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# Synthesis and structural characterization of aluminum complexes supported by NNO-tridentate ketiminate ligands: Efficient catalysts for ring-opening polymerization of l-lactide

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# A R T I C L E I N F O

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# ABSTRACT

Four NNO-tridentate ketiminate derivatives ( ${}^{H}L$ -H,  ${}^{F}L$ -H,  ${}^{OMe}L$ -H and  ${}^{tBu}L$ -H) were prepared through the condensation reaction of 1-(4-chlorophenyl)-4-(4-X-benzoyl)-3-methyl-1H-pyrazol-5(4H)-one (X = H, F, OMe, {}^{tBu}) with N,N-dimethylenediamine (1.1 molar equiv) under reflux condition. Further reaction of AlMe<sub>3</sub> (1.2 molar equiv) with  ${}^{H}L$ -H,  ${}^{F}L$ -H,  ${}^{OMe}L$ -H and  ${}^{tBu}L$ -H, respectively, affords penta-coordinated mono-adduct aluminum complexes [( ${}^{H}L$ )AlMe<sub>2</sub>] (1), [( ${}^{F}L$ )AlMe<sub>2</sub>] (2), [( ${}^{OMe}L$ )AlMe<sub>2</sub>] (3), and [( ${}^{tBu}L$ )AlMe<sub>2</sub>] (4) in high yield. Experimental results indicate complexes 1–4 are active catalysts for ring-opening polymerization of L-lactide (L-LA) in the presence of benzyl alcohol (BnOH). Al complex 2 catalyzes efficiently not only in a "living" fashion but also an "immortal" manner, giving polymers with the expected molecular weights and narrow PDIs.

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Over the past two decades, there has been considerable attention focused on the development of catalytic systems for ring-opening polymerization (ROP). ROP using metal complexes provides a promising method to prepare biodegradable polymers, such as  $poly(\varepsilon$ caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers. These metal complexes have been mainly designed to realize the single active site for minimizing the side reaction, and a variety of catalytic systems supported by various ancillary ligands such as β-diketiminate, Schiff base, amino-bis(phenolate), bisphenolate [1], anilido-aldiminate [2], and benzotriazole phenolate [3] have been reported to achieve great catalytic activities with living properties. For instance, NNOtridentate Schiff-base zinc alkoxides demonstrated the excellent catalytic activity (0 °C, 6 min) and the greater controlled manner (PDI≦1.10) toward the polymerization of L-lactide (L-LA), and their activities are dramatically affected by the substituents on the imine carbon of the NNO-ligands [4].

Encouraged by the excellent catalytic systems derived from NNOtridentate ligands, our current interest has been to design and to prepare NNO-tridentate ketiminate ligands bearing aluminum, magnesium and zinc alkoxides and to apply these complexes as initiators for ROP of L-LA [5]. Most recently, the pyrazole containing ketiminate derivative, (4Z)-4-{[(2-(dimethylamino) ethylamino](phenyl)methylene}-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one was successfully synthesized via one-step condensation, and magnesium and zinc benzylalkoxides incorporating such a ligand catalyzes the ROP of LA with not only good catalytic activities in a controlled character but also the excellent stereo-selectivity ( $P_r = 0.87$ ) [6]. However, no aluminum complex of NNO-tridentate ketiminate ligands has been isolated to date, and the electronic effect of the substituents on the NNO-tridentate ketiminate derivatives might result in dramatic differences of polymerization activity and controlled character. Herein, we report the synthesis, crystal structure and ROP catalytic studies of novel aluminum derivatives based on NNO-tridentate ketiminate ligands of this kind.

