### Accepted Manuscript

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PII:	S0277-5387(17)30256-5
DOI:	http://dx.doi.org/10.1016/j.poly.2017.03.058
Reference:	POLY 12573
To appear in:	Polyhedron
Received Date:	16 February 2017
Revised Date:	30 March 2017
Accepted Date:	30 March 2017



Please cite this article as: Z. Guo, Y. Wang, J. Yang, X. Wei, Lithium complex of 2-amino-functionalized benzoylpyrrole: Synthesis, structure, and catalytic activity for the cyclotrimerization of isocyanates, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.03.058

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#### Lithium complex of 2-amino-functionalized benzoylpyrrole:

Synthesis, structure, and catalytic activity for the cyclotrimerization

### of isocyanates

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#### Abstract:

Lithium complex stabilised by 2-amino-functionalized benzoylpyrrole was synthesized, and its structural features were provided. The molecular structure shows a novel tetrameric cage structure, which includes a eight-membered (LiN)<sub>4</sub> ring and a eight-membered (LiO)<sub>4</sub> ring with the coordinating pyrrolyl ligands. It was proved to an efficient catalyst for the cyclotrimerisation of isocyanates in good to excellent yields under mild conditions.

Keywords: benzoylpyrrole, synthesis, cyclotrimerization, isocyanate.

#### **1. Introduction**

Due to stable six-cyclic structure without an active hydrogen atom, isocyanurates, the typical isocyanate cyclotrimerized products, could enhance the physical properties of polyurethanes, copolymer resins and coating materials [1], such as increased thermal and chemical resistance, water-resistance, impact resistance, hydrolytic stability, transparency, specific rigidity [2]. Because these products are of commercial significance and are widely used in polymeric processes of industry, the cyclotrimerization of isocyanate has been studied thoroughly and many new types of catalysts have been developed to obtain the isocyanurates in quantitatively yields. For example, traditional Lewis-basic catalysts including N-heterocyclic carbenes [3],

phosphines [4], amines [5], fluoride anions [6], p-toluenesulfinate [7] carbamate anions [8] and alkoxyalkenes [9], metal catalysts including organozinc amines and alkoxides [10], alkoxy niobium [11] and zirconium compounds [12], organotin (II) and (IV) compounds [13] and Ti(bipyridyl)<sub>3</sub> [14], copper and nickel halides [15], rare earth metal amides [16], palladium (0) systems [17] and manganese (II) and iron(II) diaryl complexes[18].

On the other hand, the chemistry and structural diversity of various metal complexes incorporating pyrrole-based multifunctinal ligands have attracted increasing attention. Such as alkylzinc complexes incorporating the corresponding N,N-bifunctional ligand [19], N,O-didentate pyrrole-based ligand [20]. NNN-tridentate pyrrole-based ligand [21], pyrrole-based macrocyclic ligand [22] and so on. Our previous studies also show that the substituted pyrroles are versatile supporting proligands [23]. As a part of our ongoing interest in the development of new reaction systems based on lithium complexes supported by multidentate pyrrole-based ligands, herein we have focused on the versatile bonding modes of monoanionic pyrrolate ligands, and demonstrated that lithium complex stabilised by 2-amino-functionalized benzoylpyrrole efficient precatalyst for is the cyclotrimerisation of isocyanates. It offers high activity, selectivity towards aryl isocyanates, and high selectivity to the formation of isocyanurate products.

