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Metal and Ligand-Substituent Effects in the Immortal Polymerization of *rac*-Lactide with Li, Na, and K Phenoxo-imine Complexes

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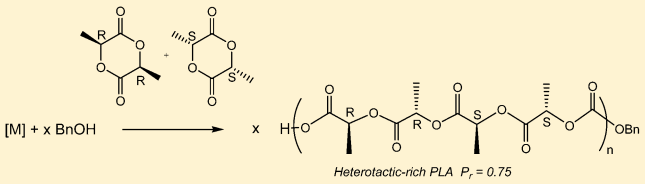
Supporting Information

ABSTRACT: A series of lithium, sodium, and potassium complexes with phenoxo-imine ligands M[(O-2-(RN═CH)-C_6H_4] [R = C_6H_5; 2-^{t}BuC_6H_5; 2,6-^{i}Pr$_2C_6H_3$] and [O-2-(RN═CH)-4,6-^{t}Bu$_2C_6H_4$] [R = C_6H_5; 2-^{t}BuC_6H_5; 2,6-^{i}Pr$_2C_6H_3$] **1**−**3**(**a**−**f**) have been synthesized. The molecular structures in the solid state of some of these complexes have been determined by X-ray diffraction. These compounds show different nuclearities and geometries around the metal center depending on the nature and the pocket of the ligand substituents. Of particular interest is the structure of compound **3e**, being the first example of a potassium cubane complex obtained with this kind of ligand. The structural behavior in solution has also been studied by diffusion-ordered NMR spectroscopy (DOSY), showing a direct correlation between aggregation behavior and polymerization activity. Compounds **1**−**3**(**a**−**f**) are extremely active catalysts in the ring-opening polymerization (ROP) of *rac*-lactide, achieving conversions of 100% in less than 1 min and heterorich-PLA that is modified by the metal atom and the ligand substituents. BnOH was used as co-initiator, and the presence of large amounts of the alcohol produces the immortal polymerization of *rac*-lactide in a more controlled process. Stoichiometric reactions involving the catalysts, BnOH, and lactide demonstrated an activated monomer mechanism for the polymerization of *rac*-lactide.



INTRODUCTION

The development of petroleum-based plastics has made our lives easier and more comfortable due to their properties and high performance. In addition, their synthesis and processing are both easy and inexpensive. However, their use has led to an important environmental pollution problem. For this reason, in recent years, the synthesis of polyesters derived from cyclic esters such as lactide (LA) has gained increasing interest because LA can be obtained from naturally renewable resources such as corn, wheat, or sugar beets.[1] Moreover, polylactide (PLA) is biodegradable and biocompatible and can be used in a wide variety of applications including thermoplastics, films, and fibers. As well, since PLA is biocompatible, it has found many uses in the medical field as drug delivery systems, resorbable sutures, and medical implants.[2]

The most efficient method for the production of PLA is the ring-opening polymerization (ROP) process initiated by metal-based complexes. Different research groups have demonstrated that by following this process well-controlled molecular weight and low polydispersity (PDI) polymers are achieved.[3] Discrete complexes of a wide range of metal centers such as Al, Zn, or lanthanide have been evaluated as catalysts for the ROP of lactide.[4] The amount of catalyst left in the resultant polymers is usually high, which may raise concerns regarding potential health issues associated with the toxicity of some metal-based residues. In this sense, alkaline earth metal derivatives such as Mg or Ca complexes have been reported recently as catalysts for the ROP of lactide owing to their nontoxic nature.[5] However, few examples with alkali metals[6] such as Li, Na, and K have been described, even though the alkali metal precursors are cheap and easily available and their synthesis is accessible. Morever, the new concept of immortal ring-opening polymerization (*i*ROP), initially named as such by Inoue,[7] allows one to carry out the ROP with minimized amounts of a catalytic system upon utilization of very large excess of chain transfer agent such as BnOH. In the context of green and sustainable chemistry, the "catalytic" *i*ROP strategy thus appears highly attractive.[5h]

On the other hand, Schiff bases are very interesting ligand precursors due to their straightforward preparation, high yield, and easy purification.[8] These molecules generate ligands that are able to coordinate to different metals, and many catalytic systems are based on them.[9] Their success in various catalytic polymerization processes is due to the scope for suitable tuning of the steric hindrance and the electronic properties of the ligand precursors. As such, by changing the position and nature of the phenyl ring substituents in the ligand it is possible to cause variations in the catalytic properties of the complexes formed.[4d,i,5b,9]

This work reports the preparation of a series of alkali metal complexes bearing phenoxo-imine ligands with different

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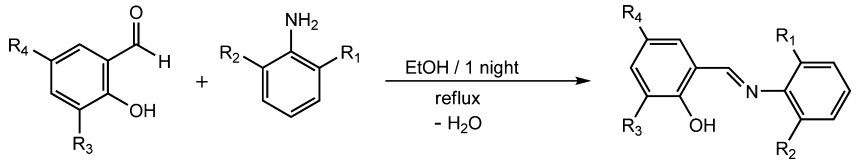
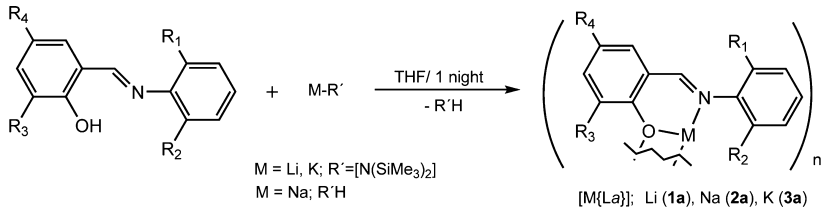
Scheme 1. Synthesis of Phenol-imine Compounds



{L*a*}H; R_1= R_2= R_3= R_4= H
{L*b*}H; R_1= R_2= H; R_3= R_4= ^{t}Bu
{L*c*}H; R_1= ^{t}Bu; R_2= R_3= R_4= H
{L*d*}H; R_2= H; R_1= R_3= R_4= ^{t}Bu
{L*e*}H; R_1= R_2= ^{i}Pr; R_3= R_4= H
{L*f*}H; R_1= R_2= ^{i}Pr; R_3= R_4= ^{t}Bu

Scheme 2. Synthesis of the Alkali Metal Derivatives[a]



M = Li, K; R´=[N(SiMe$_3$)$_2$]
M = Na; R´H

[M{L*a*}]; Li (**1a**), Na (**2a**), K (**3a**)
[M{L*b*}]; Li (**1b**), Na (**2b**), K (**3b**)
[M{L*c*}]; Li (**1c**), Na (**2c**), K (**3c**)
[M{L*d*}]; Li (**1d**), Na (**2d**), K (**3d**)
[M{L*e*}]; Li (**1e**), Na (**2e**), K (**3e**)
[M{L*f*}]; Li (**1f**), Na (**2f**), K (**3f**)

[a]Li: **1a**–**f**; Na: **2a**–**f**; K: **3a**–**f**.

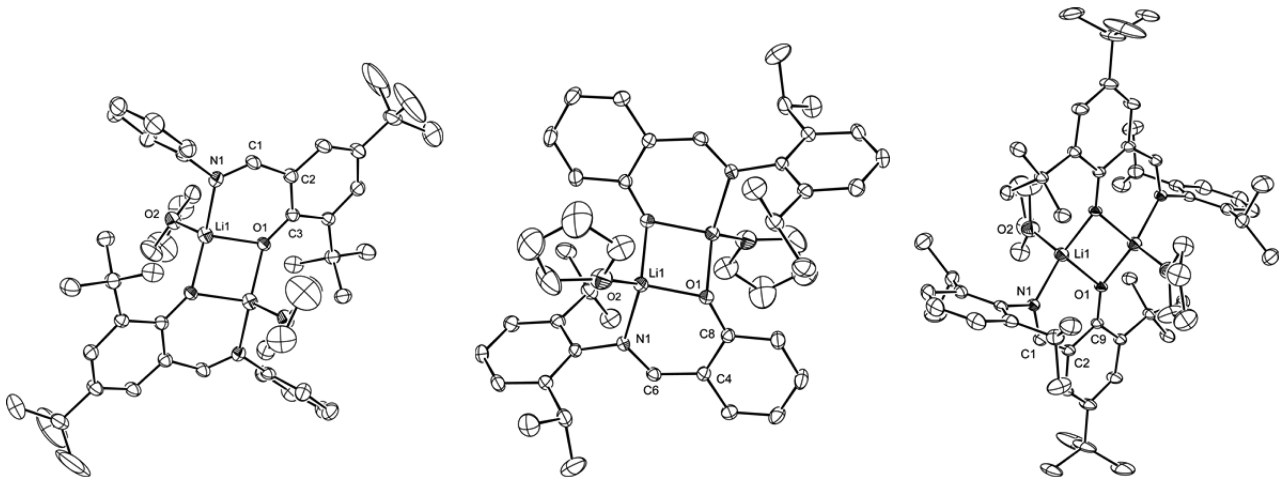


Figure 1. Molecular structure of [**1b**(THF)]$_2$, [**1e**(THF)]$_2$, and [**1f**(THF)]$_2$.

substituents to compare their activity and stereocontrol in the ROP polymerization of *rac*-lactide. Characterization studies by ^{1}H-DOSY NMR spectroscopy to explore the true nature of these complexes in solution and by X-ray diffraction to determine the structural disposition in the solid state are also reported. Their catalytic activity in *rac*-lactide polymerization has been analyzed, and the reaction mechanism of the polymerization process has also been investigated, indicating that the polymerization process depends on the presence or not of initiator.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The phenol-imine compounds have been tailored considering the effect that the bulky substituents in the aromatic rings could play in the polymerization reaction. The condensation reaction between the desired salicylaldehyde with a primary amine allows us to obtain the corresponding phenol-imine compounds with different steric hindrance, {L*a*}H–{L*f*}H (Scheme 1).[10] The ^{1}H NMR spectra of these compounds show the characteristic low-field signal corresponding to the OH proton in the range δ 12.50–14.00, which evidences the acidity of this group as a consequence of intramolecular O–H···N hydrogen interactions.[7] The proton resonance of the imine group appears in the δ 8.50–9.00 range (see the Experimental Section).

