPr)$_2$ produced atactic PLA. The aluminium imino complexes Al(**4**-**9**)Me_x (x=1,2) gave a greater range of tacticities with Al(**4**-**5**)Me_2 and Al(**9**)Me yielding heterotactic PLA (P_r = 0.68-0.69); Al(**6**)Me_2 and Al(**7**)Me preferentially formed PLA with a slight isotactic bias (P_r = 0.38-0.39). We are further investigating other bis-ligated complexes for the controlled ROP of lactide and other cyclic esters.

Experimental

Materials and methods

General Experimental. The preparation and characterisation of all metal complexes was carried out under inert argon atmosphere using standard Schlenk or glovebox techniques. All chemicals used were purchased from Aldrich and used as received except for *rac*-LA which was recrystallised from dry toluene and Ti(O^iPr)$_4$ which was vacuum distilled before use. 3,5-di-tert-butyl-2-hydroxybenzylbromide, 3,5-dimethylsalicylaldehyde and 3-(1-adamantyl)-5-methylsalicylaldehyde were prepared *via* literature methods.[15] Dry solvents used in handling metal complexes were obtained *via* SPS (solvent purification system). ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual solvent peaks. $CDCl_3$ was dried over CaH_2 prior to use with metal complexes. Coupling constants are given in Hertz. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University. MALDI ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionized using NaOAc.

Crystallography. All data were collected on a SuperNova, EOS detector diffractometer using radiation CuKα (λ= 1.54184 Å) or Mo-Kα (λ= 0.71073 Å) or a Nonius kappa diffractometer using Mo-Kα (λ= 0.71073 Å) all recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealized positions and refined using the riding model, all refinement details are given in the .cif file.

General Polymerisation Procedure. Polymerisations were carried out in a Young's ampoule under inert argon conditions. For a typical solution based polymerisations, *rac*-lactide (1.0 g, 0.69 mmol) was dissolved in toluene (10 ml) with required amount of initiator ([M]:[I] 100:1); When required, a benzyl alcohol co-initiator (typically [I]:[BnOH] 1:1, 7.2 µl) was added. The ampoule was then placed in an oil bath (80 °C) for the set time. After polymerisation, solvent was removed *in vacuo* and a crude ^{1}H NMR recorded. The polymer was then purified by washing with methanol to remove initiator and unreacted monomer. For solvent free polymerisations, a higher initiator ratio was employed (300:1) and the reaction performed at 130 °C. After polymerisation, the product was dissolved in CH_2Cl_2 which was then removed *in vacuo* and a crude ^{1}H NMR recorded. The polymer was then purified in the same fashion as for solution polymerisations.

All purified polymers were characterised by a combination of gel permeation chromatography (GPC) and homonuclear decoupled ^{1}H NMR spectroscopy. GPC was carried out at 1 ml min^{-1} at 35 °C with a THF eluent and referenced against polystyrene standards (RI). Tacticity was determined *via* ^{1}H NMR spectroscopy ($CDCl_3$) analysis of the homonuclear decoupled methine region utilizing the relationships demonstrated by Coates *et al*.[5b]

Ligand synthesis

Synthesis of 3,5-dihalosalicylaldehyde/2-(aminomethyl)piperidine based salans (1-3H$_2$). 2-(Aminomethyl)piperidine (1 ml, 8.24 mmol) was added dropwise to a solution of 3,5-dihalosalicylaldehyde (8.24 mmol) in methanol (50 ml). After stirring for 30 minutes, solvent was removed and the resultant yellow/orange solid washed with cold methanol to yield precursor ligand. Two products observed at a ratio of 2:1 (^{1}H NMR). Without further purification, the precursor ligand (5.23 mmol) was dissolved in THF (50 ml) and 3,5-di-tert-butyl-2-hydroxybenzylbromide (1.55 g, 5.23 mmol) was added. Triethylamine (2eq, 1 ml, 10.4 mmol) was added dropwise and the solution heated to reflux (70 °C) and stirred for 3 hours. The suspension was removed *via* filtration and the resultant supernatant reduced *in vacuo* to afford an orange oil from which a colored solid was precipitated from methanol.

1H$_2$:

Isolated as a pale yellow powder (2.23 g, 4.41 mmol, 84 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 11.83 (s, 1H; ArOH), 9.40 (s, 1H; ArOH), 7.22 (d, *J* = 2.5 Hz, 1H; ArH), 7.18 (d, *J*=2.5 Hz, 1H; ArH), 6.78 (d, *J* = 2.5 Hz, 1H; ArH), 6.45 (d, *J* = 2.5 Hz, 1H; ArH), 4.00 (s, 1H; Ar*C*HN_2), 3.93 (d, *J* = 13.0 Hz, 1H; ArCH_2), 3.87 (d, *J* = 13.0 Hz, 1H; ArCH_2), 3.08 (dd, *J* = 10.5, 6.5 Hz, 1H; CH_2), 3.00 (t, *J* = 10.0 Hz, 1H; CH_2), 2.89 (br d, *J* = 11.0 Hz, 1H; CH_2), 2.61 (m, 1H; CH), 2.15 (dt, *J* = 11.5, 3.0 Hz, 1H; CH_2), 1.93 (m, 2H; CH_2), 1.76 (m, 1H; CH_2), 1.64 (m, 1H; CH_2), 1.37 (m, 2H CH_2), 1.44 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ= 153.7, 152.4, 140.7, 135.7, 130.2, 129.0, 123.4, 123.1, 122.7, 122.7,121.7, 120.7, (Ar), 87.9 (ArCHN_2), 61.2 (N*C*H$(CH_2)_2$), 58.5, 57.2, 48.7 (CH_2), 34.7, 34.1 (*C*$(CH_3)_3$), 31.6, 29.5 (C(*C*$H_3)_3$), 28.6, 24.7, 23.3 (CH_2). ESI-MS (MeOH): Calcd *m/z* $[C_{28}H_{39}N_2O_2Cl_2]^+$=505.2366, found *m/z* = 505.2389.

2H$_2$:

Isolated as a yellow powder (2.02 g, 3.39 mmol, 65 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 12.00 (s, 1H; ArOH), 9.40 (s, 1H; ArOH), 7.49 (d, *J* = 2.5 Hz, 1H; ArH), 7.18 (d, *J* = 2.5 Hz, 1H; ArH), 6.75 (d, *J* = 2.5 Hz, 1H; ArH), 6.58 (d, *J* = 2.5 Hz, 1H; ArH), 3.97 (s, 1H; Ar*C*HN_2), 3.91 (d, *J* = 13.5 Hz, 1H; ArCH_2), 3.86 (d, *J* = 13.5 Hz, 1H; ArCH_2), 3.08 (dd, *J* = 10.5 Hz, 6.5 Hz, 1H; CH_2), 2.99 (t, *J* = 10.5 Hz, 1H; CH_2), 2.88 (br d, *J* = 10.5 Hz, 1H; CH_2), 2.61 (m, 1H; CH), 2.15 (dt, *J* = 12.0, 3.0 Hz, 1H; CH_2), 1.92 (m, 2H; CH_2), 1.76 (m, 1H; CH_2), 1.63 (m, 1H; CH_2), 1.37 (m, 2H; CH_2), 1.29 (s, 9H; $C(CH_3)_3$), 1.28 (s, 9H; $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 153.8, 153.7, 140.7, 135.7, 135.6, 132.5, 123.6, 123.1, 122.7, 120.7, 111.3, 110.4 (Ar), 87.8 (ArCHN_2), 61.2 (N*C*H$(CH_2)_2$), 58.6, 57.3, 48.7 (CH_2), 34.8, 34.1 (*C*$(CH_3)_3$), 31.7, 28.6 (C(*C*$H_3)_3$), 28.6, 24.7, 23.4 (CH_2). ESI-MS (MeOH): Calcd *m/z*$[C_{28}H_{39}N_2O_2Br_2]^+$ =593.1378, found *m/z* = 593.1391.