#### 2. Experimental

#### 2.1. General methods and materials

Unless otherwise noted, all syntheses and manipulations of air-sensitive materials were performed under a purified nitrogen atmosphere using the standard Schlenk techniques. Tetrahydrofuran diethyl distilled and ether were from sodium-benzophenone under nitrogen. Hexane and toluene is dried using sodium potassium alloy and distilled under nitrogen prior to use. All chemicals were sublimed, recrystallized or distilled before use. <sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75.5 MHz) and 'Li NMR (116.6 MHz) spectra of the compounds were recorded on a Bruker DRX 300 instrument in CDCl<sub>3</sub> or C<sub>5</sub>D<sub>5</sub>N at 298 K and referenced internally to the residual solvent resonances (<sup>1</sup>H,  $^{13}$ C) or externally (<sup>7</sup>Li). Elemental analyses were

performed on a Vario EL-III instrument. Melting points were determined on a STUART SMP10 melting point apparatus and uncorrected. The IR spectra were determined on a FTIR8400S IR spectrophotometer (SHIMADZU) by dispersing samples in KBr disks.

# 2.2. Synthesis of phenyl-(5-piperidin-1-ylmethyl-1H-pyrrol-2-yl)-methanone (LH)

The ligand was prepared by published procedures [19]. 83.4% yield, mp 102-103°C, <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.76 (br, 1H, N*H*), 7.87 (d, J = 6.9, 2H, C<sub>6</sub>H<sub>5</sub>), 7.44-7.57 (m, 3H, C<sub>6</sub>H<sub>5</sub>), 6.79 (d, J = 3.3, 1H, C<sub>4</sub>H<sub>2</sub>N), 6.12 (d, J = 3.0, 1H, C<sub>4</sub>H<sub>2</sub>N), 3.51 (s, 2H, CH<sub>2</sub>), 2.40 (s, 4H, C<sub>5</sub>H<sub>10</sub>N), 1.55-1.60 (m, 4H, C<sub>5</sub>H<sub>10</sub>N), 1.45 (s, 2H, C<sub>5</sub>H<sub>10</sub>N); <sup>13</sup>C NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 25.1 (*C*<sub>5</sub>H<sub>10</sub>N), 26.9 (*C*<sub>5</sub>H<sub>10</sub>N), 55.6 (*C*<sub>5</sub>H<sub>10</sub>N), 56.9 (*C*H<sub>2</sub>), 110.8 (*C*<sub>4</sub>H<sub>2</sub>N), 121.1(*C*<sub>4</sub>H<sub>2</sub>N), 129.2 (*C*<sub>6</sub>H<sub>5</sub>), 129.8 (*C*<sub>6</sub>H<sub>5</sub>), 131.3 (*C*<sub>6</sub>H<sub>5</sub>), 132.5 (*C*<sub>4</sub>H<sub>2</sub>N), 139.1 (*C*<sub>6</sub>H<sub>5</sub>), 139.5 (*C*<sub>6</sub>H<sub>5</sub>), 185.2 (*C*=O). IR<sub>vmax</sub> (KBr, cm<sup>-1</sup>): 3249.8, 2935.5, 1612.4, 1573.8, 1496.7, 1407.9, 1338.5, 1230.5, 1041.5, 983.6, 883.3, 811.9, 723.3, 698.2, 682.8. Anal. Calc. for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O: C, 76.09; H, 7.51; N, 10.44. Found: C, 75.90; H, 7.38; N, 10.21.