The reaction of the phenol-imine compounds with a stoichiometric quantity of the appropriate metallic precursor, [Li{N(SiMe$_3$)$_2$}], NaH, or [K{N(SiMe$_3$)$_2$}] has been carried

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Table 1. Selected Bond Lengths and Angles for $[\mathbf{1b}(THF)]_2$, $[\mathbf{1e}(THF)]_2$, and $[\mathbf{1f}(THF)]_2$

$[\mathbf{1b}(THF)]_2$		$[\mathbf{1e}(THF)]_2$		$[\mathbf{1f}(THF)]_2$	
		Bond Distances (Å)			
Li(1)−O(1)	1.923(7)	Li(1)−O(1)	1.874(3)	Li(1)−O(1)	1.906(4)
Li(1)−O(1)#1	1.915(7)	Li(1)−O(1)#1	1.921(3)	Li(1)−O(1)#1	1.911(4)
Li(1)−N(1)#1	2.042(7)	Li(1)−N(1)	2.032(3)	Li(1)−N(1)	2.071(4)
Li(1)−O(2)	1.956(7)	Li(1)−O(2)	1.976(3)	Li(1)−O(2)	1.961(4)
N(1)−C(1)	1.258(4)	N(1)−C(6)	1.285(2)	N(1)−C(1)	1.288(2)
		Bond Angles (deg)			
O(1)−Li(1)−N(1)	94.0(3)	O(1)−Li(1)−N(1)	93.32(14)	O(1)−Li(1)−N(1)	93.89(16)
O(1)#1−Li(1)−O(2)	112.9(3)	O(1)−Li(1)−O(2)	125.44(19)	O(1)−Li(1)−O(2)	105.70(19)
O(1)−Li(1)−O(1)#1	98.0(3)	O(1)−Li(1)−O(1)#1	93.88(14)	O(1)−Li(1)−O(1)#1	100.86(16)
O(2)−Li(1)−N(1)#1	107.9(3)	N(1)−Li(1)−O(2)	110.50(16)	N(1)−Li(1)−O(2)	115.26(18)
N(1)#1−Li(1)−O(1)	134.4(3)	N(1)−Li(1)−O(1)#1	129.15(18)	N(1)−Li(1)- O(1)#1	132.3(2)
O(1)−Li(1)−O(2)	107.4(3)	O(2)−Li(1)−O(1)#1	105.55(16)	O(2)−Li(1)−O(1)#1	103.93(18)
Li(1)#1-N(1)−C(1)	119.5(3)	Li(1)−N(1)−C(6)	122.33(15)	Li(1)−N(1)−C(1)	116.03(15)
C(10)−N(1)−Li(1)#1	125.3(3)	Li(1)−N(1)−C(3)	118.06(14)	Li(1)−N(1)−C(10)	128.68(15)

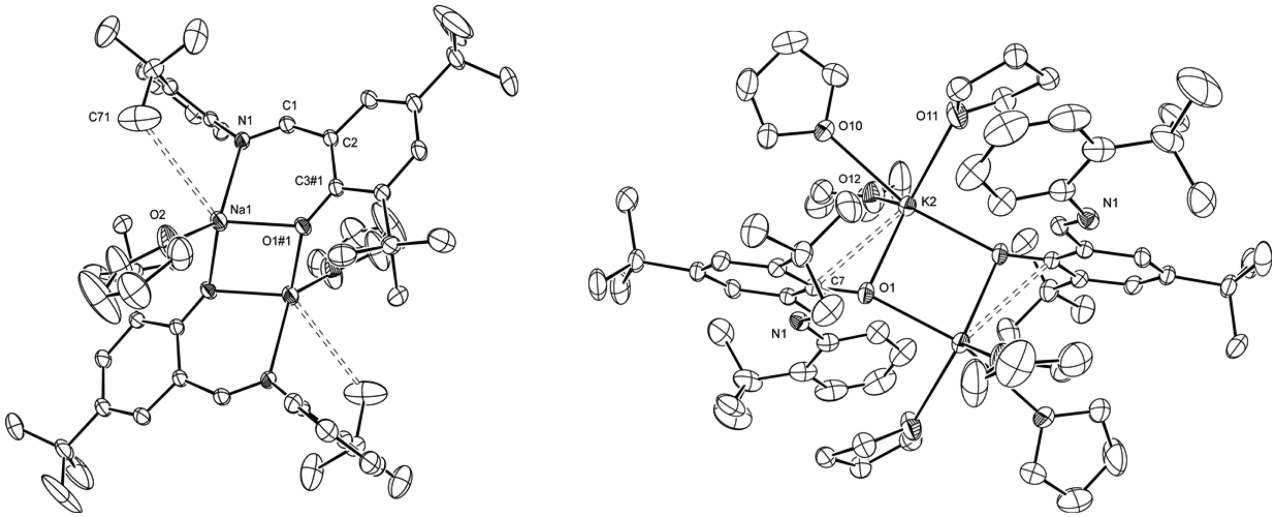

Figure 2. Molecular structure of $[\mathbf{2d}(THF)]_2$ and $[\mathbf{3d}(THF)_3]_2$.

out in dry THF. After removing the solvent, the alkali metal complexes **1**(**a**−**f**), **2**(**a**−**f**), and **3**(**a**−**f**) are isolated with high purity and good yields (Scheme 2).

The ^{1}H NMR spectra for all complexes (DMSO-d_6 at 295 K) indicate the presence of sharp signals with the expected multiplicity, as expected for the presence of the phenoxo-imine ligands, which confirmed that the metal derivatives have been synthesized with high purity. Compared to the starting phenol-imine compounds, the chemical shifts in the alkali complexes were located at higher fields. Despite that the synthesis has been carried out in THF, after drying all these compounds under vacuum, no solvent is observed in the ^{1}H NMR spectra. In ^{13}C NMR spectra, the most interesting signal is due to the carbon atom bonded to the oxygen atom, which is downfield shifted with respect to the ligand precursors (δ ca. 170.0 vs 159.0 ppm), confirming the ligand coordination (see the Experimental Section).

Solid-State Structure Determination. The molecular structures in the solid state for three lithium, **1b**, **1e**, and **1f**, two sodium, **2d** and **2e**, and two potassium complexes, **3d** and **3e**, have been determined by single-crystal X-ray crystallography. Suitable single crystals of **1b**, **1f**, and **2d** were obtained from a THF/toluene solution, while complexes **1e**, **2e**, **3d**, and **3e** were crystallized from a concentrated THF solution. In all the cases these complexes coordinate THF in the crystallization process.

The molecular structures of the three lithium complexes are very similar and show a dinuclear disposition where the lithium atoms are bridged by the oxygen atom of the phenoxo ligand, giving a Li_2O_2 core (see Figure 1). The nitrogen atom from the imine group also establishes a donor interaction with the metal center, generating a six-membered chelating ring, $LiNC_3O$. The lithium atoms complete their coordination sphere with a THF molecule, giving a distorted tetrahedral environment due to the restrictions imposed by the chelate ring. The distances within the $LiNC_3O$ ring are very similar for the three complexes (Table 1) and are within the range for this kind of derivative.[11] The $LiNC_3O$ ring is nearly planar, affected by the trigonal planar geometry of the nitrogen atom from the imine group. This ring is placed almost coplanar to the phenoxo group, while the phenyl group bonded to the nitrogen atom is in a plane nearly perpendicular to this $LiNC_3O$ ring. The values of the dihedral angle between the $LiNC_3O$ ring and the Li_2O_2 central core are 42.85° for $[\mathbf{1b}(THF)]_2$, 49.96° for $[\mathbf{1e}(THF)]_2$, and 35.6° for $[\mathbf{1f}(THF)]_2$.

Sodium and potassium complexes bearing the **L*d*** ligand, $[\mathbf{2d}(THF)]_2$ and $[\mathbf{3d}(THF)_3]_2$, are also dinuclear like the previously described lithium derivatives (Figure 2). The sodium

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Table 2. Selected Bond Lengths and Angles for $[2d(THF)]_2$ and $[3d(THF)_3]_2$[a]

$[2d(THF)]_2$		$[3d(THF)_3]_2$	
	Bond Distances (Å)		
Na(1)−O(1)#1	2.2011(17)	K(2)−O(1)	2.675(3)
Na(1)−O(1)	2.231(2)	K(2)−O(1)#2	2.599(2)
Na(1)−O(2)	2.291(2)	K(2)−O(10)	2.767(3)
Na(1)−N(1)	2.4536(19)	K(2)−O(11)	2.770(3)
N(1)−C(1)	1.284(3)	K(2)−O(12)	2.769(3)
O(1)−C(3)	1.290(3)		
	Bond Angles (deg)		
O(1)#1−Na(1)−O(1)	96.39(7)	O(1)−K(2)−O(1)#2	84.08(7)
O(1)#1−Na(1)−O(2)	118.70(8)	O(1)−K(2)−O(10)	118.06(9)
O(1)−Na(1)−O(2)	104.61(10)	O(1)−K(2)−O(11)	102.81(8)
O(1)−Na(1)−N(1)	111.80(8)	O(1)−K(2)−O(12)	125.39(12)
C(1)−N(1)−C(22)	114.62(18)	O(1)#2−K(2)−O(10)	113.59(8)
N(1)−C(1)−C(2)	129.4(2)	O(1)#2−K(2)−O(11)	163.56(8)
O(1)−C(3)−C(2)#1	120.87(19)	O(1)#2−K(2)−O(12)	86.02(8)
		O(10)−K(2)−O(11)	76.63(10)
		O(10)−K(2)−O(12)	114.98(11)
		O(11)−K(2)−O(12)	77.82(9)
		K(2)−O(1)−K(2)#2	95.92(7)
		C(7)−O(1)−K(2)#2	158.11(19)
		C(7)−O(1)−K(2)	104.23(18)