3H$_2$:

Isolated as a yellow powder (2.56 g, 3.71 mmol, 71%). ^{1}H NMR ($CDCl_3$, 400MHz) δ= 12.17 (s, 1H; ArOH), 9.45 (s, 1H; ArOH), 7.85 (d, *J* = 2.0 Hz, 1H; ArH), 7.19 (d, *J* = 2.5 Hz, 1H; ArH), 6.75 (d, *J* = 2.0 Hz, 1H; ArH), 6.73 (d, *J* = 2.5 Hz, 1H; ArH), 3.90 (s, 1H; Ar*C*HN_2), 3.89 (d, *J* = 13.0 Hz, 1H; ArCH_2), 3.85 (d, *J* = 13.0 Hz, 1H; ArCH_2), 3.08 (dd, *J* = 10.0, 7.0 Hz, 1H; CH_2), 2.99 (t, *J* = 10.5 Hz, 1H; CH_2), 2.88 (br d, *J* = 11.0 Hz, 1H; CH_2), 2.61 (m, 1H; CH), 2.14 (dt, *J* = 3.0, 12.0 Hz, 1H; CH_2), 1.92 (m, 2H; CH_2), 1.76 (m, 1H; CH_2), 1.63 (m, 1H; CH_2), 1.37 (m, 2H CH_2), 1.29 (s, 9H; $C(CH_3)_3$), 1.28 (s, 9H; $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ= 156.9, 153.7, 146.7, 140.6, 139.4, 135.6, 123.6, 122.8, 122.7, 120.7, 86.4, 80.7 (Ar), 87.6 (ArCHN_2), 61.1 (N*C*H$(CH_2)_2$), 58.6, 57.3, 48.7 (CH_2), 34.8, 34.1 (*C*$(CH_3)_3$), 31.7, 29.5 (C(*C*$H_3)_3$), 28.6, 24.7, 23.4 (CH_2). ESI-MS(MeOH): Calcd *m/z* $[C_{28}H_{39}N_2O_2I_2]^+$ =689.1101, found *m/z* = 689.1082.

Synthesis of 3,5-dialkylsalicylaldehyde/2-aminopiperidine based half salalens (4-6H). 2-(Aminomethyl)piperidine (1.0 ml, 8.24 mmol) was added dropwise to a solution of 3,5-dialkylsalicylaldehyde (8.24 mmol) in methanol (50 ml). After stirring for 1 hour, solvent was removed to afford an orange oil. Two products were observed with a ratio dependent on aryl substituents (^{1}H NMR). Note: For aluminium complexations, the condensation was carried out in a Schlenk tube on a 2 mmol scale and was used directly after drying *in vacuo.* Reaction of 3-(1-adamantyl)-5-methyl-2-salicylaldehyde was performed on 2.7 mmol scale.

4H:

Isolated as an orange oil (99% unpurified yield, 9:1 imine:cyclic product). Major product (Imine): ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 13.63 (s, 1H; ArOH), 8.36 (s, 1H; ArCHN), 7.37 (d, *J* = 2.4 Hz, 1H; ArH), 7.07 (d, *J* = 2.5 Hz, 1H; ArH), 3.68 (ddd, *J* = 12.0, 4.5, 1.5 Hz, 1H; NC*H*$_2$CH), 3.39 (dd, *J* = 12.0, 8.0 Hz, 1H; NC*H*$_2$CH), 3.09 (m, 1H CH_2), 2.84 (m, 1H; CH), 2.65 (m, 1H; CH_2), 1.83 (m, 1H; CH_2), 1.74 (m, 1H; C*H*$_2$) 1.63 (m, 1H; CH_2), 1.44 (s, 9H; $C(CH_3)_3$), 1.34 (m, 2H; CH_2), 1.29 (s, 9H; $C(CH_3)_3$), 1.23 (m, 1H; CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ= 167.3 (Ar*C*HN), 157.9, 140.1, 136.6, 126.9, 125.9, 117.7 (Ar), 66.2 (CH_2), 56.6 (N*C*H$(CH_2)_2$), 46.8 (CH_2), 35.0, 34.0 (*C*$(CH_3)_3$), 31.4 (C(*C*$H_3)_3$), 30.7 (CH_2), 29.4 (C(*C*$H_3)_3$), 26.2, 24.5 (CH_2). Minor product (Cyclic): ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 11.60 (s, 1H; ArOH), 7.24 (d, *J* = 2.5 Hz, 1H; ArH), 6.93 (d, *J* = 2.5 Hz, 1H; ArH), 4.16 (s, 1H; Ar*C*HN_2), 3.21(dd, *J* = 9.5, 7.0 Hz, 1H; NC*H*$_2$CH), 2.96 (m, 2H; CH_2), 2.84 (m, 1H; CH_2), 2.43 (m, 1H; CH), 2.06 (m, 2H; CH_2), 1.95 (m, 2H; CH_2), 1.87 (m, 1H; CH_2), 1.40 (s, 9H; $C(CH_3)_3$), 1.26 (s, 9H; $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ= 153.9, 140.3, 136.1, 124.9, 124.0, 120.5 (Ar), 84.0 (Ar*C*HN_2), 63.5 (N*C*H$(CH_2)_2$), 50.5, 48.4 (CH_2), 35.0, 34.0 (*C*$(CH_3)_3$), 31.6, 29.5 (C(*C*$H_3)_3$), 29.0, 24.8, 23.8 (CH_2). ESI-MS(MeOH): Calcd *m/z* $[C_{21}H_{34}N_2ONa]^+$ = 353.2569, found *m/z* = 353.2551

5H:

Isolated as an orange oil (98 % unpurified yield, 3:1 imine:cyclic product). Major product (Imine): ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 13.26 (s, 1H; ArOH), 8.24 (s, 1H; ArCHN) 6.97 (s, 1H; ArH), 6.83 (s, 1H; ArH), 3.61 (ddd, *J* = 12.0, 4.5, 1.5 Hz, 1H; NC*H*$_2$CH), 3.36 (ddd, *J* = 12.0, 8.0, 1.0 Hz, 1H; NC*H*$_2$CH), 3.01 (br d, *J* = 12.0 Hz, 1H; CH), 2.79 (m, 1H; CH_2), 2.59 (d t, *J* = 12.0, 3.0 Hz, 1H; CH_2), 2.22 (s, 6H; 2×CH_3), 1.79 (m, 1H; CH_2), 1.68 (m, 1H; CH_2), 1.58 (m, 1H; CH_2), 1.37 (m, 2H; CH_2), 1.19 (m, 1H; CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ= 166.4 (Ar*C*HN), 157.0, 134.4, 129.0, 127.2, 125.6, 117.6 (Ar), 66.1 (CH_2), 56.7 (N*C*H$(CH_2)_2$), 46.8, 30.7, 26.2, 24.5 (CH_2), 20.3, 15.4 (CH_3) Minor product (Cyclic): ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 11.44 (s, 1H; ArOH), 6.85 (s, 1H; ArH), 6.68 (s, 1H; ArH), 4.09 (s, 1H; Ar*C*HN_2), 3.14 (dd, *J* = 9.0, 6.5 Hz, 1H; CH_2), 2.88 (m, 2H; CH_2), 2.18 (s, 3H; CH_3), 2.16 (s, 3H; CH_3), 2.00

(dd, *J* = 12.0, 3.0 Hz, 1H; CH_2), 1.90 (m, 1H; CH_2), 1.79 (m, 1H; CH_2), 1.68 (m, 1H; CH_2), 1.58 (m, 1H; CH_2), 1.37 (m, 2H; CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 131.7, 128.1 (Ar), 83.1 (Ar*C*HN_2), 63.6 (N*C*H$(CH_2)_2$), 50.4, 48.5, 29.1, 25.0, 23.8 (CH_2), 20.3, 15.6 (CH_3). ESI-MS (MeOH): Calcd *m/z* $[C_{15}H_{23}N_2O_2]^+$ =247.1810, found *m/z* = 247.1807.

6H:

Isolated as a yellow powder (0.92 g, 2.5 mmol, 93 %, 9:1 imine:cyclic product). Major product (Imine): ^1H NMR ($CDCl_3$, 400 MHz) δ= 13.60 (s, 1H; ArOH), 8.33 (s, 1H; ArCHN), 7.08 (d, *J* = 2.0 Hz, 1H; ArH), 6.90 (d, *J* = 1.5 Hz, 1H; ArH), 3.70 (dd, *J* = 12.0, 4.5 Hz, 1H; CH_2), 3.42 (m, 1H; CH_2), 3.08 (br d, *J* = 11.5 Hz, 1H; CH), 2.90 (m, 1H; CH_2), 2.67 (td, *J* = 12.0, 3.0 Hz, 1H; CH_2), 2.28 (s, 3H; CH_3), 2.24 (t, *J* = 3.4 Hz, 1H; CH_2), 2.18 (br s, 6H; $CH_{2\ Ad}$), 2.09 (br s, 4H; CH_2/$CH_{\ ad}$), 1.83 (m, 1H; CH_2), 1.78 (br s, 8H; CH_2/$CH_{2\ ad}$), 1.68 (m, 1H; CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 167.3 (Ar*C*HN), 158.3, 137.4, 130.6, 129.5, 126.8, 118.3 (Ar), 66.0 (CH_2), 56.6 (N*C*H$(CH_2)_2$), 46.7 (CH_2), 40.3, 37.1 ($CH_{2\ Ad}$), 36.9 ($C_{\ ad}$), 30.5 (CH_2), 29.1 ($CH_{\ ad}$), 25.9, 24.4 (CH_2), 20.7 (CH_3). ESI-MS (MeOH): Calcd *m/z* $[C_{24}H_{34}N_2O_1Na]^+$= 389.2569, found *m/z* = 389.2572.