#### 2.3. Synthesis of lithium complex (LLi)

An n-BuLi hexane solution (3.0 mmol, 2.2 M) was added dropwise to a hexane (20 mL) solution of LH (g, 3.0 mmol) at 0 °C under nitrogen. After the reaction mixture was stirred at room temperature for 3 h. The white solid was isolated by filtration and recrystallized from a saturated hexane/Et<sub>2</sub>O solution to yield colorless crystals of 1. <sup>1</sup>H NMR (300MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$ (ppm) 8.23 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.42 (m, 3H, C<sub>6</sub>H<sub>5</sub>), 7.35 (d, 1H, C<sub>4</sub>H<sub>2</sub>N), 6368 (d, 1H, C<sub>4</sub>H<sub>2</sub>N), 3.73 (s, 2H, -CH<sub>2</sub>-), 2.44 (m, 4H, C<sub>5</sub>H<sub>10</sub>N), 1.45 (m, 4H, C<sub>5</sub>H<sub>10</sub>N), 1.31 (m, 4H, C<sub>5</sub>H<sub>10</sub>N); <sup>13</sup>C NMR (75MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$ (ppm) 184.86 (CO), 149.62 (C<sub>4</sub>H<sub>2</sub>N), 140.38 (C<sub>6</sub>H<sub>5</sub>), 138.99 (C<sub>6</sub>H<sub>5</sub>), 128.60 (C<sub>4</sub>H<sub>2</sub>N), 127.99 (C<sub>6</sub>H<sub>5</sub>), 126.58 (C<sub>6</sub>H<sub>5</sub>), 112.12 (C<sub>4</sub>H<sub>2</sub>N), 59.816 (-CH<sub>2</sub>-), 53.48 (C<sub>5</sub>H<sub>10</sub>N), 24.77 (C<sub>5</sub>H<sub>10</sub>N), 23.21 (C<sub>5</sub>H<sub>10</sub>N); <sup>7</sup>Li NMR (116.6 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$ (ppm) 0.71. Anal. Calc. for C<sub>71</sub>H<sub>83</sub>Li<sub>4</sub>N<sub>8</sub>O<sub>4</sub>: C, 74.79; H, 7.34; N, 9.83. Found: C, 75.20; H, 7.38; N, 10.01.

#### 2.4. X-ray crystallography

Reflection intensity data for compounds were collected on a Bruker Smart Apex CCD diffractometer using monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å. Each structure was solved by direct method and refined on  $F^2$  by full matrix least squares (SHELX97) [24] using all unique data. Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL) [25]. Crystal and structure refinement data are shown in Table 1. Selected bond lengths and bond angles are ruled out in Table 2.

	Ligand	Lithium complex
Empirical formula	C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O	C <sub>71</sub> H <sub>83</sub> Li <sub>4</sub> N <sub>8</sub> O <sub>4</sub>
Formula weight	268.35	1140.21
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a/Å	25.743(4)	12.206(3)
b/Å	6.1040(8)	12.637(3)
c/Å	20.136(3)	21.775(5)
α (°)	90.00	83.740(5)
β (°)	107.317(2)	88.999(4)
γ (°)	90.00	77.255(4)
Volume (Å <sup>3</sup> ), Z	3020.6(7), 8	3256.2(13), 2
$\rho_{calc}/g \text{ cm}^{-3}$	1.18	1.163
$\mu/\text{mm}^{-1}$	0.074	0.072
F(000)	1152	1218
$\theta$ range/°	2.12-25.05	0.94 to 25.05
Reflections collected	8034	14330
Independent reflections	2637 [R(int) = 0.0279]	11534 [R(int) = 0.0252]

Table 1 Crystal data and structure refinement details of and ligand its complexes.

Data/restraints/parameters	2673/0/182	11534/0/785
Goodness-of-fit on F2	1.016	1.010
Final R indices $[I > 2s (I)]$	R1 = 0.0404, wR2= 0.0982	R1 = 0.0526, wR2 = 0.1209
R indices (all data)	R1 = 0.0584, wR2= 0.1080	R1 = 0.1167, wR2 = 0.1571

Table 2 Selected bond lengths (Å) and angles (°) for complexes

Ligand			
N1-C4	1.352(18)	C4-N1-C1	110.34(13)
N1-C1	1.372(19)	C5-N2-C10	109.87(13)
N2-C5	1.458(2)	C5-N2-C6	111.31(13)
N2-C10	1.457(2)	C10-N2-C6	110.78(14)
N2-C6	1.459(2)	N1-C1-C11	121.37(13)
01-C11	1.234(17)	N1-C4-C5	122.09(15)
C1-C2	1.385(2)	N2-C5-C4	112.92(14)
C3-C4	1.377(2)	01-C11-C1	121.36(14)
C4-C5	1.491(2)	O1-C11-C12	119.70(13)
		C1-C11-C12	118.91(13)
Lithium complex			
Li1-04	1.957(4)	O4-Li1-N5	94.95(19)
Li1-01	2.096(4)	04-Li1-O1	137.2(2)
Li1-N5	2.245(5)	01-Li1-N5	83.86(17)
Li1-N1	2.251(5)	O4-Li1-N1	88.49(19)
Li1-N6	2.263(5)	01-Li1-N1	77.85(16)
N1-C4	1.338(3)	N5-Li1-N1	156.3(2)
N1-C1	1.394(3)	O4-Li1-N6	123.2(2)
N2-C6	1.458(3)	O1-Li1-N6	99.28(18)
N2-C5	1.471(3)	N5-Li1-N6	83.39(17)