The synthetic routes of NNO-tridentate ketiminate ligands (**L**-H) and their Al complexes (1–4) are outlined in Scheme 1. According to the previous literatures [7], pyrazole containing ketiminate ligands can be prepared via two-step synthesis starting from 1-phenyl-pyrazol-5-one and benzoyl chloride derivatives as shown in Scheme 1(a). Four NNO-ketiminate derivatives with 4-substitutited phenyl group (HL-H. **FL-H**, **OME**L-H, and **tBU**L-H) were prepared in moderate to high yield (≧70%) on condensation of diketone (L') with N,N-dimethylenediamine under refluxing absolute ethanol. These ligands were isolated as pale yellow solids and were characterized by <sup>1</sup>H, <sup>13</sup>C NMR and mass spectra as well as microanalyses. For instances, the <sup>1</sup>H NMR spectra of  $^{OMe}$ L-H displayed resonances at  $\delta$  3.24 ppm for the methylene protons of  $-NHCH_2CH_2$ , and signals of methylene ( $\delta = 2.47$  ppm) or methyl ( $\delta = 2.21$  ppm) protons of  $-CH_2CH_2N(CH_3)_2$ , indicating the formation of the desired NNO-tridentate ketiminate ligand. The broad N-H signal at the down field of ~11.2 ppm indicates a hydrogen bond between N-H and O(carbonyl), which was further confirmed by X-ray structural determination. Single crystals suitable for X-ray determination of compound <sup>OMe</sup>L-H were obtained from a

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Scheme 1. Synthetic routes of ligands L-H and complexes (1)-(4).

saturated EtOH solution. The solid-state structure of  $^{OMe}$ L-H [8] (Fig. 1) shows an intramolecular hydrogen bond of N—H<sup>...</sup>O between the amine and amide groups. The distance of O<sup>...</sup>H (1.994(4) Å) is substantially shorter than the Van der Waals distance of 2.72 Å for the O and H atom. The six-membered ring (O(1), C(14), C(13), C(5), N(3),



**Fig. 1.** ORTEP drawing of <sup>OMe</sup>L–H with probability ellipsoids drawn at level 50%. Selected bond lengths/Å and angles/deg: N(3)–C(5) 1.321(2), C(5)–C(13) 1.403(3), C(13)–C(14) 1.443(2), O(1)–C(14) 1.245(2), N(2)–C(14) 1.382(2), N(1)–N(2) 1.411(2), N(1)–C(15) 1.310(2), C(13)–C(15) 1.431(3), O(1) ···H(3A) 1.994(4), N(3)–H(3A) ···O(1) 138.8(3).

H(3A)) formed from the N—H<sup>...</sup>O hydrogen-bond is almost coplanar with mean deviation of 0.0454 Å. Complexes **1–4** were further synthesized via alkane elimination in toluene. Treatment of the ligand (L-H) with AlMe<sub>3</sub> (1.2 molar equiv) yields the mono-adduct aluminum complex (**1**: [(<sup>*H*</sup>L)AlMe<sub>2</sub>] [9]; **2**: [(<sup>*F*</sup>L)AlMe<sub>2</sub>] [10]; **3**: [(<sup>*OMe*</sup>L)AlMe<sub>2</sub>] [11]; **4**: [(<sup>*tBu*</sup>L)AlMe<sub>2</sub>] [12]) in high yield, respectively. The formation of expected complexes **1–4** were demonstrated by the disappearance of the N-H signal of the L-H group at ~11.2 ppm and the appearance of the resonance for methyl protons of Al-Me in the region of -0.78 ppm for **1**, -0.79 ppm for **2** and **3** in NMR spectra. All these compounds were isolated as white crystalline solids and were characterized by spectroscopic studies as well as microanalyses. The structures of complexes **2** and **3** were further verified with X-ray single crystal measurements.

Suitable crystals of complexes 2 and 3 suitable for X-ray structural determinations were grown from their toluene/hexane solutions. Oak Ridge thermal-ellipsoid plots (ORTEP) display selected bond lengths and angles of the molecular structures of 2 [13] and 3 [14] in Figs. 2 and 3, respectively. The molecular structures of compounds **2** and **3** are isostructural, except either a fluoro (-F) or a methoxy (-OMe) substituent at the 4-position of the phenyl group. Both complexes exhibit a monomeric feature with a penta-coordinated Al center, containing one six- and one five-membered chelating ring. The geometry around Al atom is distorted from trigonal-bipyramidal environment with one oxygen atom, two nitrogen atoms from the NNO-tridentate ketiminate ligand, and two C atoms from two methyl groups. Their principal structural features include ketiminate nitrogen atom N(2) and carbon atoms C(1), C(2) occupying the equatorial plane; the angles (O(1)-Al(1)-N(1)) formed by the axial bonds are  $166.76(7)^{\circ}$  for **2** and  $166.13(5)^{\circ}$  for **3**, respectively. The distances between the Al atom and atoms O(1), N(1), N(2), C(1) and C(2) are 1.9152(15), 2.2232(18), 2.0405(17), 1.970(2) and 1.976(2) Å for 2, which are all longer than bond lengths observed for the four-coordinated aluminum complex bearing a NO-bidentate ketiminate derivative [15]. In comparison, the Al-containing bond distances of Al(1) - O(1) = 1.8942(12) Å, Al(1) - O(1) = 1.8942(12) Å, Al(1) - O(1) = 0.0000N(1) = 2.1896(14) Å, Al(1) - N(2) = 2.0403(13) Å, Al(1) - C(1) =