Synthesis of 3,5-dialkylsalicylaldehyde/2-aminopiperidine based full salalens (7-9H_2). Without purification, the isolated half salalen (**4**-**6**H) was dissolved in THF (50ml) and 3,5-di-tert-butyl-2-hydroxybenzylbromide (2.45 g, 8.24 mmol) was added. Triethylamine (2eq, 2.3 ml, 16.4 mmol) was added dropwise and the solution heated to reflux (70 °C) and stirred for 3 hours. The suspension was filtered and the resultant supernatant reduced *in vacuo* to afford an orange oil from which the product was isolated *via* recrystallisation from methanol. Note: Reaction of 3-(1-adamantyl)-5-methyl-2-salicyladehyde adduct was carried out on 2 mmol scale.

7H_2:

Isolated as a yellow powder (2.85 g, 5.18 mmol, 63%). ^1H NMR ($CDCl_3$, 400 MHz) δ= 13.51 (s, 1H; ArOH), 11.10 (s, 1H; ArOH), 8.29 (s, 1H; ArCHN), 7.39 (d, *J* = 2.5 Hz, 1H; ArH), 7.20 (d, *J* = 2.5 Hz, 1H; ArH), 7.04 (d, *J* = 2.5 Hz, 1H; ArH), 6.86 (d, *J* = 2.5 Hz, 1H; ArH), 4.27 (br s, 1H; N*C*H$(CH_2)_2$), 3.97 (dd, *J* = 12.5, 3.5 Hz, 1H; NCH_2), 3.74 (dd, *J* = 12.5, 7.0 Hz, 1H; NCH_2), 3.56 (m, 1H; CH_2), 2.87 (m, 1H; CH), 2.78 (m, 1H; CH_2), 2.33 (br s, 1H; CH_2), 1.72 (br m, 6H; CH_2), 1.46 (s, 9H; $C(CH_3)_3$), 1.37 (s, 9H; $C(CH_3)_3$), 1.31 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 167.3 (Ar*C*HN), 157.9, 154.4, 140.3, 140.0, 136.6, 135.5, 127.0, 126.0, 123.1, 122.6, 121.1, 117.8 (Ar), 58.5 (CH_2), 56.7 (N*C*H$(CH_2)_2$), 35.0, 34.8, 34.11, 34.09 (*C*$(CH_3)_3$), 31.7, 31.5, 29.5, 29.4 (C(*C*$H_3)_3$), 20.0 (CH_2). ESI-MS (MeOH): Calcd *m/z* $[C_{36}H_{56}N_2O_2\,Na]^+$ = 571.4240, found *m/z* = 571.4230.

8H_2:

Isolated as a yellow powder (2.62 g, 5.67 mmol, 69%). ^1H NMR ($CDCl_3$, 400 MHz) δ= 13.19 (s, 1H; ArOH), 11.07 (br s, 1H; ArOH), 8.23 (s, 1H; ArCHN), 7.19 (d, *J* = 2.5 Hz, 1H; ArH), 7.01 (s, 1H; ArH), 6.86 (d, *J* = 2.5 Hz, 1H; ArH), 6.84 (d, *J* = 2.5 Hz, 1H; ArH), 4.26 (br s, 1H; N*C*H$(CH_2)_2$), 3.99 (dd, *J* = 12.5, 4.0 Hz, 1H; $ArCH_2$), 3.71 (dd, *J* = 12.2, 7.2 Hz, 1H; $ArCH_2$), 3.56 (br s, 1H; CH_2), 2.86 (m, 2H; CH_2), 2.25 (s, 6H; 2×CH_3), 2.22 (m, 1H; CH_2), 1.84 (m, 1H; CH_2), 1.62 (m, 5H; CH_2), 1.37 (s, 9H; $C(CH_3)_3$), 1.28 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 166.4 (Ar*C*HN), 156.9, 154.4, 140.4, 135.5, 134.3, 129.0, 127.1, 125.6, 123.1, 122.7, 121.1, 117.7 (Ar), 58.5 (CH_2), 56.7 (N*C*H$(CH_2)_2$), 34.8, 34.1 (*C*$(CH_3)_3$), 31.7, 29.5 (C(*C*$H_3)_3$), 25.0 (CH_2), 20.3, 15.4 (CH_3). ESI-MS (MeOH): Calcd *m/z* $[C_{30}H_{44}N_2O_2\,Na]^+$ = 487.3301, found *m/z* = 487.3332.

9H_2:

Isolated as a yellow powder (1.02 g, 1.74 mmol, 87 %). ^1H NMR ($CDCl_3$, 400 MHz) δ= 13.45 (s, 1H; ArOH), 11.15 (br s, 1H; ArOH), 8.24 (s, 1H; ArCHN), 7.20 (d, *J* = 2.2 Hz, 1H; ArH), 7.07 (d, *J* = 2.0 Hz, 1H; ArH), 6.86 (d, *J* = 1.5 Hz, 1H; ArH), 6.84 (d, *J* = 2.5 Hz, 1H; ArH), 4.26 (br s, 1H; N*C*H$(CH_2)_2$), 3.98 (br d, *J* = 13.0 Hz, 1H; $ArCH_2$), 3.69 (dd, *J* = 13.0, 7.5 Hz, 1H; $ArCH_2$), 2.93 (m, 2H; CH_2), 2.28 (s, 3H; CH_3), 2.18 (br s, 7H; $CH_{2\ Ad}$), 2.08 (br s, 4H; CH_2/$CH_{\ ad}$), 1.80 (m, 10H; CH_2/$CH_{2\ ad}$), 1.64 (m, 2H; CH_2), 1.39 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 167.1 (Ar*C*HN), 158.2, 154.4, 140.3, 137.4, 135.5, 130.5, 129.5, 126.7, 123.2, 122.6, 121.1, 118.3 (Ar), 58.5 (CH_2), 56.7 (N*C*H$(CH_2)_2$), 40.2, 37.1 ($CH_{2\ ad}$), 34.8, 34.1 (*C*$(CH_3)_3$), 31.7 ($CH_{\ ad}$), 29.5, 29.1 (C(*C*$H_3)_3$), 25.0 (CH_2), 20.6 (CH_3). ESI-MS (MeOH): Calcd *m/z* $[C_{30}H_{45}N_2O_2]^+$ = 585.4420, found *m/z* = 585.4562.

Complex synthesis

Synthesis of Zirconium complexes Zr(*trans*-1-3)$_2$. $Zr(O^iPr)_4OH^iPr$ (0.388 g, 1 mmol) was dissolved in hexane (10 ml) and ligand **1**-**3**H_2 (2 mmol) was added. The solution was heated to reflux (70 °C) for 24 hours before purification by filtration or crystallization.

Zr(1)$_2$:

Product precipitated from solution during complexation and collected *via* filtration as a white powder (0.857 g, 0.78 mmol, 78 %). Crystals isolated from hexane/CH_2Cl_2 mixture. ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.11 (d, *J* = 2.5 Hz, 2H; ArH), 7.08 (d, *J* = 2.5 Hz, 2H; ArH), 7.04 (d, *J* = 2.5 Hz, 2H; ArH), 6.06 (d, *J* = 2.5 Hz, 1H; ArH), 5.19 (d, *J* = 12.0 Hz, 2H; Ar*C*H_2N), 3.83 (t, *J* = 11.5 Hz, 2H; CH_2), 3.60(d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.56 (s, 2H; Ar*C*HN_2) 3.12 (dd, *J* = 12.0 ,5.0 Hz, 2H; CH_2), 2.48 (br d, *J* = 10.5 Hz, 2H; CH), 2.37 (m, 2H; CH_2), 1.82 (m, 4H; CH_2), 1.74 (m, 2H; CH_2), 1.62 (m, 2H; CH_2), 1.53 (m, 3H; CH_2), 1.35 (s, 18H; $C(CH_3)_3$), 1.29 (m, 3H; CH_2), 1.18 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.0, 153.1, 141.6, 136.0, 129.1, 128.4, 125.6, 124.6, 124.6, 124.2, 124.2, 121.5 (Ar), 92.3 ($ArCHN_2$), 62.9, 61.9 (CH_2), 60.1 (N*C*H$(CH_2)_2$), 49.5 (CH_2), 34.9, 34.2 (*C*$(CH_3)_3$), 31.8, 30.1 (C(*C*$H_3)_3$), 27.3, 24.5, 23.4 (CH_2). Elemental analysis ($C_{56}H_{72}Cl_4N_4O_4Zr_1$) Calcd in %: C, 61.24; H, 6.61; N, 5.10. Found: C, 61.16; H, 6.70; N, 5.13.