01-C11	1.267(3)	N1-Li1-N6	114.15(19)
C1-C2	1.407(3)	N1-Li4-N2	84.25(17)
C2-C3	1.376(4)	Li4-N1-Li1	81.12(18)

#### 3. Results and discussion

**3.1.** Crystal structures

#### 3.1.1. Crystal structure of LH



Fig. 1 (a) The ORTEP view of **LH** at the 25% probability level with hydrogen atoms omitted for clarity. (b) The  $N_{pyrrole}$ -H···O hydrogen bridges of **HL**.

The single crystals of **LH** suitable for X-ray diffraction studies were obtained by recrystallization from a saturated THF/hexane solution at room temperature, and the ORTEP drawing is presented in Fig. 1(a), along with selected bond lengths and angles Table 2. The crystal structure of HL reveals an intermolecular N<sub>pyrrole</sub>-H-O hydrogen bond using oxygen atom of the carboxyl group as the hydrogen-bonding receptor, the pyrrole rings are well-established as hydrogen-bonding donors and are largely employed for anion bonding. The N-H-O bonds [H(N)-O(1) = 2.045 Å, N(1)-H-O(1)

= 158.06] responsible for the crystal packing of the ligand compound.

#### 3.1.2. Crystal structure of LLi



Fig. 2 (a) The ORTEP view of **LLi** at the 25% probability level with hydrogen atoms and solvent omitted for clarity. (b) Alternative views showing the core structure of **LLi**.

Lithium complex stabilised by 2-amino-functionalized benzoylpyrrole (LLi) were crystallized from a saturated  $Et_2O$ /hexane solution, as illustrated in Fig. 2a. In the solid state, it is a novel tetrameric cage structure, which includes a

eight-membered (LiN)<sub>4</sub> ring and a eight-membered (LiO)<sub>4</sub> ring with the coordinating pyrrolyl ligands. Different from the common tetrameric eight-membered (LiN)<sub>4</sub> ring motifs of lithium amides [26], all three donor atoms of the O,N,N-ligand coordinate to a lithium and each sodium is coordinated by three nitrogen and two bridging oxygen atoms. The eight-membered (LiO)<sub>4</sub> ring exhibits an interesting V-shaped (Fig. 2b). The Li-O-Li bond angle range is between 84.37(17) and 88.55(18)° and the Li-O bond lengths range from 1.951(5) to 2.249(5) Å, which fall within the normal range found in lithium oxide compounds. In addition, the Li-N distances within eight-membered (LiN)<sub>4</sub> ring range from 2.078(4) to 2.251(5) Å. The Li-N-Li bond angles fall in the range of 79.93(17) - 81.12(18)°, which are much smaller than those in (LiO)<sub>4</sub> ring.