[a]Symmetry transformations used to generate equivalent atoms: for $[2d(THF)]_2$: #1 $-x+1, -y+1, -z$; for $[3d(THF)_3]_2$ #1 $-x+1, -y+1, -z+1$; #2 $-x+2, -y+2, -z$.

complex **2d** shows a structure very similar to the lithium counterparts, the most remarkable differences being the distances within the Na_2O_2 core and the bond distances from the sodium atoms due to the bigger size of the metal (Table 2). Also, because of the bigger size of sodium compared to lithium, the metal establishes a Na···Me interactions with one methyl group from the ^{t}Bu substituent in order to saturate its coordination sphere (Na···C distance 3.252 Å).[11]

For the potassium derivative $[3d(THF)_3]_2$ (Figure 2) important differences are observed with respect to the lithium and sodium complexes. In this case the potassium atom saturates its coordination sphere by coordinating three THF molecules exhibiting a pentacoordinated disposition. The phenoxo-imine ligand now acts only as a bridging ligand through the oxygen atom, and no chelating nitrogen coordination is observed; consequently the phenyl imine group is located in a plane nearly perpendicular to the central K_2O_2 core and in the same plane as the phenoxo ring. The distance of the α-phenoxo carbon atom to the metal center is quite short (3.35 Å) (Table 2) and could be described as an η^2-C−O bond to potassium. Similar interactions have been observed in heterometallic potassium and zinc derivatives described by Mulvey and Hevia,[12] where the $K-C_{phenoxo}$ distance is even shorter, 3.141 Å. This interaction could be responsible for the perpendicular disposition of the phenoxo ring with respect to the K_2O_2 core that hampers the coordination of the imine nitrogen to the metal. No intermolecular Me···K interactions are present, similar to that observed in the sodium compound.

The structures for sodium and potassium compounds with the L*e* ligand, $[2e(THF)]_4$ (see the Supporting Information) and $[3e(THF)]_4$, have been also determined by X-ray diffraction methods, although the quality of the data is poor, but the connectivity and the nuclearity of the compounds in the solid state can be accurately determined. In both cases the compound structure is formed by four metal atoms bridged by four phenoxo-imine ligands through the phenoxo moiety. The metals saturate their coordination sphere by coordinating to the imine nitrogen atom and one molecule of THF (Figure 3). Examples of this kind of structure for sodium have been previously described.[11] Nevertheless $[3e(THF)]_4$ constitutes the first example of a potassium cubane structure bearing this type of phenoxo-imine ligand. As in $[3d(THF)_3]_2$, in $[3e(THF)]_4$ an interaction between the potassium atom and the α-phenoxo carbon atom of the nonchelating ligand is also observed.

Diffusion-Ordered NMR Spectroscopy (DOSY) Studies. The study of the molecular structure and aggregation degree of the metallic complexes in solution is a very useful tool to understand their behavior in polymerization processes under these conditions. ^{1}H-DOSY is a powerful method to estimate the degree of aggregation and the molecular mass through the measurement of the diffusion coefficient, *D*.[13] These measurements strongly depend on experimental conditions such as viscosity changes or temperature fluctuations. Thus, to achieve reliable molecular mass an internal reference method has been chosen to obtain this value by their relative diffusion coefficient. In our study we chose as internal reference standards[13b] *N*-benzylideneaniline (PhN=CHPh; FW = 181.2), 1-phenylnaphtalene (PhN, FW = 204.7), and 1,2,3,4-tetraphenylnaphthalene (TPhN, FW = 432.6), which present good solubilities, minimal overlapping of signals, and no reactivity with our complexes.

In order to obtain a further understanding of the true nature of these complexes in the lactide polymerization process, we have studied complexes **1e**−**3e** in the same conditions as in the polymerization reactions, that is, in CD_2Cl_2 and in the presence of benzyl alcohol together with the three reference standards in an equimolar ratio. A correlation between log *D* and log FW of the linear least-squares fit to the internal references can be set up for each complex as shown in Table 3 (log $D = A$ log FW + B).[13b,14] The ^{1}H-DOSY *D*−FW plots have a high correlation

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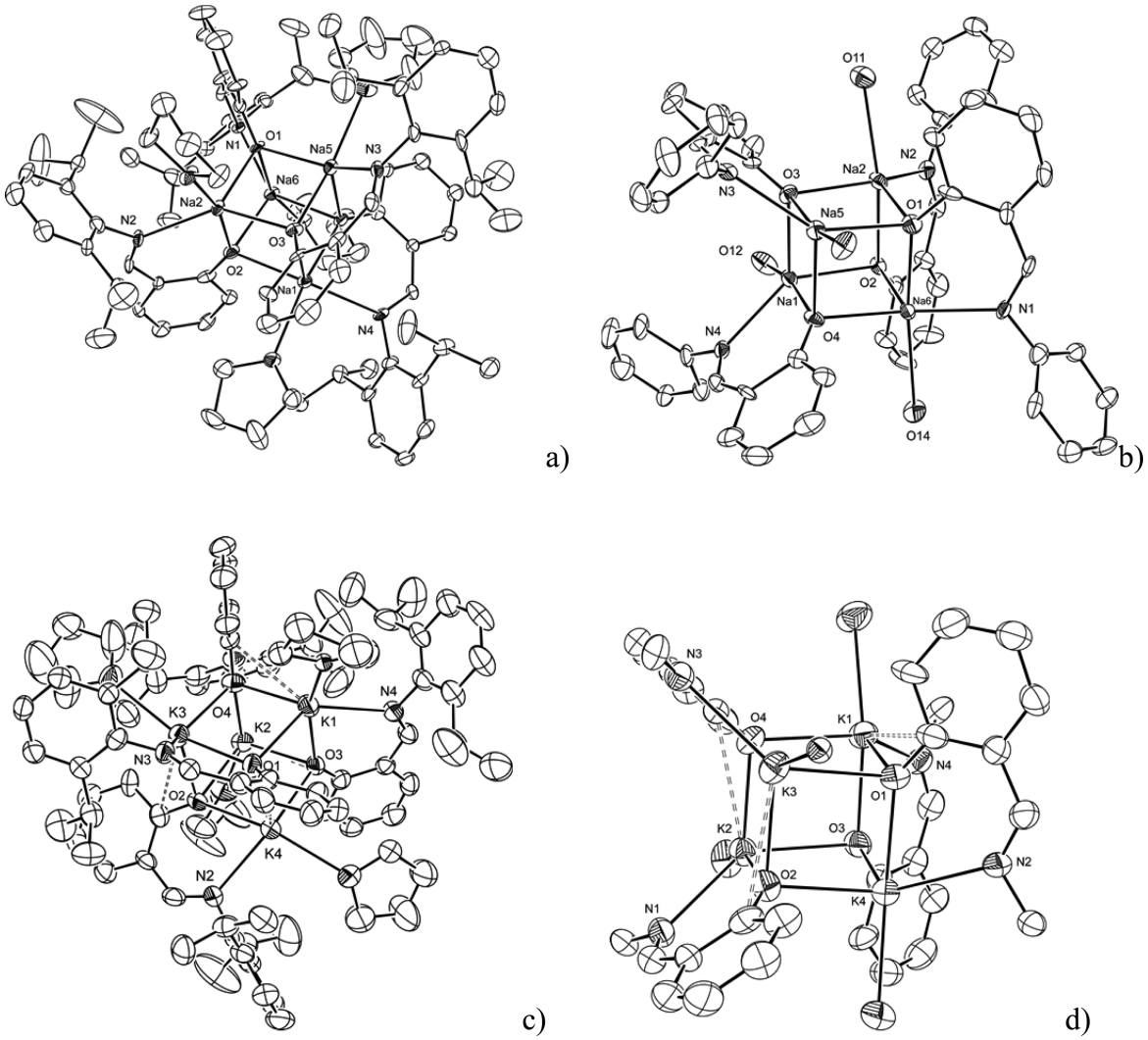


Figure 3. Molecular structure of $[\mathbf{2e}(\mathbf{THF})]_4$ (a and b) and $[\mathbf{3e}(\mathbf{THF})]_4$ (c and d).

Table 3. Diffusion Coefficients and Molecular Mass (m) in CD_2Cl_2 in the Presence of BnOH for 1e−3e

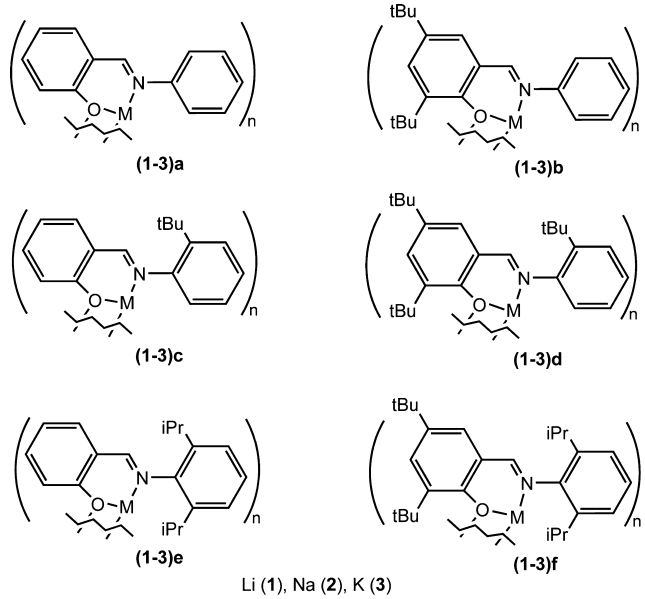
entry	estim. complex	m (g/mol)[a]	D (m^2/s)	m* (g/mol)[b]	% error
1	$[\mathbf{1e}\cdot(\mathbf{BnOH})]_2$	790.94	6.714×10^{-10}	752	4.9
2	$[\mathbf{2e}\cdot(\mathbf{BnOH})]_2$	823.02	6.194×10^{-10}	862	−4.7
3	$[\mathbf{3e}\cdot(\mathbf{BnOH})]_2$	855.24	6.095×10^{-10}	887	−3.7

[a]Predicted molecular mass. [b]Experimental molecular mass.