Zr(2)$_2$:

Product precipitated from solution during complexation and collected *via* filtration as a white powder (1.06 g, 0.82 mmol, 82 %). Crystals isolated from hexane. ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.39 (d, *J* = 2.5 Hz, 2H; ArH), 7.09 (d, *J* = 2.5 Hz, 2H; ArH), 7.03 (d, *J* = 2.5 Hz, 2H; ArH), 6.22 (d, *J* = 2.5 Hz, 1H; ArH), 5.27 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.80 (t, *J* = 11.5 Hz, 2H; CH_2), 3.60 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.54 (s, 2H; $ArCHN_2$) 3.11 (dd, *J* = 12.0, 5.0 Hz, 2H; CH_2), 2.46 (br d, *J* = 10.5 Hz, 2H; CH), 2.36 (m, 2H; CH_2), 1.81 (m, 4H; CH_2), 1.72 (m, 2H; CH_2), 1.62 (m, 2H; CH_2), 1.51 (m, 3H;

CH_2), 1.36 (s, 18H; $C(CH_3)_3$), 1.30 (m, 3H; CH_2), 1.17 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.0, 154.4, 141.6, 136.0, 134.5, 131.9, 126.0, 124.6, 124.3, 124.1, 115.4, 108.7 (Ar), 93.2 ($ArCHN_2$), 63.0, 62.0 (CH_2), 60.9 ($NCH(CH_2)_2$), 49.5 (CH_2), 34.9, 34.2 ($C(CH_3)_3$), 31.9, 30.3 ($C(CH_3)_3$)), 27.3, 24.5, 23.4 (CH_2). Elemental analysis ($C_{56}H_{72}Br_4N_4O_4Zr_1$) Calcd in %: C, 52.71; H, 5.69; N, 4.39. Found: C, 52.64; H, 5.56; N, 4.51.

Zr(trans-3)$_2$:

Product precipitated from solution during complexation and collected *via* filtration as a white powder (0.96 g, 0.66 mmol, 66%). ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.75 (d, *J* = 2.0 Hz, 2H; ArH), 7.10 (d, *J* = 2.5 Hz, 2H; ArH), 7.02 (d, *J* = 2.5 Hz, 2H; ArH), 6.39 (d, *J* = 2.0 Hz, 2H; ArH), 5.47 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.75 (t, *J* = 12.0 Hz, 2H; CH_2), 3.57 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.47 (s, 2H; $ArCHN_2$), 3.08 (dd, *J* = 12.0, 5.0 Hz; 2H; CH_2), 2.40 (br d, *J* = 10.5, 2H; CH), 2.34 (m, 2H; CH_2), 1.80 (m, 4H; CH_2), 1.69 (m, 3H; CH_2), 1.58 (m, 3H; CH_2), 1.51 (m, 4H; CH_2), 1.37 (s, 18H; $C(CH_3)_3$), 1.18 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.5, 157.0, 145.6, 141.5, 138.9, 136.0, 125.6, 124.7, 124.3, 124.0, 93.1 (Ar), 92.4 ($ArCHN_2$), 78.6 (Ar), 63.4, 62.0 (CH_2), 60.9 ($NCH(CH_2)_2$), 49.5 (CH_2), 35.0, 34.3 ($C(CH_3)_3$), 32.0, 30.5 ($C(CH_3)_3$), 27.2, 24.5, 23.4 (CH_2). Elemental analysis ($C_{56}H_{72}I_4N_4O_4Zr_1$) Calcd in %: C, 45.94; H, 4.96; N, 3.83. Found: C, 45.99; H, 5.07; N, 3.71.

Zr(cis-3)$_2$:

$Zr(O^iPr)_4OH^iPr$ (0.388 g, 1 mmol) was dissolved in CH_2Cl_2 (10 ml) and ligand **3**H_2 (1.38g, 2 mmol) was added. After 3 hours, solvent was removed *in* vacuo and product recrystallised from hot hexane mixture as colourless crystals (0.144 g, 0.10 mmol, 10 %). ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.74 (d, *J* = 2.0 Hz, 1H; ArH), 7.66 (d, *J* = 2.0 Hz, 1H; ArH), 7.60 (d, *J* = 2.0 Hz, 1H; ArH), 7.14 (d, *J* = 2.0 Hz, 1H; ArH), 7.06 (d, *J* = 2.0 Hz, 1H; ArH), 6.98 (d, *J* = 2.0 Hz, 1H; ArH), 6.54 (d, *J* = 2.0 Hz, 1H; ArH), 6.15 (d, *J* = 2.0 Hz, 1H; ArH), 5.47 (s, 1H; $ArCHN_2$), 5.21 (d, *J* = 12.0 Hz, 1H; $ArCH_2N$), 4.90 (dd, *J* = 9.5, 8.0 Hz, 1H; CH_2), 4.02 (d, *J* = 14.0 Hz, 1H; $ArCH_2N$), 3.78 (t, *J* = 11.5 Hz, 1H; CH_2), 3.65 (dd, *J* = 12.0, 6.0 Hz, 2H; CH_2), 3.59 (s, 1H; $ArCHN_2$), 3.33 (br d, *J* = 10.5 Hz, 1H; CH_2), 3.15 (dd, *J* = 12.0, 6.0 Hz, 1H; CH_2), 2.70 (br q, *J* = 8.0 Hz, 1H; CH), 2.41 (m, 3H; CH/CH_2), 2.27 (m, 1H; CH_2), 1.85 (m, 8H; CH_2), 1.63 (m, 1H; CH_2), 1.46 (s, 9H; $C(CH_3)_3$), 1.37 (s, 9H; $C(CH_3)_3$), 1.31 (m, 4H; CH_2), 1.23 (s, 9H; $C(CH_3)_3$), 1.21 (s, 9H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 161.2, 158.0, 156.0, 155.9, 146.2, 145.8, 141.8, 140.2, 138.9, 136.3, 135.4, 135.0, 125.7, 125.3, 124.7, 124.1, 124.0, 123.8, 123.7, 122.8, 92.7 (Ar), 92.6 ($ArCHN_2$), 87.8 (Ar), 82.1 ($ArCHN_2$), 80.8, 78.3 (Ar), 63.9 ($NCH(CH_2)_2$), 63.3, 63.2, 63.1, 61.2 (CH_2), 60.7 ($NCH(CH_2)_2$), 50.5, 48.7 (CH_2), 34.8, 34.7, 34.3, 34.0 ($C(CH_3)_3$), 32.0, 31.6, 30.3, 30.2 ($C(CH_3)_3$), 29.7, 28.0, 25.0, 24.7, 24.2, 23.5 (CH_2). Elemental analysis ($C_{56}H_{72}I_4N_4O_4Zr_1$) Calcd in %: C, 45.94; H, 4.96; N, 3.83. Found: C, 45.85; H, 5.01; N, 3.84.

Synthesis of Hafnium complexes Hf(1-3)$_2$:

$Hf(O^iPr)_4OH^iPr$ (0.415 g, 1 mmol) was dissolved in hexane (10 ml) and ligand **1**-**3**H_2 (2 mmol) was added. The solution was heated to reflux (70°C) for 24 hours before purification by recrystallisation.

Hf(1)$_2$:

Recrystallised from hexane/CH_2Cl_2/toluene mixture as colourless crystals. (0.875 g, 0.738 mmol, 74 %). ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.12 (d, *J* = 2.5 Hz, 2H; ArH), 7.11 (d, *J* = 2.5 Hz, 2H; ArH), 7.02 (d, *J* = 2.5 Hz, 2H; ArH), 6.05 (d, *J* = 2.5 Hz, 2H; ArH), 5.26 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.84 (t, *J* = 12.0 Hz, 2H; CH_2), 3.64 (s, 2H; $ArCHN_2$), 3.59 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.13 (dd, *J* = 12.5, 5.0 Hz, 2H; CH_2), 2.49 (br d, *J* = 10.5 Hz, 2H; CH), 2.37 (m, 2H; CH_2), 1.83 (m, 4H; CH_2), 1.74 (m, 2H; CH_2), 1.63 (m, 2H; CH_2), 1.54 (m, 3H; CH_2), 1.35(s, 18H; $C(CH_3)_3$), 1.31 (m, 3H; CH_2), 1.19 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.2, 153.2, 141.3, 136.6, 129.0, 128.2, 125.5, 125.2, 124.5, 124.2, 123.9, 121.5 (Ar), 92.4 ($ArCHN_2$), 63.1, 62.1 (CH_2) 60.9 ($NCH(CH_2)_2$), 49.5 (CH_2), 34.8, 34.1 ($C(CH_3)_3$), 31.8, 30.1 ($C(CH_3)_3$), 27.2, 24.5, 23.3 (CH_2). Elemental analysis ($C_{56}H_{72}Cl_4N_4O_4Hf_1$) Calcd in %: C, 56.74; H, 6.12; N, 4.73. Found: C, 56.59; H, 6.27; N, 4.62. Note: CH_2Cl_2 present in the crystal unit cell and ^1H NMR spectra.