**Fig. 2.** ORTEP drawing of complex **2** with probability ellipsoids drawn at level 50%. Selected bond lengths/Å and angles/deg: Al(1)-O(1) 1.9152(15), Al(1)-N(1) 2.2232(18), Al(1)-N(2) 2.0405(17), Al(1)-C(1) 1.970(2), Al(1)-C(2) 1.976(2), O(1)-Al(1)-N(1) 166.76(7), O(1)-Al(1)-N(2) 89.09(6), N(1)-Al(1)-N(2) 77.95(7), O(1)-Al(1)-C(1) 93.05(9), O(1)-Al(1)-C(2) 91.66(9), N(1)-Al(1)-C(1) 95.10(8), N(1)-Al(1)-C(2) 92.70(8), N(2)-Al(1)-C(1) 116.17(9), N(2)-Al(1)-C(2) 120.96(9), C(1)-Al(1)-C(2) 122.71(10).

1.9826(16) Å and Al(1)—C(2) = 1.9923(16) Å in **3** are all similar to those found in complex **2** and other aluminum complexes [16–18]. The sixmembered rings, Al(1)O(1)C(15)C(14)C(7)N(2), consisting of an Al center coordinated by the oxygen atom O(1) and nitrogen atom N(2) of the ketiminate ligand are nearly coplanar with mean deviation of 0.0840 Å for **2** and 0.0202 Å for **3**. It is interesting to note that the torsion angles between the six-membered chelating ring and the aromatic ring attached to the carbon atom C(7) are 91.2° for **2** and 88.3° for **3**, respectively.

On the basis of lactone polymerizations catalyzed with 0,0-bidentate dipyrazolate aluminum complex [16], dimethyl aluminum anilidooxazolinate [17] or anilido-pyrazolate complexes [18], mono-adduct Al methyl complexes 1-4 have the potential to perform as catalysts toward the ROP of L-lactide (L-LA) in the presence of benzyl alcohol (BnOH). Similar conditions following our previous studies [2c] were first utilized to examine the catalytic activities of L-LA polymerizations using **1–4** as catalyst precursors under dry N<sub>2</sub>. Representative results of L-LA polymerizations under varied conditions are listed in Table 1. It was found that a great catalytic activity and a "controlled" character were achieved with a Al:BnOH molar ratio of 1:2 in toluene at 110 °C. Experimental results indicated that complexes 1-4 exhibited good activities and is somewhat higher than the activity of [(MMPEP)  $Al(\mu$ -OBn)]<sub>2</sub>, which required 48 h to reach 87% conversion [19]. Among them, complex 2 showed the greater "controlled" character than other complexes. As a result, polymerizations catalyzed by 2 were systematically investigated the "living" character (Table 1, entries 2, 5–7). The monomer conversion attained  $\geq$  91% in toluene within 14 h with [L-LA]<sub>0</sub>/[BnOH]<sub>0</sub> ratio in a range 25–150. As depicted in Fig. 4, a linear relationship was demonstrated between actual molecular weight  $M_{\rm p}$  ( $M_{\rm p}$ (GPC) value corrected by a factor of 0.58)