($r^2 > 0.99$).[15] By interpolating the corresponding D value in the respective calibration curve for each compound, an approximate value of the molecular weight in solution can be obtained[14b] (see Supporting Information). In this study, all the complexes show a dinuclear structure with one BnOH molecule coordinated per metallic center. Thus, it can be considered that in the polymerization process these structures might be responsible for the beginning of the ROP in CH_2Cl_2.

Ring-Opening Polymerization of *rac*-Lactide. The polymerization of *rac*-lactide with complexes **1a** to **3f** (Chart 1) in the presence of benzyl alcohol as co-initiator has been tested in CH_2Cl_2, and the results are summarized in Table 4.

Chart 1. Metal Complexes Tested in the ROP of *rac*-Lactide



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Preliminary polymerization experiments have been carried out to study the influence of the metal center and the ligand substituents on the ROP activity and stereoselectivity.

Table 4. Polymerization of *rac*-Lactide (Preliminary Results)[a]

entry	complex	[LA]/[cat]/[I]	t (min)	conv (%)[c]	P_r[d]
1	**1a**	100:1:1	60	91	0.71
2	**2a**	100:1:1	1	99	0.64
3	**3a**	100:1:1	0.5	99	atactic
4	**1b**	100:1:1	45	99	0.64
5	**2b**	100:1:1	1	99	0.53
6	**3b**	100:1:1	0.5	99	atactic
7	**1c**	100:1:1	45	97	0.74
8	**2c**	100:1:1	1	99	0.56
9[b]	**2c**	100:1:1	5	99	0.68
10	**3c**	100:1:1	0.5	99	atactic
11	**1d**	100:1:1	60	88	0.64
12	**2d**	100:1:1	1	99	0.56
13	**3d**	100:1:1	0.5	99	atactic
14	**1e**	100:1:1	30	98	0.75
15	**2e**	100:1:1	1	99	0.50
16[b]	**2e**	100:1:1	5	98	0.68
17	**3e**	100:1:1	0.5	99	atactic
18	**1f**	100:1:1	45	98	0.62
19	**2f**	100:1:1	1	99	0.58
20	**3f**	100:1:1	0.5	99	atactic

[a]General conditions: 100:1:1 mixture of the lactide, [M], and BnOH, CH_2Cl_2 (5 mL), [LA] = 1 M, RT. [b]T = −30 °C. [c]Obtained from ^{1}H NMR analysis. [d]Calculated from homonuclear decoupled ^{1}H NMR analysis.

Few alkali complexes have been used in the polymerization of *rac*-lactide, and in the reported studies very poor stereoselectivity has been observed. As such, some sodium aryloxo derivatives produce a racemic enchainment in the range 0.37−0.49, while potassium bis(phenolate) complexes generate atactic polymers.[6a,b] Lithium and sodium bis(phenolate) complexes were tested only in the polymerization of L-lactide.[6d]

In our tests, the general tendency is that sodium **2** and potassium **3** complexes are extremely active catalysts, reaching total conversion in less than 1 min, while lithium **1** complexes need more than 30 min to obtain high conversions. These differences could be ascribed to the size of the different alkali metal atoms. The nature of the ligand substituents (Chart 1) seems to have less influence than the metal center on the activity, and for this parameter no clear tendencies are observed.

The selectivity in the polymerization of *rac*-lactide is also highly influenced by the metal center, with the highest selectivity being observed for the slowest catalysts.[5c,16] The ligand substituent also plays an interesting role in this process property. The lithium complexes **1a**, **1c**, and **1e** give the best P_r values, producing heterotactic-rich PLA (P_r = 0.71, 0.74, and 0.75, entries 1, 7, and 14) at 25 °C. These complexes with no substituents in the phenoxo ring afford more stereoregular polymers than complexes **1b**, **1d**, and **1f**, containing substituents in the phenoxo ring (P_r = 0.64, 0.64, and 0.62, entries 4, 11, and 18). As a general tendency, the complexes with bulky substituents in the imine ring group afford better selectivities when no substituents in the phenoxo ring are present (P_r = 0.74 and 0.75, entries 7 and 14) in comparison with the complexes with both substituted rings (P_r = 0.64 and 0.62, entries 11 and 18).

In the polymerizations with sodium complexes, when the temperature was decreased to −30 °C, heterorich-PLA polymers are also obtained (P_r = 0.68 for **2c** and **2e**, entries 9 and 16). The potassium complexes do not present any

Table 5. Immortal Polymerization of *rac*-Lactide Initiated by 1e and 2e with Different Amounts of BnOH[a]

entry	complex	[LA]/[cat]/[I]	t (min)	conv (%)[d]	P_r[e]	$M_{n,theo}$[f]	$M_{n,GPC}$[g]	PDI[g]
21	**1e**	100:1:0	90	96	0.80	13 877	11 594	2.03
22	**1e**	100:1:1	30	98	0.75	14 230	8305	1.55
23	**1e**	100:1:2	30	99	0.70	7243	8342	1.54
24	**1e**	100:1:4	15	99	0.68	3676	3007	1.45
25	**1e**	100:1:8	5	99	0.65	1892	2067	1.54
26	**1e**	100:1:16	1	99	atactic	892	1223	1.32
27	**1e**	100:1:20	1	99	atactic	822	841	1.26
28	**1e**	200:1:40	3	99	atactic	822	804	1.33
29	**1e**	400:1:80	7	99	atactic	822	715	1.33
30	**2e**	100:1:0	1	99	0.68	14 342	14 022	3.19
31[b]	**2e**	100:1:0	5	98	0.68	14 126	16 350	2.13
32[c]	**2e**	100:1:1	5	98	0.68	14 230	7544	1.40
33	**2e**	100:1:1	1	99	atactic	14 380	9489	1.54
34	**2e**	100:1:2	1	99	atactic	7243	10 710	1.60
35	**2e**	100:1:4	0.5	99	atactic	3676	4367	1.70
36	**2e**	100:1:8	0.5	99	atactic	1892	2555	1.72
37	**2e**	100:1:16	0.5	99	atactic	892	1380	1.79
38	**2e**	100:1:20	0.5	99	atactic	822	1517	1.65
39	**2e**	200:1:40	2	99	atactic	822	907	1.54
40	**2e**	400:1:80	4	99	atactic	822	783	1.49

[a]General conditions: 100:1:1 mixture of the lactide, [M], and BnOH, CH_2Cl_2 (5 mL), [LA] = 1 M, 25 °C. [b]T = 0 °C. [c]T = −30 °C. [d]Obtained from ^{1}H NMR analysis. [e]Calculated from homonuclear decoupled ^{1}H NMR analysis. [f]$M_{n,theo}$ = {[M_w(lactide) × [LA]/[cat] × conv/no. equiv BnOH} + M_n(BnOH) or $M_{n,theo}$ = {[LA] × [LA]/[cat] × conv}. [g]Determined by GPC calibrated versus polystyrene standards using a correction factor of 0.58.[17]

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selectivity under the reaction conditions used. As described, the potassium complex **3d** shows, in the solid state, a structural disposition with the imine group of the ligand uncoordinated, while three molecules of THF are coordinated to the potassium atom. Therefore, the chelating coordination of the phenoxo-imine ligand in the potassium complexes must be weaker than in the analogous lithium or sodium derivatives. A plausible explanation for the absence of tacticity observed for the potassium complexes, besides their larger size, could be that in the presence of donor molecules, such as lactide, the absence of a chelating disposition of the phenoxo ligand prevents the induction of stereoselectivity.

In view of these results, complexes **1e** and **2e** were selected for a more detailed study (Table 5) since lithium complexes provide the highest tacticity and sodium complexes show a very high activity with some tacticity. These experimental polymerization tests were explored with different reagent stoichiometries and temperatures, and the resulting polymers were analyzed by GPC and NMR spectroscopy. The GPC analysis for the *rac*-PLA obtained in dichloromethane in the presence of BnOH at various molar rates shows a monomodal weight distribution ranging from 1.26 to 1.55 for the lithium complex **1e** (entries 22−29) being more controlled with an excess of BnOH. In the case of the sodium derivative **2e** the polymerization is less controlled, giving polydispersities between 1.49 and 1.79 (entries 33−40). Molecular weights, obtained by GPC, for the resulting polymers when using a catalyst:BnOH ratio of 1:1 are lower than those expected assuming one growing chain per metal atom, indicating the presence of inter- and intratransesterification reactions, which were confirmed by MALDI-TOF experiments (separation peaks of Δ (m/z) = 72 g·mol^{-1}).[18] However, when the molar ratio [**1e**−**2e**:BnOH] is 1:x (x = 2, 4, 8, 16, 20), the obtained PLA polymers exhibit similar molecular weights to those calculated, indicating that one H-[PLA]-OR polymer chain is formed per added ROH and grows continually through the immortal ROP in a more controlled process.[19] The ^{1}H NMR spectra of the resulting polymers show the corresponding peaks of PLA including the terminal groups HOC(H)Me− and −C(O)OBn. On increasing the concentration of lactide with respect to the metal complex in a ratio of 200:1:40 and 400:1:80 (entries 28, 29, 39, and 40), the polymerization is also controlled and the activity does not decrease significantly.