Hf(2)$_2$:

Recrystallised from hexane/CH_2Cl_2 mixture as colourless crystals. (0.481 g, 0.353 mmol, 35 %). ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.42 (d, *J* = 2.5 Hz, 2H; ArH), 7.12 (d, *J* = 2.5 Hz, 2H; ArH), 7.03 (d, *J* = 2.5 Hz, 2H; ArH), 6.22 (d, *J* = 2.5 Hz, 2H; ArH), 5.34 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.82 (t, *J* = 11.5 Hz, 2H; CH_2), 3.62 (s, 2H; $ArCHN_2$), 3.58 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.13 (dd, *J* = 12.0, 4.5 Hz; 2H; CH_2), 2.46 (br d, *J* = 10.0 Hz, 2H; CH), 2.37 (m, 2H; CH_2), 1.83 (m, 4H; CH_2), 1.72 (m, 2H; CH_2), 1.63 (m, 2H; CH_2), 1.54 (m, 3H; CH_2), 1.36(s, 18H; $C(CH_3)_3$), 1.31 (m, 3H; CH_2), 1.19 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.3, 154.6, 141.3, 136.7, 134.5, 131.8, 125.9, 124.5, 124.2, 124.0, 116.0, 108.7 (Ar), 92.4 ($ArCHN_2$), 63.2, 62.1 (CH_2), 60.9 ($NCH(CH_2)_2$), 49.5 (CH_2), 34.9, 34.2 ($C(CH_3)_3$), 31.9, 30.2 ($C(CH_3)_3$), 27.2, 24.5, 23.4 (CH_2). Elemental analysis ($C_{56}H_{72}Br_4N_4O_4Hf_1$) Calcd in %: C, 49.34; H, 5.32; N, 4.11. Found: C, 49.59; H, 5.49; N, 4.09. Note: CH_2Cl_2 present in the crystal unit cell and ^1H NMR spectra.

Hf(trans-3)$_2$:

First recrystallisation from hexane/CH_2Cl_2 mixture yield isomer as colourless crystals. (0.293g, 0.189 mmol, 19 %). ^1H NMR ($CDCl_3$, 400 MHz), δ= 7.77 (d, *J* = 2.0 Hz, 2H; ArH), 7.11 (d, *J* = 2.5 Hz, 2H; ArH), 7.02 (d, *J*=2.5 Hz, 2H; ArH), 6.39 (d, *J* = 2.0 Hz, 2H; ArH), 5.53 (d, *J* = 12.0 Hz, 2H; $ArCH_2N$), 3.78 (t, *J* = 11.5 Hz, 2H; CH_2), 3.58 (m, 4H; $ArCHN_2/ArCH_2N$), 3.10 (dd, *J* = 12.5, 5.0 Hz; 2H; CH_2), 2.46 (br d, *J* = 10.5 Hz, 2H; CH), 2.34 (m, 3H; CH_2), 1.81 (m, 5H; CH_2), 1.70 (m, 2H; CH_2), 1.61 (m, 2H; CH_2), 1.52 (m, 2H; CH_2), 1.37 (s, 18H; $C(CH_3)_3$), 1.31 (m, 2H; CH_2), 1.18 (s, 18H; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 157.6, 157.2, 145.6, 141.2, 138.8, 136.6, 125.5, 124.5, 124.1, 124.0, 93.6, 78.6 (Ar), 92.5 ($ArCHN_2$), 63.5, 62.2 (CH_2), 60.8 ($NCH(CH_2)_2$), 49.5 (CH_2), 34.9, 34.2 ($C(CH_3)_3$), 32.2, 30.4 ($C(CH_3)_3$), 27.1, 24.5, 23.3 (CH_2). Elemental analysis ($C_{56}H_{72}I_4N_4O_4Hf_1$) Calcd in %: C, 43.36; H, 4.68; N, 3.61. Found: C, 43.24; H, 4.74; N, 3.55.

Hf(cis-3)$_2$:

Second recrystallisation from hexane/CH_2Cl_2 mixture as colourless crystals (0.429 g, 0.277 mmol, 28 %). ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.75 (d, *J* = 2.0 Hz, 1H; ArH), 7.66 (d, *J* = 2.0 Hz, 1H; ArH), 7.58 (d, *J* = 2.0 Hz, 1H; ArH), 7.15 (d, *J* = 2.5 Hz, 1H; ArH), 7.07 (d, *J* = 2.5 Hz, 1H; ArH), 6.97 (d, *J* = 2.5 Hz, 1H; ArH), 6.53 (d, *J* = 2.0 Hz, 1H; ArH), 6.15 (d, *J* = 2.5 Hz, 1H; ArH), 5.50 (s, 1H; $ArCHN_2$), 5.28 (d, *J* = 12.0 Hz, 1H; $ArCH_2N$), 4.96 (dd, *J* = 10.0, 8.0 Hz, 1H; CH_2), 4.07 (d, *J* = 14.0 Hz, 1H; $ArCH_2N$), 3.76 (m, 2H; CH_2),

3.67 (s, 1H; ArCHN_2), 3.64 (d, *J* = 12.5 Hz, 1H; CH_2), 3.34 (br d, *J* = 11.0 Hz, 1H; CH_2), 3.16 (dd, *J* = 12.0, 6.0 Hz, 1H; CH_2), 2.70 (br q, *J* = 8.0 Hz, 1H; CH), 2.40 (m, 3H; CH/CH_2), 2.28 (m, 1H; CH_2), 1.92 (br d, *J* = 12.0 Hz, 1H; CH_2), 1.82 (m, 7H; CH_2), 1.63 (m, 2H; CH_2), 1.45 (s, 9H; C(CH_3)$_3$), 1.37 (s, 9H; C(CH_3)$_3$), 1.22 (s, 9H; C(CH_3)$_3$), 1.21 (s, 9H; C(CH_3)$_3$), 1.19 (m, 3H; CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ= 161.7, 158.1, 156.4, 155.9, 146.2, 145.8, 141.4, 140.1, 138.8, 136.8, 136.1, 134.9, 125.5, 125.3, 124.7, 124.1, 124.0, 123.7, 123.4, 122.6, 93.2 (Ar), 92.7 (ArCHN_2), 88.5 (Ar), 82.0 (ArCHN_2), 80.6, 78.4 (Ar), 63.9 (N*C*H(CH_2)$_2$), 63.5, 63.4, 63.3, 61.4 (CH_2), 60.6 (N*C*H(CH_2)$_2$), 50.6, 48.7 (CH_2), 34.8, 34.7, 34.2, 33.9 (*C*(CH_3)$_3$), 32.1, 31.6, 30.2, 30.18 (C(*C*H_3)$_3$). 29.7, 28.0, 25.0, 24.7, 24.2, 23.5 (CH_2). Elemental analysis ($C_{56}H_{72}I_4N_4O_4Hf_1$) Calcd in %: C, 43.36; H, 4.68; N, 3.61. Found: C, 43.24; H, 4.75; N, 3.62.

Synthesis of Titanium complex Ti(1)(O^{i}Pr)$_2$:

Ti(O^{i}Pr)$_4$ (0.30 ml, 1 mmol) was added to ligand, **1**H_2 (0.504 g, 1 mmol) in toluene (10ml). After 1 hour, solvent was removed *in vacuo* and complex recrystallised from hexane to yield yellow crystals (0.353g, 0.523 mmol, 53%). ^1H NMR ($CDCl_3$, 400 MHz), δ=7.31 (d, *J* = 2.4 Hz, 1H; ArH), 7.21 (d, *J* = 2.4 Hz, 1H; ArH), 7.17 (d, *J* = 2.4 Hz, 1H; ArH), 6.85 (d, *J* = 2.3 Hz, 1H; ArH), 5.09 (2×sept, *J* = 6.1 Hz, 2H; (CH_3)$_2$*CH*), 4.66 (s, 1H; ArC*H*N_2), 3.43 (dd, *J* = 10.1 Hz, 7.0 Hz, 1H; CH_2), 3.37 (br d, *J* = 10.4, 1H; CH_2), 3.26 (d, *J* = 12.7 Hz, 1H; ArC*H*$_2$N), 3.14 (d, *J* = 12.7 Hz, 1H; ArC*H*$_2$N), 2.39 (t, *J* = 10.6 Hz, 1H; CH_2), 2.30 (br q, *J* = 9.8 Hz, 1H; CH_2), 1.91 (m, 2H; CH_2), 1.78 (m, 3H; CH_2), 1.47 (s, 9H; C(CH_3)$_3$), 1.45 (d, *J*= 4.6 Hz, 3H; (C*H*$_3$)$_2$CH), 1.44 (d, *J* = 4.8 Hz, 3H; (C*H*$_3$)$_2$CH), 1.37 (m, 2H; CH_2), 1.25 (m (s, 2xd), 15H; C(CH_3)$_3$/(C*H*$_3$)$_2$CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz,) δ= 158.8, 158.5, 141.7, 135.4, 128.9, 126.7, 125.0, 124.6, 124.5, 123.1, 123.0, 121.8 (Ar), 81.8, 80.8, 79.7 (CH), 65.3 (CH_2) 57.2 (CH), 55.5, 51.5 (CH_2), 34.9, 34.2 (*C*(CH_3)$_3$), 31.6, 29.7 (C(*C*H_3)$_3$), 29.2 (CH_2), 26.3, 26.1, 25.94, 25.91 (CH_3), 24.7, 24.4 (CH_2). Elemental analysis ($C_{34}H_{50}Cl_2N_2O_4Ti_1$) Calcd in %: C, 60.99; H, 7.53; N, 4.18. Found: C, 60.88; H, 7.68; N, 4.26.