**Fig. 3.** ORTEP drawing of complex **3** with probability ellipsoids drawn at level 50%. Selected bond lengths/Å and angles/deg: Al(1)-O(1) 1.8942(12), Al(1)-N(1) 2.1896(14), Al(1)-N(2) 2.0403(13), Al(1)-C(1) 1.9826(16), Al(1)-C(2) 1.9923(16), O(1)-Al(1)-N(1) 166.13(5), O(1)-Al(1)-N(2) 89.45(5), N(1)-Al(1)-N(2) 79.26(5), O(1)-Al(1)-C(1) 96.60(6), O(1)-Al(1)-C(2) 89.16(6), N(1)-Al(1)-C(1) 94.90(6), N(1)-Al(1)-C(2) 91.55(6), N(2)-Al(1)-C(1) 110.55(6), N(2)-Al(1)-C(2) 128.28(7), C(1)-Al(1)-C(2) 120.96(7).

and  $[L-LA]_0/[BnOH]_0$ , and the PDIs of PLLAs catalyzed by **2** range from 1.13 to 1.23, which indicate that polymerizations proceed in a "living" fashion. The <sup>1</sup>H NMR spectrum of PLLA-25 (25 indicate

#### Table 1

Ring-opening polymerization of L-lactide (L-LA) catalyzed by complexes  $1{-}4$  in the presence of BnOH.



Entry	Cat.	[L-LA] <sub>0</sub> /[Cat.] <sub>0</sub> / [BnOH] <sub>0</sub>	t (h)	Conv. (%) <sup>a</sup>	Mn (calcd.) <sup>b</sup>	Mn (obsd.) <sup>c</sup>	Mn (NMR) <sup>d</sup>	PDI <sup>e</sup>
1 <sup>f</sup>	1	100/1/2	14	93	6800	7700	7400	1.16
2 <sup>f</sup>	2	100/1/2	14	91	6600	7100	6300	1.16
3 <sup>f</sup>	3	100/1/2	14	91	6700	6000	6200	1.20
$4^{f}$	4	100/1/2	14	90	6600	6300	6100	1.15
5 <sup>f</sup>	2	50/1/2	14	91	3400	3500	3200	1.23
6 <sup>f</sup>	2	200/1/2	14	93	13500	15100	11000	1.22
7 <sup>f</sup>	2	300/1/2	14	92	20000	18800	14400	1.13
8 <sup>g</sup>	2	200/1/10	9	92	2800	2100	2900	1.17
9 <sup>g</sup>	2	400/1/20	8	93	2800	2300	2900	1.14
10 <sup>h</sup>	2	1000/1/50	12	92	2800	2400	2700	1.13

<sup>a</sup> Obtained from <sup>1</sup>H NMR determination.

<sup>b</sup> Calculated from the molecular weight of L-LA times [L-LA]<sub>0</sub>/[BnOH]<sub>0</sub> times conversion yield plus the molecular weight of BnOH.

<sup>c</sup> Obtained from GPC analysis times 0.58 [20].

<sup>d</sup> Obtained from <sup>1</sup>H NMR analysis.

<sup>e</sup> Obtained from GPC analysis.

<sup>f</sup> 0.1 mmol complexes, 10 mL toluene, 110 °C.

 $^{\rm g}~$  0.05 mmol complexes, 10 mL toluene, 110 °C.

h 0.05 mmol complexes, 20 mL toluene, 110 °C.



**Fig. 4.** Polymerization of L-LA catalyzed by **2** in toluene at 110 °C. The relationship between  $Mn(\blacksquare)(PDI(\bullet))$  of polymer and the initial molar ratio  $[L-LA]_0/[BnOH]_0$  is shown.

the  $[L-LA]_0/[BnOH]_0$  ratio, Fig. 5) displays that the PLLA chain is capped by one benzyl ester and one hydroxyl chain end with the integration ratio ~5:1 between  $H_a$  and  $H_d$ . Based on the <sup>1</sup>H NMR spectrum of PLLA, it was believed that the [(L)AIMe<sub>2</sub>]/BnOH system could result in situ formation of a metal-benzylalkoxy species, and the insertion of an benzylalkoxy group into L-LA occurred to initiate the polymerization. Complex 2 catalyzes the ROP of L-LA in not only a "living" fashion but also an "immortal" manner. The "immortal" character was further investigated using excess equiv. ratios of BnOH (up to 50 equiv.) as the chain transfer agent (entry 8–10). For instance, 50-fold BnOH can be added to  $[L - LA]_0/[Al]_0 = 1000$ for 12 h, producing a narrow PDI polymer with  $M_{\rm n}$  only ~1/5 that for the addition of  $[L-LA]_0/[AI]_0/[BnOH]_0 = 200/1/2$  (Table 1, entry 10 vs 6). It is worthy of note that complex **2** in the presence of excess amounts of BnOH (>10 equiv.) showed the improved catalytic activity (conv.  $\geq$  92%;  $t \leq$  12 h) and the better controlled behavior (PDI < 1.20) at 110 °C (Table 1, entries 8-10). The "immortal" character of complex 2

provides an efficient way by using only small amounts of catalyst to synthesize PLLA with a narrow PDI, and the metal residues are eventually reduced in the isolated polymer.