As a comparison, polymerization reactions of *rac*-lactide with **1e** and **2e** were carried out in the absence of benzyl alcohol. Under these conditions, the process was slower, leading to higher heterorich-PLA (P_r = 0.80 for compound **1e**, entry 21) and greater molecular weight but with broader PDIs (from 2.03 to 3.19, entries 21, 30, and 31). No terminal polymer end-groups were identified by ^{1}H NMR spectroscopy, indicating the cyclic nature of the polymers,[18c,19a,b] which was confirmed by MALDI-TOF experiments. These results suggest that the nature of the propagating species in the presence and absence of BnOH is not the same.

In order to obtain insight into the polymerization mechanism, the stoichiometric reactions involving the metal derivatives **1e**, **2e**, and **3e**, BnOH, and *rac*-lactide have been studied in dichloromethane-d_2 at 303 K. Initially, a mixture of the metal derivative and BnOH (1:1) was monitored, but no reaction was detected, and the formation of neither {L*e*}H nor BnO-M (M = Li, Na, K) was observed. When the reactions were performed adding *rac*-LA to generate a 1:1:1 mixture, the products formed correspond to the ring-opening insertion of BnOH into the monomer, while the metal complex appears intact at the end of the reaction. These results together with the ^{1}H-DOSY NMR experiments (Table 3) are in accordance with an activated monomer mechanism.[5a,13h,19c,20] As described before, in the absence of initiator the mechanism seems to be different, so we also have checked the stoichiometric reaction under these conditions. When the reactions of a 1:1 mixture of (**1**−**3**)**e** and *rac*-lactide were studied by NMR spectroscopy, no terminal groups are observed in the oligomers formed. MALDI-TOF experiments confirmed the cyclic nature as mentioned below. Hence it can be suggested that in the absence of BnOH the polymerization mechanism occurs by insertion of the monomer into the M−O bond via a coordination−insertion mechanism followed by a ring-closing termination step, producing cyclic polymers as reported by Kozak[18c] and Kerton.[19a] Therefore, for our systems, the absence of BnOH produces *rac*-lactide polymerization giving cyclic polymers, while the presence of BnOH as co-initiator plays an important role in the polymerization, giving a more controlled process with benzyl end-groups in an immortal ROP reaction.

CONCLUSIONS

A series of phenoxo-imine complexes with nontoxic alkali metals Li, Na, and K have been synthesized and fully characterized. In the solid state, the lithium derivatives show a dinuclear structure, while the sodium and potassium complexes exhibit di- or tetranuclear dispositions depending on the ligand nature. This tetranuclear structure is not preserved in solution in the presence of BnOH, as shown by ^{1}H-DOSY NMR studies that reveal a dinuclear structure for **1e**−**3e** under these conditions with one benzyl alcohol molecule coordinated per metal center. All complexes are very active toward ROP of *rac*-lactide, and the activity of the catalysts increases with the size of the metal center (K > Na > Li), pointing to the nature of the metal center as a critical factor in the polymerization reaction. A clear effect is exerted by the substituents of the phenyl rings, which modifies the tacticities of the polymer chain. The few examples of alkaline complexes in the polymerization of *rac*-lactide described in the literature at room temperature presented very poor stereoselectivity, but in our case, heterorich-PLA are obtained with lithium complexes (P_r = 0.75).

The BnOH acts as a chain transfer agent with metal catalysts leading to the rapid immortal ROP of cyclic esters, to produce some of the most active ROP catalysts known to date. In the presence of BnOH, an activated monomer mechanism is suggested, while in the absence of co-initiator, a coordination−insertion mechanism followed by a ring-closing termination is proposed, giving heterorich-PLA (P_r = 0.80) with high M_w and broader polydispersities. GPC and MALDI-TOF analysis show that transesterification reactions occur when a 1:1 ratio of catalyst to BnOH is used, but with higher amounts of BnOH, an *i*ROP process, a more controlled polymerization reaction takes place.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere using standard Schlenk-line techniques (O_2 < 3 ppm) and in an MBraun MB-20G glovebox (O_2 < 0.6 ppm). Solvents were dried by conventional procedures and freshly distilled prior to use. Deuterated solvents were degassed by freeze−vacuum−thaw cycles and stored in a glovebox in the presence of molecular sieves (4 Å). All reagents were purchased from Aldrich and used as received.

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Sodium hydride was washed twice with hexane due to the commercial reagent being an oil suspension. *rac*-Lactide was purified by recrystallization from toluene twice and subsequent sublimation under vacuum. NMR spectra were recorded with a Bruker 400 Ultrashield (^{1}H 400 MHz, ^{13}C 101 MHz) at room temperature. All chemical shifts were determinated using the residual signal of solvents and were reported versus $SiMe_4$. Assignment of signals was carried out with 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H–^{13}C HSQC) NMR experiments. Elemental analyses were performed with a PerkinElmer 2400 CHNS/O analyzer Series II and were the average of a minimum of two independent measurements. Molecular weights of polymers were determined by gel permeation chromatography (GPC) in a Varian HPL apparatus with a Plgel Mixed-D (30 cm × 7.5 mm × 5 μm) column and a light scattering detector (Pl-ELS 1000) in THF at room temperature calibrated with respect to polystyrene standards and corrected with a factor of 0.58.[17] MALDI-TOF MAS analysis was performed using a MALDI Agilent TOF LC/MS, and the ionization source was Masstech AP/MALDI. The mass spectrum was recorded in positive mode. 1,8,9-Anthracenetriol was used as matrix, and sodium iodide was added as a cationization agent.

Synthesis of (C_6H_5N=CHC_6H_4OH), {La}H. A solution of aniline (4.79 g, 0.05 mol) in ethanol (150 mL) was prepared, and to it was added 2-hydroxybenzaldehyde (6.41 g, 0.05 mol). This mixture was refluxed for 18–20 h under stirring. The resultant solution was concentrated under vacuum to just 50 mL, and $MgSO_4$ was added to eliminate H_2O. After filtration, it was concentrated under vacuum and stored at −20 °C for a night to give a yellow powder, which was characterized as compound **{La}H**. Yield: 9.17 g, 91%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 13.15 (s, 1H, O*H*), 8.94 (s, 1H, *H*C=N), 7.65 (d, 1H, C_6H_4), 7.47–7.39 (m, 5H, Ar*H*), 7.30 (s, 1H, C_6H_5), 6.95 (d, 2H, C_6H_5). ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 163.9 (*C*=N), 160.8 (*C*-OH), 148.5, 138.1, 133.7, 133.1, 129.9, 127.4, 121.8, 119.7, 119.5, 117.1 (Ar-*C*). Anal. Calcd for $C_{13}H_{11}NO$ (197.23 g/mol): C 79.16, H 5.57, N 7.10. Found: C 78.76, H 5.51, N 6.99.

Synthesis of (C_6H_5N=CH-3,5-^{t}Bu$_2C_6H_2OH$), {Lb}H. Using the same method as that for **{La}H** but using aniline (3.01 g, 0.032 mol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (7.57 g, 0.032 mol), compound **{Lb}H** was obtained as a yellow powder. Yield: 9.44 g, 94%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 13.95 (s, 1H, O*H*), 8.98 (s, 1H, *H*C=N), 7.50 (d, 1H, C_6H_2), 7.48–7.42 (m, 4H, C_6H_5), 7.40 (d, 1H, C_6H_2), 7.30 (t, 1H, C_6H_5), 1.40 [s, 9H, C(CH_3)$_3$], 1.29 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 165.6 (*C*=N), 158.0 (*C*-OH), 148.2, 140.6, 136.3, 129.9, 128.1, 127.8, 127.3, 121.8, 118.7 (Ar-*C*), 35.1, 34.4 [*C*(CH$_3$)$_3$], 31.7, 29.7 [C(CH_3)$_3$]. Anal. Calcd for $C_{21}H_{27}NO$ (309.47 g/mol): C 81.50, H 8.73, N 4.53. Found: C 81.17, H 8.51, N 4.44.

Synthesis of (2-^{t}BuC_6H_4N=CHC_6H_4OH), {Lc}H. Using the same method as that for **{La}H** but using 2-*tert*-butylaniline (6.02 g, 0.040 mol) and 2-hydroxybenzaldehyde (4.93 g, 0.040 mol), compound **{Lc}H** was obtained as a yellow powder. Yield: 8.72 g, 87%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 12.53 (s, 1H, O*H*), 8.69 (s, 1H, *H*C=N), 7.72 (d, 1H, C_6H_4), 7.41 (m, 2H, C_6H_4O-C_6H_4N), 7.29 (t, 1H, C_6H_4O), 7.22 (t, 1H, C_6H_4N), 7.01 (m, 3H, C_6H_4O-C_6H_4N), 1.37 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 162.6 (*C*=N), 160.0 (*C*-OH), 149.6, 142.4, 133.7, 132.4, 127.8, 126.7, 126.44, 121.4, 120.4, 119.7, 116.9 (Ar-*C*), 35.4 [*C*(CH$_3$)$_3$], 30.9 [C(CH_3)$_3$]. Anal. Calcd for $C_{17}H_{19}NO$ (253.34 g/mol): C 80.59, H 7.49, N 5.53. Found: C 80.34, H 7.72, N 5.56.