Synthesis of bisphenolate Aluminium complexes, Al(1-3)Me: $AlMe_3$ (2M, 0.5 ml, 1 mmol) was added dropwise to a solution of **1**-**3**H_2 (1 mmol) in toluene (10 ml) at 40 °C. After complete addition, the solution was then heated to 80 °C and complexation allowed for 3 hours. Solvent was then removed *in vacuo* and the product recrystallised from hexane.

Al(1)Me:

Isolated as colorless crystals (0.160 g, 0.29 mmol, 29 %). ^1H NMR (d_8-tol, 400MHz), δ= 7.48 (d, *J* = 2.5 Hz, 1H; ArH), 7.31 (d, *J* = 2.5 Hz, 1H; ArH), 6.73 (d, *J* = 2.5 Hz, 1H; ArH), 6.58 (d, *J* = 2.5 Hz, 1H; ArH), 3.40 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 2.97 (s, 1H; ArCHN_2), 2.71 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 2.55 (dd, *J* = 11.0, 8.0 Hz, 1H; NC*H*$_2$CH), 2.19 (br d, *J* = 10.5 Hz, 1H; NCH_2C*H*'), 2.05 (dd, *J* = 11.0, 9.5 Hz, 1H; CH_2), 1.60 (s, 9H; C(CH_3)$_3$), 1.41 (s, 9H; C(CH_3)$_3$), 1.29 (m, 3H; CH_2), 1.04 (m, 5H; CH_2), -0.39 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR (d_8-tol, 100MHz) δ= 155.9, 154.2, 139.7, 138.8, 131.7, 129.8, 126.8, 125.1, 123.9, 121.5, 121.0, 120.6, (Ar), 90.8 (ArCHN_2), 61.3 (N*C*H(CH_2)$_2$), 57.1, 55.4, 48.3 (CH_2) 35.4, 34.3 (*C*(CH_3)$_3$), 32.0, 30.1 (C(*C*H_3)$_3$), 28.0, 24.4, 24.1 (CH_2), -12.4 (AlMe). Elemental analysis ($C_{29}H_{39}Cl_2N_2O_2Al_1$) Cald in %: C, 63.85; H, 7.21; N, 5.14. Found: C, 63.77; H, 7.31; N, 5.07. Note: ArH ^{13}C resonance obscured by d_8-toluene.

Al(2)Me:

Isolated as colorless crystals (0.362 g, 0.57 mmol, 57%). ^1H NMR (d_8-tol, 400 MHz), δ= 7.66 (d, *J* = 2.5 Hz, 1H; ArH), 7.48 (d, *J* = 2.5 Hz, 1H; ArH), 6.76 (d, *J* = 2.5 Hz, 1H; ArH), 6.73 (d, *J* = 2.5 Hz, 1H; ArH), 3.38 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 2.94 (s, 1H; ArCHN_2), 2.67 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 2.55 (dd, *J* = 11.0, 8.0 Hz, 1H; NC*H*$_2$CH'), 2.18 (br d, *J* = 10.0 Hz, 1H; NCH_2C*H*'), 2.04 (dd, *J* = 11.0, 9.5 Hz, 1H; CH_2), 1.60 (s, 9H; C(CH_3)$_3$), 1.42 (s, 9H; C(CH_3)$_3$), 1.28 (m, 3H; CH_2), 1.04 (m, 4H; CH_2), 0.81 (m, 1H; CH_2), -0.38 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR (d_8-tol, 100 MHz) δ= 156.0, 155.5, 139.7, 138.8, 137.3, 133.4, 125.1, 123.9, 120.99, 120.95, 117.3, 108.6, (Ar), 90.8 (ArCHN_2), 61.3 (N*C*H(CH_2)$_2$), 57.1, 55.4, 48.3 (CH_2), 35.4, 34.3 (*C*(CH_3)$_3$), 32.1, 30.1 (C(*C*H_3)$_3$), 28.0, 24.4, 24.1 (CH_2), -12.4 (AlMe). Note: ArH ^{13}C resonance obscured by d_8-toluene. Elemental analysis ($C_{29}H_{39}Br_2N_2O_2Al_1$) Cald in %: C, 54.90; H, 6.20; N, 4.42. Found: C, 54.78; H, 6.33; N, 4.33.

Al(3)Me:

Isolated as colorless crystals (0.517 g, 0.71 mmol, 71%). ^1H NMR (d_8-tol, 400 MHz), δ=8.11 (d, *J* = 2.0 Hz, 1H; ArH), 7.50 (d, *J* = 2.2 Hz, 1H; ArH), 6.97 (d, *J* = 2.0 Hz, 1H; ArH), 6.73 (d, *J* = 2.5 Hz, 1H; ArH), 3.34 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 2.87 (s, 1H; ArCHN_2), 2.59 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 2.51 (dd, *J* = 11.0, 8.0 Hz, 1H; NC*H*$_2$CH'), 2.16 (br d, *J* = 10.5 Hz, 1H; NCH_2C*H*'), 2.02 (dd, *J* = 11.0, 9.5 Hz, 1H; CH_2), 1.61 (s, 9H; C(CH_3)$_3$), 1.42 (s, 9H; C(CH_3)$_3$), 1.25 (m, 3H; CH_2), 1.05 (m, 4H; CH_2), 0.78 (m, 1H; CH_2), -0.38 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR (d_8-tol, 100 MHz) δ= 158.2, 155.9, 148.5, 140.4, 139.6, 138.7, 125.1, 123.9, 121.0, 120.3, 94.3 (Ar) 90.6 (ArCHN_2), 78.3 (Ar), 61.2 (N*C*H(CH_2)$_2$), 56.9, 55.2, 48.3 (CH_2), 28.0, 24.3, 24.1 (CH_2), 35.4, 34.3 (*C*(CH_3)$_3$), 32.1, 30.1 (C(*C*H_3)$_3$), -13.1 (AlMe). Note: ArH $^{13}C/^1H$ resonance obscured by d_8-toluene. Elemental analysis ($C_{29}H_{39}I_2N_2O_2Al_1$) Calcd in %: C, 47.82; H, 5.40; N, 3.85. Found: C, 47.96; H, 5.37; N, 3.67.

Synthesis of monophenolate Aluminium complexes, Al(4-6)Me$_2$: $AlMe_3$ (2M, 1 ml, 2 mmol) was added to a solution of **4**-**6**H (2 mmol) in toluene (10 ml). After complete addition, the solution was stirred for 1 hour before purification *via* filtration or recrystallisation.

Al(4)Me$_2$:

Product precipitated from solution during complexation and collected by filtration as a yellow solid (0.557g, 1.44 mmol, 72%). Crystals isolated from a hot toluene/hexane mixture. ^1H NMR (400 MHz, d_8-tol) δ= 7.64 (d, *J* = 2.5 Hz, 1H; ArH), 7.41 (s, 1H;ArCHN), 6.81 (d, *J* = 2.5 Hz, 1H; ArH), 2.78 (br d, *J* = 13.5 Hz, 1H; CH_2), 2.48 (m, 2H; CH_2), 2.25 (m, 2H; CH/CH_2), 1.68 (s, 9H C(CH_3)$_3$), 1.39 (m, 1H; CH_2),1.37 (s, 9H C(CH_3)$_3$), 1.21 (br d, *J* = 13.0 Hz, 1H; CH_2), 1.11 (br dd, *J* = 13.5, 3.0 Hz, 1H; CH_2), 0.98 (t q, *J* = 13.0, 4.0 Hz, 1H; CH_2), 0.77 (q t, *J* = 13.0, 4.0 Hz, 1H; CH_2), 0.55 (d t, *J* = 12.0, 3.0 Hz, 1H; NH), 0.34 (q d, *J* = 13.0, 4.0 Hz, 1H; CH_2) -0.37 (s, 3H; AlMe), -0.50 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR (d_8-tol, 100 MHz) δ= 172.0 (Ar*C*HN), 165.8, 141.0, 136.1, 131.1, 127.7 117.6 (Ar), 62.7 (CH_2), 54.4 (N*C*H(CH_2)$_2$), 44.6 (CH_2), 35.6, 34.1 (*C*(CH_3)$_3$), 31.6, 29.7 (C(*C*H_3)$_3$), 26.5, 23.4 (CH_2), -6.8, -9.4 (AlMe). Note: ArH ^{13}C resonance obscured by d_8-toluene. Elemental analysis ($C_{23}H_{39}AlN_2O$) Calcd in %: C, 71.46; H, 10.17; N, 7.25. Found: C, 71.35; H, 10.29; N, 7.24.