In conclusion, three novel aluminum complexes bearing NNOtridentate ketiminate ligands have been synthesized and structurally characterized by spectroscopic studies as well as X-ray single crystal determinations. Experimental results indicate that Al complex **2** catalyzes the ROP of L-LA in the presence of BnOH with the "living" and "immortal" characters. The "immortal" manner of **2** has paved a way to synthesize as much as 50-fold polymer chains of PLLA with a narrow PDI in the presence of small amounts of catalyst.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2012.01.004.

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Fig. 5. <sup>1</sup>H NMR spectrum of PLLA-25 (Table 1, entry 4) in CDCl<sub>3</sub>.

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- [9] [(<sup>H</sup>L)AlMe<sub>2</sub>] (1): Yield: 0.67 g (76 %). Anal. calc. for C<sub>23</sub>H<sub>28</sub>AlClN<sub>4</sub>O: N, 12.76; C, 62.94; H, 6.43. Found: N, 12.30; C, 64.77; H, 6.99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.96 (2H, d, J = 8.8 Hz, ArH), 7.53 (3H, m, ArH), 7.35 (2H, d, J = 8.8 Hz, ArH), 7.22 (2H, d, J = 6.4 Hz, ArH), 3.18 (2H, t, J = 6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.67 (2H, t, J = 6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.26 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.35 (3H, s, CH<sub>3</sub>C = N), -0.78 (6H, s, Al(CH<sub>3</sub>)<sub>2</sub>).
  <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 174.69, 160.86, 148.83, 137.38, 136.28, 129.38, 129.04, 128.74, 128.22, 125.77, 121.00 (Ar and Py), 101.50 (C = C-NH), 55.28 (NHCH<sub>2</sub>CH<sub>2</sub>), 44.93 (NHCH<sub>2</sub>CH<sub>2</sub>), 46.72 (N(CH<sub>3</sub>)<sub>2</sub>), 14.72 (N = C-CH<sub>3</sub>), -8.58 (Al(CH<sub>3</sub>)<sub>2</sub>).
- [10] [(<sup>F</sup>L)AlMe<sub>2</sub>] [2): Yield: 0.73 g (80 %). Anal. calc. for C<sub>23</sub>H<sub>27</sub>AlClFN<sub>4</sub>O: N, 12.66; C, 60.46; H, 5.96. Found: N, 12.22; C, 60.35; H, 5.53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.94 (2H, d, J=8.8 Hz, ArH), 7.36 (2H, d, J=8.8 Hz, ArH), 7.25 (4H, m, ArH),

3.17 (2H, t, J = 6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.68 (2H, t, J = 6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.27 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.39 (3H, s, CH<sub>3</sub>C = N), -0.79 (6H, s, Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$  173.71, 164.30, 161.81, 160.84, 148.55, 137.28, 132.21, 130.16, 128.76, 127.86, 121.00, 116.78, 116.57 (*Ar* and *Py*), 101.65 (*C* = C-NH), 55.21 (NHCH<sub>2</sub>CH<sub>2</sub>), 46.78 (NHCH<sub>2</sub>CH<sub>2</sub>), 45.52 (N(CH<sub>3</sub>)<sub>2</sub>), 14.97 (N = C-CH<sub>3</sub>), -8.56 (Al(CH<sub>3</sub>)<sub>2</sub>).