Synthesis of (2-^{t}BuC_6H_4N=CH-3,5-^{t}Bu$_2C_6H_2OH$), {Ld}H. Using the same method as that for **{La}H** but using 2-*tert*-butylaniline (4.12 g, 0.027 mol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (6.47 g, 0.027 mol), compound **{Ld}H** was obtained as a yellow powder. Yield: 8.97 g, 89%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 13.59 (s, 1H, O*H*), 8.68 (s, 1H, *H*C=N), 7.53 (s, 1H, C_6H_2), 7.41 (s, 2H, C_6H_2), 7.31 (m, 1H, C_6H_4), 7.24 (m, 1H, C_6H_4), 7.08 (d, 1H, C_6H_4), 1.43 [s, 9H, C(CH_3)$_3$], 1.39 [s, 9H, C(CH_3)$_3$], 1.30 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 165.6 (*C*=N), 157.5 (*C*-OH), 149.1, 142.4, 140.8, 136.2, 128.2, 127.9, 126.8, 126.5, 122.0, 119.1 (Ar-*C*), 35.3, 35.1, 34.4 [*C*(CH$_3$)$_3$], 31.7, 30.9, 29.7 [C(CH_3)$_3$]. Anal. Calcd for $C_{25}H_{35}NO$ (365.56 g/mol): C 82.13, H 9.57, N 3.83. Found: C 82.29, H 9.71, N 4.01.

Synthesis of (2,6-^{i}Pr$_2C_6H_3N$=CH-C_6H_4OH), {Le}H. Using the same method as that for **{La}H** but using 2,6-diisopropylaniline (7.05 g, 0.036 mol) and 2-hydroxybenzaldehyde (4.46 g, 0.036 mol), compound **{Le}H** was obtained as a yellow powder. Yield: 8.69 g, 86%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 12.69 (s, 1H, O*H*), 8.57 (s, 1H, *H*C=N), 7.66 (d, 1H, C_6H_4), 7.43 (m, 1H, C_6H_4), 7.17 (m, 3H, C_6H_3), 6.98 (m, 2H, C_6H_4), 2.89 [m, 2H, *H*C(CH$_3$)$_2$], 1.12 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 167.5 (*C*=N), 160.7 (*C*-OH), 146.8, 138.4, 133.9, 132.7, 125.6, 123.5, 119.6, 119.3, 117.1 (Ar-*C*), 28.1 [HC(CH$_3$)$_2$], 23.6 [HC(*CH*$_3$)$_2$]. Anal. Calcd for $C_{19}H_{23}NO$ (281.42 g/mol): C 81.11, H 8.24, N 4.98. Found: C 81.20, H 8.38, N 5.23.

Synthesis of (2,6-^{i}Pr$_2C_6H_3N$=CH-3,5-^{t}Bu$_2C_6H_2OH$), {Lf}H. Using the same method as that for {L*a*}H, but using 2,6-diisopropylaniline (5.08 g, 0.026 mol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (6.10 g, 0.026 mol), compound **{Lf}H** was obtained as a yellow powder. Yield: 5.22 g, 53%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 13.57 (s, 1H, O*H*), 8.55 (s, 1H, *H*C=N), 7.47 (s, 1H, C_6H_2), 7.42 (s, 1H, C_6H_2), 7.19 (m, 3H, C_6H_3), 2.89 [m, 2H, *H*C(CH$_3$)$_2$], 1.43 [s, 9H, C(*CH*$_3$)], 1.28 [s, 9H, C(*CH*$_3$)$_3$], 1.13 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 169.5 (*C*=N), 158.0 (*C*-OH), 146.2, 140.8, 138.6, 136.3, 128.1, 127.9, 125.8, 123.5, 118.2 (Ar-*C*), 35.1, 34.4 [*C*(CH$_3$)$_3$], 31.7, 29.8 [C(*CH*$_3$)$_3$], 28.2 [HC(CH$_3$)$_2$], 23.7 [HC(*CH*$_3$)$_2$]. Anal. Calcd for $C_{27}H_{39}NO$ (393.64 g/mol): C 82.39, H 9.99, N 3.56. Found: C 82.71, H 10.09, N 3.68.

Synthesis of Li[(O-2-{(C_6H_5)N=CH}C_6H_4)] [Li{La}] (1a). At room temperature a mixture of **{La}H** (1.5 g, 7.60 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (1.31 g, 7.60 mmol) in THF (50 mL) was stirred for one night. The resultant solution was filtered and concentrated under reduced pressure, obtaining a white powder, which was characterized as compound **1a**. Yield: 1.46 g, 94%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.29 (s, 1H, *H*C=N), 7.32 (m, 2H, C_6H_5), 7.21 (m, 3H, C_6H_5/C_6H_4), 7.11 (m, 1H, C_6H_4), 6.98 (m, 1H, C_6H_4), 6.36 (d, 1H, C_6H_5), 6.13 (m, 1H, C_6H_5). ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 172.7 (*C*-O), 164.7 (*C*=N), 153.6, 135.9, 133.4, 129.3, 124.8, 123.5, 122.5, 121.7, 109.3 (Ar-*C*). Anal. Calcd for $C_{13}H_{10}NOLi$ (203.180 g/mol): C 76.47, H 4.89, N 6.89. Found: C 76.53, H 4.60, N 6.79.

Synthesis of Na[(O-2-{(C_6H_5)N=CH}C_6H_4)] [Na{La}] (2a). The procedure was as described for **1a** but using **{La}H** (1.5 g, 7.60 mmol) and NaH (0.182 g, 7.60 mmol) in THF (50 mL). A pale yellow powder was obtained, which was characterized as compound **2a**. Yield: 1.61 g, 96%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.77 (s, 1H, *H*C=N), 7.51 (m, 1H, C_6H_4), 7.29 (m, 2H, C_6H_5), 7.06 (m, 3H, C_6H_4/C_6H_5), 6.87 (m, 1H, C_6H_4), 6.25 (m, 1H, C_6H_5), 5.99 (m, 1H, C_6H_4). ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.5 (*C*-O), 161.6 (*C*=N), 154.9, 133.1, 129.4, 128.9, 124.2, 123.4, 123.2, 121.4, 109.2 (Ar-*C*). Anal. Calcd for $C_{13}H_{10}NONa$ (219.22 g/mol): C 71.23, H 4.56, N 6.39. Found: C 70.88, H 4.54, N 6.13.

Synthesis of K[(O-2-{(C_6H_5)N=CH}C_6H_4)] [K{La}] (3a). The procedure was as described for **1a** but using **{La}H** (1.5 g, 7.60 mmol) and K[N{Si(CH$_3$)$_3$}$_2$] (1.60 g, 7.60 mmol) in THF (50 mL). A yellow powder was obtained, which was characterized as compound **3a**. Yield: 1.60 g, 89%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.78 (s, 1H, *H*C=N), 7.51 (m, 1H, C_6H_4), 7.29 (m, 2H, C_6H_5), 7.03 (m, 3H, C_6H_4/C_6H_5), 6.80 (m, 1H, C_6H_4), 6.12 (m, 1H, C_6H_5), 5.84 (m, 1H, C_6H_4).^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 175.8 (*C*-O), 161.2 (*C*=N), 155.4, 133.1, 129.3, 127.5, 124.0, 123.6, 123.4, 121.3, 106.9 (Ar-*C*). Anal. Calcd for $C_{13}H_{10}NOK$ (235.327 g/mol): C 66.35, H 4.28, N 5.95. Found: C 66.53, H 4.61, N 6.22.

Synthesis of Li[(O-2-{(C_6H_5)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [Li{Lb}] (1b). The same method as that for **1a** was used but with **{Lb}H** (1.47 g, 4.75 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (0.82 g, 4.75 mmol). Yield (**1b**): 1.50 g, 99%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8,23 (s, 1H, *H*C=N), 7,32 (m, 2H, C_6H_5), 7.24 (m, 2H, C_6H_5), 7.10 (m, 2H, C_6H_5/C_6H_2), 6.99 (s, 1H, C_6H_2), 1.40 [s, 9H, C(CH$_3$)$_3$], 1.22 [s, 9H, C(CH$_3$)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 170.7 (*C*-O), 165.7 (*C*=N), 154.2, 140.0, 130.0, 129.3, 127.2, 124.3, 121.7, 120.8 (Ar-*C*), 35.5, 33.8 [*C*(CH$_3$)$_3$], 32.1, 30.0 [C(CH$_3$)$_3$]. Anal. Calcd for

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$C_{21}H_{26}NOLi$ (315.39 g/mol): C 79.80, H 8.31, N 4.44. Found: C 79.82, H 8.29, N 4.38.

*Synthesis of Na[(O-2-{(C_6H_5)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**Na{Lb}**] (**2b**).* The same method as that for **1a** was used but with {**Lb**}**H** (1.49 g, 4.83 mmol) and NaH (0.108 g, 4.83 mmol). Yield (**2b**): 1.54 g, 96%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.77 (s, 1H, *H*C=N), 7.36 (s, 1H, C_6H_2), 7.25 (m, 2H, C_6H_5), 6.98 (m, 3H, C_6H_5), 6.93 (s, 1H, C_6H_2), 1.31 [s, 9H, C(CH_3)$_3$], 1.18 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 163.2 (*C*-O), 139.7 (*C*=N), 129.2, 128.6, 126.6, 125.7, 123.5, 121.3, 121.0 (Ar-*C*), 35.3, 33.8 [*C*(CH$_3$)$_3$], 32.1, 30.0 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{21}H_{26}NONa$ (331.45 g/mol): C 76.10, H 7.91, N 4.23. Found: C 76.25, H 8.09, N 4.31.