Al(5)Me$_2$:

Recrystallised from a toluene/hexane mixture to yield yellow crystals (0.177 g, 0.586 mmol, 29%). ^{1}H NMR (400 MHz, d_8-tol) δ= 7.41 (s, 1H; ArCHN), 6.94 (s, 1H; ArH), 6.50 (s, 1H; ArH), 2.78 (br d, *J* = 13.5 Hz, 1H; CH_2), 2.63 (dd, *J* = 13.5, 4.5 Hz, 1H; CH_2), 2.54 (t, *J* = 12.0, 1H; CH_2), 2.31 (s, 3H; CH_3), 2.27 (m, 1H; CH), 2.27 (m, 1H; CH_2), 2.15 (s, 3H; CH_3), 1.42 (br d, *J* = 13.0 Hz, 1H; CH_2), 1.23 (br d, *J* = 13.0 Hz, 1H; CH_2), 1.14 (br dd, *J* = 13.0, 3.0 Hz, 1H; CH_2), 1.0 (q t, *J* = 13.0, 4.0 Hz, 1H; CH_2), 0.85 (q t, *J* = 13.0, 4.0 Hz, 1H; CH_2), 0.61 (br d t, *J* = 10.5, 2.0 Hz, 1H; NH), 0.42 (q d, *J* = 12.5 Hz, 4.0 Hz, 1H; CH_2), -0.39 (s, 3H; AlMe), -0.51 (s, 3H; AlMe). ^{13}C{^{1}H} NMR (d_8-tol, 100 MHz) δ= 171.3 (Ar*C*HN), 164.9, 138.3, 130.8, 130.6, 123.1, 116.9 (Ar), 63.0 (CH_2), 54.5 (N*C*H(CH_2)$_2$), 44.9, 30.0, 26.6, 23.6 (CH_2), 20.3, 16.5 (CH_3), -6.3, -8.6 (AlMe). Elemental analysis ($C_{17}H_{27}AlN_2O$) Calcd in %: C, 67.52; H, 9.00; N, 9.26. Found: C, 67.48; H, 9.13; N, 9.18. Note: Ar-CH_3 ^{13}C resonance obscured by d_8-toluene.

Al(6)Me$_2$:

Recrystallised from hot toluene to yield yellow crystals (0.320 g, 0.74 mmol, 37 %). ^{1}H NMR (400 MHz, d_8-tol) δ= 7.40 (s, 1H; ArCHN), 7.19 (d, *J* = 2.5 Hz, 1H; ArH), 6.54 (d, *J* = 2.0 Hz, 1H; ArH), 2.80 (br d, *J* = 14.0 Hz, 1H; CH_2), 2.45 (m, 5H; CH_2 /$CH_{2\ ad}$), 2.27 (s, 3H; CH_3), 2.21 (m, 2H; CH_2/CH), 2.17 (m, 3H; CH_{ad}), 1.97 (br d, *J* = 11.5 Hz, 3H; $CH_{2\ ad}$), 1.83 (br d, *J* = 12.0 Hz, 3H; $CH_{2\ ad}$), 1.37 (br d, *J* = 13.5 Hz, 1H; CH_2), 1.20 (br d, *J* = 13.5 Hz, 1H; CH_2), 1.09 (br d, *J* = 12.5 Hz, 1H; CH_2), 0.97 (q t, *J* = 13.0, 3.5 Hz, 1H; CH_2), 0.76 (q t, *J* = 13.0, 3.5 Hz, 1H CH_2), 0.56 (d t, *J* = 12.0, 2.5 Hz, 1H; NH), 0.32 (q d, *J* = 12.5, 3.5, 1H; CH_2), -0.37 (s, 3H; AlMe), -0.54 (s, 3H; AlMe). ^{13}C{^{1}H} NMR (d_8-tol, 100 MHz) δ= 171.5 (Ar*C*HN), 166.0, 141.6, 134.8, 131.2, 122.8, 118.3 (Ar), 62.6 (CH_2), 54.5 (N*C*H(CH_2)$_2$), 44.6 (CH_2), 40.61, 37.9 ($CH_{2\ Ad}$), 37.5 (C_{ad}), 29.9 (CH_{ad}), 29.8, 26.5, 23.4 (CH_2), 20.9 (CH_3), -6.2, -9.0 (AlMe). Elemental analysis $C_{26}H_{39}AlN_2O$) Calcd in %: C, 73.90; H, 9.30; N, 6.63. Found: C, 73.73; H, 9.40; N, 6.54.

Synthesis of bisphenolate Aluminium complexes, Al(7-9)Me: $AlMe_3$ (2M, 0.5 ml, 1 mmol) was added dropwise to a solution of **7**-**9**H_2 (1 mmol) in toluene (10 ml) at 40 °C. After complete addition, the solution was then heated to 80 °C and complexation allowed for 3 hours. Solvent was then removed *in vacuo* and the product recrystallised from hexane.

Al(7)Me:

Isolated as yellow crystals (0.326 g, 0.55 mmol, 55%). Two main series at a ratio of 3:2. ^{1}H NMR (400 MHz, d_6-benzene) Major Product δ= 7.76 (m, 1H; ArH), 7.57 (d, *J* = 2.5 Hz, 1H; ArH), 7.49 (s, 1H; ArCHN), 6.99 (d, *J* = 2.5 Hz, 1H; ArH), 6.88 (m, 1H; ArH), 3.83 (d, *J* = 12.5 Hz, 1H; NCH_2Ar), 3.66 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 3.13 (t, *J* = 13.0 Hz, 1H; CH_2), 2.66 (m, 2H; CH/CH_2), 2.28 (m, 2H; CH_2), 2.21 (dd, *J* = 14.0, 5.0 Hz; 1H; CH_2), 1.83 (s, 9H $C(CH_3)_3$), 1.65 (s, 9H $C(CH_3)_3$), 1.45 (s, 9H $C(CH_3)_3$), 1.36 (s/m, 10H $C(CH_3)_3$/CH_2), 0.91 (m, 2H; CH_2), 0.69 (br t, *J* = 13.0 Hz, 1H; CH_2), 0.58 (br d, *J* = 13.3 Hz, 1H; CH_2), -0.23 (s, 3H; AlMe); ^{13}C{^{1}H} NMR (d_6-benzene, 100 MHz) δ= 173.0 (Ar*C*HN), 166.0, 157.3, 141.4, 138.6, 138.3, 137.0, 131.7, 127.3, 124.3, 124.1, 121.7, 117.8 (Ar), 55.7, 55.2 (CH_2), 51.5 (N*C*H(CH_2)$_2$), 46.2 (CH_2), 35.8, 35.6, 34.3, 34.2 (*C*(CH_3)$_3$), 32.3, 31.6, 30.3, 30.1 (C(*C*H_3)$_3$), 23.6, 20.6, 17.5 (CH_2), -8.6 (AlMe).

Minor Product δ= 7.76 (m, 1H; ArH), 7.63 (d, *J* = 2.5 Hz, 1H; ArH), 7.44 (s, 1H;ArCHN), 7.03 (d, *J* = 2.5 Hz, 1H; ArH), 6.88 (m, 1H; ArH), 3.52 (d, *J* = 12.0 Hz, 1H; NCH_2Ar), 3.24 (d, *J* = 12.0 Hz, 1H; NCH_2Ar), 2.87 (t, *J* = 13.0 Hz, 1H; CH_2), 2.75 (m, *J* = 13.5 Hz, 1H; CH), 2.28 (m, 1H; CH_2), 1.87 (s, 9H $C(CH_3)_3$), 1.83 (s, 9H $C(CH_3)_3$), 1.47 (s, 9H $C(CH_3)_3$), 1.39 (s, 9H $C(CH_3)_3$), 1.36 (m, 2H; CH_2), 1.09 (m, 3H; CH_2), 0.91 (m, 2H; CH_2), 0.69 (br t, *J* = 13.0 Hz, 1H; CH_2) -0.42 (s, 3H; AlMe). ^{13}C{^{1}H} NMR (d_6-benzene, 100 MHz) δ= 173.8 (Ar*C*HN), 166.3, 157.5, 141.5, 138.5, 138.2, 137.0, 131.9, 127.3, 123.94, 123.90, 121.7, 117.9 (Ar), 57.7 (N*C*H(CH_2)$_2$), 56.7, 48.9, 44.8 (CH_2), 35.9, 35.8, 34.4 (*C*(CH_3)$_3$), 32.3, 31.7, 30.5, 30.3 (C(*C*H_3)$_3$), 20.5, 18.7, 18.4 (CH_2), -11.0 (AlMe). Elemental analysis ($C_{37}H_{57}AlN_2O_2$) Calcd in %: C, 75.47; H, 9.76; N, 4.76. Found: C, 75.33; H, 9.85; N, 4.88.