#### 3.2 lithium complex (LLi) catalyzed cyclotrimerization of isocyanates

Although cyclotrimerization of isocyanates have been studied by us utilizing different type pyrrolyl lithium complexes as catalysts. [23e, 23f] For exploiting new reaction systems based on lithium complexes supported by multidentate pyrrole-based above lithium complex stabilised by 2-amino-functionalized ligands, the benzoylpyrrole as catalysts for cyclotrimerization reactions were studied, and the results are listed in Table 3. The reaction can work well producing the isocyanurate product by carrying out the reaction in different solvents at room temperature for 0.5 h in the presence of 1 mol% of the above lithium complex as the catalyst (Table 3, entries 1-5), indicating the solvent compatibility of the catalysts though the best result was obtained when diethyl ether was employed as solvent. Pleasingly, the title complex can promoted this reaction almost quantitatively at the 0.1 to 1.0 mol% loadings (Table 3, entries 6-9). It is worth noting that the cyclotrimerization reaction also can afford 98% isolated yield after 3h when the loading of catalyst is decreased to 0.05% (Table 3, entry 10). Under the optimized reactions, the representative isocyanates, 4-chloro, 4-methyl and 4-methoxyphenyl isocyanate, were also examined using above lithium complex as a catalyst at 0.05 mol % loading (Table 3, entries 11-13). These results were comparable with those obtained by using the bidentate pyrrolyl lithium complexes  $[Li{C_4H_3N(CH_2NHCMe_3)-2}_2Li(THF)_2]$ and

 $[Li(OEt_2){C_4H_3N(CH_2NMe_2)-2}]_2$  [23e] as catalysts. A proposed mechanism for the cyclotrimerization of isocyanates catalyzed by this complex would be similar to the reaction catalyzed by Lewis base [23e].

Table 3. Lithium complex catalyzed cyclotrimerization of isocyanates<sup>a</sup>



Entry		Isocvanates	Catalyst loading	Solvent		Yield
	Linu y	isocyanacos	(mol %)	Solvent		$(\%)^{b}$
-	1	N=C=O	1.0	Et <sub>2</sub> O	0.5	>99
	2	N=C=O	1.0	THF	0.5	90
	3	N=C=O	1.0	Hexane	0.5	93
	4	N=C=O	1.0	Toluene	0.5	99
	5	N=C=O	1.0	None	0.5	99
	6	N=C=O	0.5	Et <sub>2</sub> O	0.5	99
	7	N=C=O	0.25	Et <sub>2</sub> O	0.5	99
	8	N=C=O	0.1	Et <sub>2</sub> O	0.5	97
	9	N=C=O	0.1	Et <sub>2</sub> O	3	99
	10	N=C=O	0.05	Et <sub>2</sub> O	3	98
	11	——————————————————————————————————————	0.05	Et <sub>2</sub> O	3	95
	12	H <sub>3</sub> CO-	0.05	Et <sub>2</sub> O	3	97
	13	CI-N=C=O	0.05	Et <sub>2</sub> O	3	96

<sup>a</sup>Reaction conditions: isocyanate (30 mmol), room temperature, <sup>b</sup>Isolated yield

#### 4. Conclusions

In summary, a new lithium complex stabilised by 2-amino-functionalized benzoylpyrrole was synthesized and characterised. The X-ray diffraction analyses of the complex indicated that it is a novel tetrameric cage structure, which includes a eight-membered (LiN)<sub>4</sub> ring and a eight-membered (LiO)<sub>4</sub> ring with the coordinating pyrrolyl ligands. The results demonstrated that the title complex has good compatibility for cyclotrimerisation of various aryl isocyanate in different solvents, and it is an efficient precatalyst for the cyclotrimerisation of isocyanates.

#### Acknowledgements

Financial supports from the National Natural Science Foundation of China (No. 20572065), the Coal-based Key Scientific and Technological Project (No. MH2014-07), the Special Fund for Agro-scientific Research in the Public Interest (No. 201303106) and the Natural Science Foundation of Shanxi Province (No. 2011021011-1, 2014011049-26) are gratefully acknowledged.

### Appendix A. Supplementary data

CCDC (1530934 and 1530935) contains the supplementary crystallographic data for LH and LLi, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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MAS

Lithium complex of 2-amino-functionalized benzoylpyrrole:

Synthesis, structure, and catalytic activity for the cyclotrimerization

### of isocyanates

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**Graphical abstract** 