*Synthesis of K[(O-2-{(C_6H_5)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**K{Lb}**] (**3b**).* The same method as that for **1a** was used but with {**Lb**}**H** (1.51 g, 4.89 mmol) and K[N{Si(CH$_3$)$_3$}$_2$] (1.03 g, 4.89 mmol). Yield (**3b**): 1.60 g, 94%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.81 (s, 1H, *H*C=N), 7.39 (s, 1H, C_6H_2), 7.27 (m, 2H, C_6H_5), 6.99 (m, 3H, C_6H_5), 6.94 (s, 1H, C_6H_2), 1.33 [s, 9H, C(CH_3)$_3$], 1.20 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.9 (*C*-O), 162.7 (*C*=N), 156.1, 140.4, 129.2, 126.5, 126.5, 122.9, 121.3, 121.2, 120.4 (Ar-*C*), 35.4, 33.9 [*C*(CH$_3$)$_3$], 32.3, 30.0 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{21}H_{26}NOK$ (347.54 g/mol): C 72.57, H 7.54, N 4.03. Found: C 72.81, H 7.69, N 4.41.

*Synthesis of Li[(O-2-{(2-^{t}BuC_6H_4)N=CH}C_6H_4)] [**Li{Lc}**] (**1c**).* The same procedure as that described for **1a** was followed but with {**Lc**}**H** (1.46 g, 5.78 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (1.0 g, 5.78 mmol). Yield (**1c**): 1.30 g, 86%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.75 (s, 1H, *H*C=N), 7.65 (m, 1H, C_6H_4O), 7.24 (m, 1H, C_6H_4N), 7.15 (m, 1H, C_6H_4O), 6.99 (m, 1H, C_6H_4N), 6.89 (m, 1H, C_6H_4O), 6.76 (m, 1H, C_6H_4O), 6.33 (m, 1H, C_6H_4N), 6.05 (m, 1H, C_6H_4N), 1.39 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.9 (*C*-O), 159.2 (*C*=N), 154.3, 142.2, 132.7, 127.5, 127.3, 125.7, 124.5, 123.7, 123.6, 120.5, 109.0 (Ar-*C*), 35.8 [*C*(CH$_3$)$_3$], 30.8 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{17}H_{18}NOLi$ (259.29 g/mol): C 78.75, H 7.00, N 5.40. Found: C 78.42, H 6.99, N 5.42.

*Synthesis of Na[(O-2-{(2-^{t}BuC_6H_4)N=CH}C_6H_4)] [**Na{Lc}**] (**2c**).* The same procedure as that described for **1a** was followed but with {**Lc**}**H** (1.38 g, 5.45 mmol) and NaH (0.131 g, 5.45 mmol). Yield (**2c**): 1.49 g, 91%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.64 (s, 1H, *H*C=N), 7.58 (m, 1H, C_6H_4O), 7.23 (m, 1H, C_6H_4N), 7.14 (m, 1H, C_6H_4O), 6.97 (m, 1H, C_6H_4N), 6.82 (m, 1H, C_6H_4O), 6.70 (m, 1H, C_6H_4O), 6.15 (m, 1H, C_6H_4N), 5.90 (m, 1H, C_6H_4N), 1.40 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 175.0 (*C*-O), 158.8 (*C*=N), 154.6, 142.2, 132.8, 127.5, 127.3, 125.6, 124.3, 123.8, 123.6, 120.3, 108.0 (Ar-*C*), 35.8 [*C*(CH$_3$)$_3$], 30.8 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{17}H_{18}NONa$ (275.32 g/mol): C 74.16, H 6.59, N 5.09. Found: C 73.87, H 6.64, N 5.08.

*Synthesis of K[(O-2-{(2-^{t}BuC_6H_4)N=CH}C_6H_4)] [**K{Lc}**] (**3c**).* The same procedure as that described for **1a** was used but with {**Lc**}**H** (1.48 g, 5.83 mmol) and K[N{Si(CH$_3$)$_3$}$_2$] (1.22 g, 5.83 mmol). Yield (**3c**): 1.55 g, 91%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.60 (s, 1H, *H*C=N), 7.55 (m, 1H, C_6H_4O), 7.21 (m, 2H, C_6H_4N+C_6H_4O), 6.95 (m, 1H, C_6H_4N), 6.78 (m, 1H, C_6H_4O), 6.67 (m, 1H, C_6H_4O), 6.09 (m, 1H, C_6H_4N), 5.84 (m, 1H, C_6H_4N), 1.39 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 172.5 (*C*-O), 159.0 (*C*=N), 154.8, 142.1, 132.8, 129.4, 127.5, 127.3, 125.6, 123.9, 123.4, 120.2, 107.1 (Ar-*C*), 35.8 [*C*(CH$_3$)$_3$], 30.7 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{17}H_{18}NOK$ (291.43 g/mol): C 70.06, H 6.23, N 4.81. Found: C 70.15, H 6.24, N 4.44.

*Synthesis of Li[(O-2-{(2-^{t}BuC_6H_4)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**Li{Ld}**] (**1d**).* The same method as that for **1a** was used but with {**Ld**}**H** (1.47 g, 4.04 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (0.696 g, 4.04 mmol). Yield (**1d**): 1.31 g, 87%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.74 (s, 1H, *H*C=N), 7.59 (s, 1H, C_6H_2), 7.24 (m, 1H, C_6H_4), 7.14 (m, 1H, C_6H_4), 7.04 (s, 1H, C_6H_2), 6.97 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 1.42 [s, 9H, C(CH_3)], 1.38 [s, 9H, C(CH_3)], 1.22 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 171.6 (*C*-O), 160.9 (*C*=N), 154.6, 142.1, 139.8, 128.3, 127.1, 126.2, 125.6, 123.2, 122.8, 121.7, 120.7 (Ar-*C*), 35.8, 35.4, 33.9 [*C*(CH$_3$)$_3$], 32.2, 30.8, 30.2 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{25}H_{34}NOLi$ (371.48 g/mol): C 80.83, H 9.22, N 3.77. Found: C 81.20, H 8.98, N 3.52.

*Synthesis of Na[(O-2-{(2-^{t}BuC_6H_4)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**Na{Ld}**] (**2d**).* The same method as that for **1a** was used but with {**Ld**}**H** (0.574 g, 1.55 mmol) and NaH (0.037 g, 1.55 mmol). Yield (**2d**): 0.574 g, 96%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.74 (s, 1H, *H*C=N), 7.63 (s, 1H, C_6H_2), 7.25 (m, 1H, C_6H_4), 7.15 (m, 1H, C_6H_4), 7.03 (s, 1H, C_6H_2), 6.98 (m, 1H, C_6H_4), 6.81 (m, 1H, C_6H_4), 1.44 [s, 9H, C(CH_3)], 1.38 [s, 9H, C(CH_3)], 1.24 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 172.8 (*C*-O), 160.0 (*C*=N), 154.6, 142.2, 139.8, 127.2, 126.2, 125.6, 123.1, 122.4, 121.3, 120.2 (Ar-*C*), 35.8, 35.4, 33.8 [*C*(CH$_3$)$_3$], 32.2, 30.7, 30.1 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{25}H_{34}NONa$ (387.53 g/mol): C 77.48, H 8.84, N 3.61. Found: C 76.77, H 8.99, N 3.64.

*Synthesis of K[(O-2-{(2-^{t}BuC_6H_4)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**K{Ld}**] (**3d**).* The same method as that for **1a** was used but with {**Ld**}**H** (1.50 g, 4.10 mmol) and K[N{Si(CH$_3$)$_3$}$_2$] (0.862 g, 4.10 mmol). Yield (**3d**): 1.55 g, 94%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.64 (s, 1H, *H*C=N), 7.55 (s, 1H, C_6H_2), 7.21 (m, 1H, C_6H_4), 7.13 (m, 1H, C_6H_4), 6.92 (m, 2H, C_6H_4/C_6H_2), 6.70 (m, 1H, C_6H_4), 1.41 [s, 9H, C(CH_3)], 1.33 [s, 9H, C(CH_3)], 1.19 [s, 9H, C(CH_3)]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.5 (*C*-O), 160.1 (*C*=N), 155.2, 142.1, 140.2, 127.2, 126.4, 126.0, 125.5, 122.7, 122.1, 121.1, 119.9 (Ar-*C*), 35.8, 35.4, 33.7 [*C*(CH$_3$)$_3$], 32.2, 30.7, 30.0 [C(*CH*$_3$)$_3$]. Anal. Calcd for $C_{25}H_{34}NOK$ (403.65 g/mol): C 74.39, H 8.49, N 3.47. Found: C 74.81, H 8.20, N 3.44.

*Synthesis of Li[(O-2-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}C_6H_4)] [**Li{Le}**] (**1e**).* The same procedure as that described for **1a** was followed but with {**Le**}**H** (1.50 g, 5.33 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (0.919 g, 5.33 mmol). Yield (**1e**): 1.41 g, 92%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.03 (s, 1H, *H*C=N), 7.24 (m, 1H, C_6H_4), 7.08 (m, 2H, C_6H_3), 7.03 (m, 1H, C_6H_4), 6.97 (m, 1H, C_6H_4), 6.35 (m, 1H, C_6H_3), 6.09 (m, 1H, C_6H_4), 3.03 [m, 2H, *H*C(CH$_3$)$_2$], 1.08 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 172.7 (*C*-O), 166.0 (*C*=N), 151.4, 139.1, 133.2, 133.0, 123.6, 123.3, 122.9, 122.4, 109.0 (Ar-*C*), 27.4 [HC(CH$_3$)$_3$], 24.2 [HC(*CH*$_3$)$_3$]. Anal. Calcd for $C_{19}H_{22}NOLi$ (287.35 g/mol): C 79.42, H 7.72, N 4.87. Found: C 78.92, H 7.73, N 4.88.