Al(8)Me:

Isolated as yellow crystals (0.241g, 0.477 mmol, 48%). Two series with a ratio approximately 1:1. ^{1}H NMR (400 MHz, d_6-benzene) Form 1: δ= 7.55 (s, 1H; ArH), 7.50 (s, 1H; ArCHN), 7.05 (s, 1H; ArH), 6.98 (s, 1H; ArH), 6.62 (s, 1H; ArH), 3.83 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 3.63 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 3.20 (m, 1H; CH_2), 2.57 (m, 1H; CH), 2.56 (s, 3H; CH_3), 2.54 (s, 3H; CH_3), 2.38 (m, 2H; CH_2), 2.04 (dd, *J* = 4.0 Hz, 1H; CH_2), 1.84 (s, 9H $C(CH_3)_3$), 1.61 (s, 9H $C(CH_3)_3$), 1.39 (m, 2H; CH_2), 1.08 (m, 1H; CH_2), 0.89 (m, 1H; CH_2), 0.69 (m, 1H; CH_2), 0.53 (br d, *J* = 14.4 Hz, 1H; CH_2), -0.19 (s, 3H; AlMe); ^{13}C{^{1}H} NMR (d_6-benzene, 100 MHz) δ= 172.0 (Ar*C*HN), 165.7, 157.3, 139.0, 138.5, 138.2, 131.0, 130.1, 124.1, 123.8, 123.5, 121.6, 116.7 (Ar), 56.4, 55.3 (CH_2), 51.9 (N*C*H(CH_2)$_2$), 46.2 (CH_2), 35.6, 35.3 (*C*(CH_3)$_3$), 30.1, 30.0 (C(*C*H_3)$_3$), 23.6, 20.4, 18.7 (CH_2), 16.6, 16.4 (CH_3), -8.1 (AlMe).

Form 2: δ= 7.59 (s, 1H; ArH), 7.50 (s, 1H;ArCHN), 7.07 (s, 1H; ArH), 6.98 (s, 1H; ArH), 6.62 (s, 1H; ArH), 3.27 (d, *J* = 12.0 Hz, 1H; NCH_2Ar), 3.18 (d, *J* = 12.0 Hz, 1H; NCH_2Ar), 2.84 (m, 1H; CH), 2.75 (br d, 1H; CH_2) 2.66 (br t, *J* = 13.5 Hz, 1H; CH_2), 2.38 (m, 2H; CH_2), 2.17 (s, 6H; CH_3), 1.46 (s, 9H $C(CH_3)_3$), 1.44 (s, 9H $C(CH_3)_3$), 1.39 (m, 2H; CH_2), 1.08 (m, 1H; CH_2), 0.89 (m, 1H; CH_2), 0.69 (m, 1H; CH_2), 0.69 (br t, *J* = 13.2 Hz, 1H; CH_2), -0.31 (s, 3H; AlMe). ^{13}C{^{1}H} NMR (d_6-benzene, 100 MHz) δ= 172.9 (Ar*C*HN), 165.8, 157.6, 138.7, 138.3, 137.9, 130.9, 130.3, 124.1, 123.7, 123.5, 121.3, 116.9 (Ar), 56.9 (N*C*H(CH_2)$_2$), 55.5, 48.6, 45.0 (CH_2), 34.36, 34.34 (*C*(CH_3)$_3$), 32.31, 31.27 (C(*C*H_3)$_3$), 20.7 (CH_2), 20.51, 20.47 (CH_3), 18.41 17.4 (CH_2), -10.5 (AlMe). Notes: Form 1 resonance at 3.20 ppm obscured by form 2. CH resonance at 2.57 ppm obscured by CH_3 resonance. Elemental analysis ($C_{31}H_{45}AlN_2O_2$) Calcd in %: C, 73.78; H, 8.99; N, 5.55. Found: C, 73.64; H, 9.08; N, 5.45.

Al(9)Me:

Isolated as yellow crystals (0.265 g, 0.424 mmol, 42 %). Two series with a ratio of 3:2. ^{1}H NMR (400 MHz, d_6-benzene) Major Product δ= 7.55 (d, *J* = 2.5 Hz, 1H; ArH), 7.50 (s, 1H; ArCHN), 7.32 (m, 1H; ArH), 6.99 (m, 1H; ArH), 6.62 (m, 1H; ArH), 3.96 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 3.57 (d, *J* = 13.0 Hz, 1H; NCH_2Ar), 3.15 (m, 1H; CH_2), 2.71 (m, 1H; CH), 2.66 (m, 1H; CH_2), 2.60 (m, 6H; $CH_{2\ Ad}$), 2.32 (m, 4H; CH_2/CH_{Ad}), 2.26 (s, 3H; CH_3), 2.06 (m, 3H; $CH_{2\ Ad}$), 1.97 (dd, *J* = 14.1, 5.3 Hz; 1H; CH_2), 1.90 (m, 3H; $CH_{2\ Ad}$), 1.61 (s, 9H $C(CH_3)_3$), 1.44 (s, 9H $C(CH_3)_3$), 1.43 (m, 1H; CH_2), 1.37 (m, 1H; CH_2), 1.07 (m, 1H; CH_2), 0.83 (m, 1H; CH_2), 0.68 (br t, *J* = 14.4 Hz, 1H; CH_2), 0.48 (br d, *J* = 13.9 Hz, 1H; CH_2), -0.23 (s, 3H; AlMe); ^{13}C{^{1}H} NMR (d_6-benzene, 100 MHz) δ= 173.0 (Ar*C*HN), 166.1, 157.3, 141.8, 138.5, 138.3, 135.5, 130.8, 123.9, 123.8, 123.6, 121.9, 118.4 (Ar), 55.4, 54.6 (CH_2), 50.4 (N*C*H(CH_2)$_2$), 48.7 (CH_2),

41.0, 37.9 ($CH_{2\ ad}$), 35.5, 34.3 ($C(CH_3)_3$), 32.2, 29.8 ($C(CH_3)_3$) 29.8 (CH_{ad}), 20.9 (CH_3), 20.8, 19.7, 17.5 (CH_2), -7.7 (AlMe).
Minor Product δ= 7.60 (d, *J* = 2.5 Hz, 1H; ArH), 7.48 (s, 1H; ArCHN), 7.32 (m, 1H; ArH), 6.99 (m, 1H; ArH), 6.62 (m, 1H; ArH), 3.32 (d, *J* = 12.0 Hz, 1H; NCH_2Ar), 3.15 (m, 1H; NCH_2Ar), 2.79 (m, 1H; CH), 2.66 (m, 1H; CH_2), 2.60 (m, 6H; $CH_{2\ Ad}$), 2.32 (m, 5H; CH_2/CH_{Ad}), 2.28 (s, 3H; CH_3), 2.06 (m, 3H; $CH_{2\ Ad}$), 1.90 (m, 3H; $CH_{2\ Ad}$), 1.83 (s, 9H $C(CH_3)_3$), 1.47 (s, 9H $C(CH_3)_3$), 1.37 (m, 3H; CH_2), 1.07 (m, 1H; CH_2), 0.90 (m, 1H; CH_2), 0.84 (m, 2H; CH_2), -0.42 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR (d_6-benzene, 100 MHz) δ= 173.8 (Ar*C*HN), 166.6, 157.6, 141.8 138.5, 138.2, 136.0, 131.2, 127.3, 123.94, 123.90, 121.7, 117.9 (Ar), 56.5 ($NCH(CH_2)_2$), 55.5, 45.5, 45.0 (CH_2) 41.0, 37.74 ($CH_{2\ ad}$), 37.70 (($C(CH_3)_3$), 35.9, 35.8 ($C(CH_3)_3$), 35.7 ($C(CH_3)_3$), 30.1 (CH_3), 30.0 (CH_{ad}), 23.6, 18.2, 18.0 (CH_2), -9.7 (AlMe). Elemental analysis ($C_{37}H_{57}AlN_2O_2$) Calcd in %: C, 75.47; H, 9.76; N, 4.76. Found: C, 75.33; H, 9.85; N, 4.88. Notes: $ArCH_2$ and CH_2 resonances of minor and major series overlap at 3.15 ppm.

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