- [11]  $[(^{OME}L)AIMe_2]$  (3): Yield: 0.73 g (78 %). Anal. calc. for  $C_{24}H_{30}AICIN_4O_2$ : N, 11.95; C, 61.47; H, 6.45. Found: N, 11.76; C, 61.50; H, 6.85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ 7.94 (2H, d, J=8.8 Hz, ArH), 7.34 (2H, d, J=8.8 Hz, ArH), 7.13 (2H, d, J=8.4 Hz, ArH), 7.04 (2H, d, J=8.4 Hz, ArH), 3.88 (3H, s, ArOCH<sub>3</sub>), 3.21 (2H, t, J=6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.67 (2H, t, J=6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.27 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.41 (3H, s, CH<sub>3</sub>C=N), -0.79 (6H, s, Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$  174.82, 160.74, 160.10, 149.00, 137.36, 129.80, 128.65, 128.34, 127.06, 120.84, 114.62 (Ar and Py), 101.76 (C=C-NH), 55.30 (NHCH<sub>2</sub>CH<sub>2</sub>), 55.04 (OCH<sub>3</sub>), 46.56 (NHCH<sub>2</sub>CH<sub>2</sub>), 44.84 (N(CH<sub>3</sub>)<sub>2</sub>), 14.93 (N=C-CH<sub>3</sub>), -8.54 (Al(CH<sub>3</sub>)<sub>2</sub>).
- 44.04 [N(CH<sub>3</sub>)<sub>2</sub>), 14.55 (R = C-G<sub>3</sub>), 0.5- (N(CH<sub>3</sub>)<sub>2</sub>), [12] [( $^{tBu}$ L)AIMe<sub>2</sub>] (4): Yield: 0.80 g (81 %). Anal. calc. for C<sub>27</sub>H<sub>36</sub>AlClN<sub>4</sub>O: N, 11.32; C, 65.51; H, 7.33. Found: N, 11.21; C, 66.25; H, 7.75%. <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm):  $\delta$ 7.95 (2H, d, J = 8.8Hz, ArH), 7.54 (2H, d, J = 8.4Hz ArH), 7.35 (2H, d, J = 9.2Hz, ArH), 7.13 (2H, d, J = 8.6Hz, ArH), 3.21 (2H, t, J = 13.6Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.67 (2H, t, J = 13.2Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.26 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.37 (9H, s, CH<sub>3</sub>C=N), 1.33 (3H, s, ArC(CH<sub>3</sub>)<sub>3</sub>), -0.79 (6H, s, Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR(CDCl<sub>3</sub>, ppm):  $\delta$ 175.13, 160.78, 152.79, 149.00, 137.41, 133.29, 129.98, 128.72, 126.13, 125.28, 121.00 (Ar and Py), 101.65 (C=C-NH), 55.28 (NHCH<sub>2</sub>CH<sub>2</sub>), 46.68 (NHCH<sub>2</sub>CH<sub>2</sub>), 44.92 (N(CH<sub>3</sub>)<sub>2</sub>), 34.87 (C(CH<sub>3</sub>)<sub>3</sub>), 31.29(C(CH<sub>3</sub>)<sub>3</sub>), 14.58 (N = C-CH<sub>3</sub>), -8.58 (Al(CH<sub>3</sub>)<sub>2</sub>) ppm.
- [13] Crystal data for complex 2: C23H27AlCIFN4O, M = 456.92, triclinic, space group P-1, a=10.2603(4) Å, b=10.5288(3) Å, c=12.3331(5) Å,  $\alpha$ =101.806(3)°  $\beta$ =113.387(4)°  $\gamma$ =99.609(3)° V=1150.44(7) Å3, T=110(2)K, Z=2, Dc=1.319 Mg/m3, F(000)=480, 20max=58.50° 12583 reflections collected, 5427 unique [R(int)=0.0279], no. of observed reflections 3575 (I >2 $\sigma$ (I)); R1=0.0450, wR2=0.1250.
- [14] Crystal data for complex 3: C24H30AlClN402, M = 468.95, triclinic, space group P-1, a=9.6850(5) Å, b=10.9437(5) Å, c=12.1709(5) Å,  $\alpha$ =107.185(4)°  $\beta$ =91.980(4)°  $\gamma$ =103.589(4)° V=1190.37(10) Å3, T=110(2)K, Z=2, Dc=1.308 Mg/m3, F(000) = 496, 20max = 58.88° 16126 reflections collected, 5741 unique [R(int)=0.0182], no. of observed reflections 4670 (I > 2\sigma(I)); R1 = 0.0389, wR2 = 0.1321.
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