*Synthesis of Na[(O-2-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}C_6H_4)] [**Na{Le}**] (**2e**).* The same procedure as that described for **1a** was followed but with {**Le**}**H** (1.35 g, 4.79 mmol) and NaH (0.115 g, 4.79 mmol). Yield (**2e**): 1.28 g, 88%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.44 (s, 1H, *H*C=N), 7.59 (m, 1H, C_6H_4), 7.03 (m, 2H, C_6H_3), 6.93 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 6.19 (m, 1H, C_6H_4), 5.96 (m, 1H, C_6H_3), 2.95 [m, 2H, *H*C(CH$_3$)$_2$], 1.09 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.3 (*C*-O), 162.4 (*C*=N), 152.2, 138.1, 132.7, 127.5, 123.3, 123.0, 122.8, 108.7 (Ar-*C*), 27.6 [HC(CH$_3$)$_3$], 23.8 [HC(*CH*$_3$)$_3$]. Anal. Calcd for $C_{19}H_{22}NONa$ (303.37 g/mol): C 75.23, H 7.31, N 4.62. Found: C 74.81, H 7.41, N 4.46.

*Synthesis of K[(O-2-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}C_6H_4)] [**K{Le}**] (**3e**).* The same procedure as that described for **1a** was followed but with {**Le**}**H** (1.50 g, 5.33 mmol) and K[N{Si(CH$_3$)$_3$}$_2$] (1.12 g, 5.33 mmol). Yield (**3e**): 1.47 g, 86%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ (s, 1H, *H*C=N), 7.60 (m, 1H, C_6H_4), 7.04 (m, 2H, C_6H_3), 6.93 (m, 1H, C_6H_4), 6.84 (m, 1H, C_6H_4), 6.15 (m, 1H, C_6H_4), 5.90 (m, 1H, C_6H_3), 2.97 [m, 2H, *H*C(CH$_3$)$_2$], 1.09 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 175.0 (*C*-O), 162.3 (*C*=N), 152.6, 138.1, 132.7, 127.1, 123.7, 123.4, 122.7, 122.6, 107.0 (Ar-*C*), 27.6 [HC(CH$_3$)$_2$], 23.9 [HC(*CH*$_3$)$_2$]. Anal. Calcd for $C_{19}H_{22}NOK$ (319.51 g/mol): C 71.43, H 6.94, N 4.38. Found: C 71.05, H 6.90, N 4.04.

*Synthesis of Li[(O-2-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}-3,5-^{t}Bu$_2C_6H_2$)] [**Li{Lf}**] (**1f**).* The same method as that for **1a** was used but with {**L6**}**H** (1.00 g, 2.54 mmol) and Li[N{Si(CH$_3$)$_3$}$_2$] (0.438 g, 2.54 mmol). Yield (**1f**): 0.88 g, 87%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 7.81 (s, 1H, *H*C=N), 7.09−6.98 (m, 4H, C_6H_2-C_6H_3), 6.91 (s, 1H, C_6H_2), 3.07 [m, 2H, *H*C(CH$_3$)$_2$], 1.43, 1.20 [s, 9H, C(CH_3)], 1.09 [d, 12H, HC(*CH*$_3$)$_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 170.4 (*C*-O), 168.3 (*C*=N), 151.6, 139.7, 139.6, 128.9, 127.0, 123.7, 123.0, 120.4 (Ar-*C*), 35.5, 33.7 [*C*(CH$_3$)$_3$], 32.1, 30.2 [C(*CH*$_3$)$_3$], 25.8

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$[HC(CH_3)_2]$, 23.7 $[HC(CH_3)_2]$. Anal. Calcd for $C_{27}H_{38}NOLi$ (399.55 g/mol): C 81.17, H 9.59, N 3.51. Found: C 80.85, H 9.52, N 3.47.

*Synthesis of Na[(O-2-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}-3,5-^{t}Bu$_2$C$_6$H$_2$)] [**Na{Lf}**] (**2f**).* The same method as that for **1a** was used but with {**Lf**}**H** (1.00 g, 2.54 mmol) and NaH (0.061 g, 2.54 mmol). Yield (**2f**): 0.90 g, 85%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.46 (s, 1H, *H*C=N), 7.49 (s, 1H, C_6H_2), 6.97 (m, 4H, C_6H_2-C_6H_3), 2.98 [m, 2H, $HC(CH_3)_2$], 1.34 [s, 9H, $C(CH_3)$], 1.21 [s, 9H, $C(CH_3)$], 1.10 [d, 12H, $HC(CH_3)_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 172.7 (C-O), 163.5 (C=N), 152.9, 139.9, 138.2, 126.5, 126.1, 122.6, 122.2, 121.4, 120.5 (Ar-C), 35.3, 33.8 $[C(CH_3)_3]$, 32.3, 30.1 $[C(CH_3)_3]$, 27.5 $[HC(CH_3)_2]$, 23.9, $[HC(CH_3)_2]$. Anal. Calcd for $C_{27}H_{38}NONa$ (415.60 g/mol): C 78.03, H 9.22, N 3.37. Found: C 77.76, H 9.36, N 3.22.

*Synthesis of K[(O-2-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}-3,5-^{t}Bu$_2$C$_6$H$_2$)] [**K{Lf}**] (**3f**).* Using the same method as that for **1a** but using {**Lf**}**H** (1.00 g, 2.54 mmol) and Li[N{Si$(CH_3)_3$}$_2$] (0.534 g, 2.54 mmol). Yield (**3f**): 1.01 g, 92%. ^{1}H NMR (DMSO-d_6, 400 MHz, 295 K): δ 8.47 (s, 1H, *H*C=N), 7.51 (s, 1H, C_6H_2), 7.02 (m, 2H, C_6H_3), 6.96 (s, 1H, C_6H_2), 6.89 (m, 1H, C_6H_3), 3.01 [m, 2H, $HC(CH_3)_2$], 1.33 [s, 9H, $C(CH_3)$], 1.21 [s, 9H, $C(CH_3)$], 1.10 [d, 12H, $HC(CH_3)_2$]. ^{13}C NMR (DMSO-d_6, 101 MHz, 295 K): δ 173.2 (C-O), 163.4 (C=N), 153.1, 140.0, 138.2, 126.0, 126.0, 122.6, 122.1, 121.3, 120.2 (Ar-C), 35.3, 33.8 $[C(CH_3)_3]$, 32.3, 30.1 $[C(CH_3)_3]$, 27.5 $[HC(CH_3)_2]$, 23.9 $[HC(CH_3)_2]$. Anal. Calcd for $C_{27}H_{38}NOK$ (431.732 g/mol): C 75.12, H 8.87, N 3.24. Found: C 75.54, H 8.98, N 3.24.

Typical Procedure for the Polymerization of *rac*-Lactide. In the glovebox, a Schlenk flask was charged with a solution of the complex (0.05 mmol with respect to the monometallic unit) in CH_2Cl_2 (3 mL), and when required, benzyl alcohol was added in the desired stoichiometric amount. In another Schlenk flask, a *rac*-lactide solution was prepared (721 mg, 5 mmol) in CH_2Cl_2 (2 mL). The Schlenk flasks were removed from the glovebox and manipulated with Schlenk-line techniques. The Schlenk flask was immersed in a bath at the desired temperature. The reaction time was measured when the complex mixture was added to the *rac*-lactide solution. Polymerizations with Li complexes were carried out in the glovebox. Small amounts removed with a syringe were tested to determine the conversion by ^{1}H NMR and ^{1}H NMR homonuclear decoupled experiments in $CDCl_3$. Finally the product was isolated and purified by precipitation from heptane by the addition of acidified methanol. The polymer was filtered and dried under vacuum to constant weight.

Structure Determination of Compounds [1b(THF)]$_2$, [1e(THF)]$_2$, [1f(THF)]$_2$, [2d(THF)]$_2$, [3d(THF)$_3$]$_2$, and [3e(THF)]$_4$. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in the Supporting Information. Suitable single crystals of $[\mathbf{1b}(\mathbf{THF})]_2$, $[\mathbf{1e}(\mathbf{THF})]_2$, $[\mathbf{1f}(\mathbf{THF})]_2$, $[\mathbf{2d}(\mathbf{THF})]_2$, $[\mathbf{3d}(\mathbf{THF})_3]_2$, and $[\mathbf{3e}(\mathbf{THF})]_4$ for the X-ray diffraction study were selected. Data collection was performed at 200(2) K, with the crystals covered with perfluorinated ether oil. The crystals were mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All non-hydrogen atoms were anisotropically refined, except in $[\mathbf{3e}(\mathbf{THF})]_4$. For $[\mathbf{3e}(\mathbf{THF})]_4$ the quality of the data was poor, and one coordinated THF molecule was very disordered and was refined in two positions with fixed coordinates and left isotropic without hydrogens. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for the hydrogens from the imine group that were found in the difference Fourier map and refined in compounds $[\mathbf{1e}(\mathbf{THF})]_2$, $[\mathbf{1f}(\mathbf{THF})]_2$ and $[\mathbf{3d}(\mathbf{THF})_3]_2$. For $[\mathbf{1b}(\mathbf{THF})]_2$, $[\mathbf{1f}(\mathbf{THF})]_2$, and $[\mathbf{3e}(\mathbf{THF})]_4$ disordered solvent molecules (toluene for $[\mathbf{1b}(\mathbf{THF})]_2$ and $[\mathbf{1f}(\mathbf{THF})]_2$; THF for $[\mathbf{3e}(\mathbf{THF})]_4$) are present in the unit cell; these solvent molecules were found in the difference Fourier map.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1017337 [**1b**], CCDC-1017338 [**1e**], CCDC-017339 [**1f**], CCDC-1017340 [**2d**], CCDC-1017340 [**2d**], CCDC-1017341 [**3d**], and CCDC-1017342 [**3e**]. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, X-ray crystallographic data (CIF), and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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