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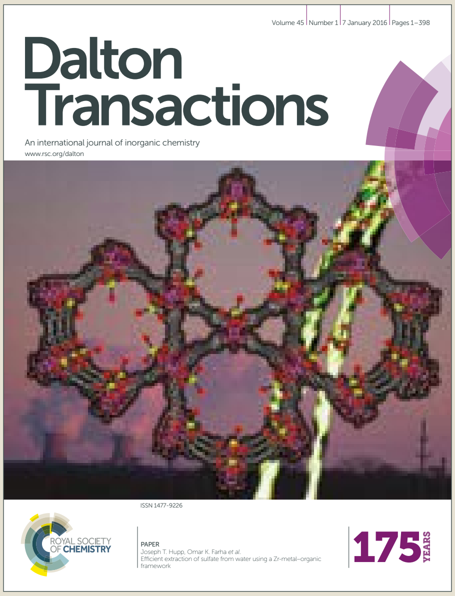

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ARTICLE

Potassium Complexes Containing Bidentate Pyrrole Ligands: Synthesis, Structures, and Catalytic Activity for the Cyclotrimerization of Isocyanates

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The bidentate pyrrolyl ligand, 2-(*t*-butyliminomethyl)pyrrole and 2-(*t*-butylaminomethyl)pyrrole, reacted with KH to give complexes $[C_4H_3N(2\text{-}CH{=}N^tBu)K(THF)]_n$ (**1**) and $[C_4H_3N(2\text{-}CH_2NH^tBu)K]_n$ (**2**), respectively. Each has been characterized by satisfactory C, H and N microanalysis, NMR spectroscopy, and single crystal X-ray structural analysis. The X-ray structure of complex **1** ($n \geq 1$) demonstrated that it exists as a 1D zig-zag coordination polymer in the solid state. Conversely, the structure of complex **2** ($n \geq 1$) showed that it is a 2D supramolecular network. They proved to be an effective class of catalysts for cyclotrimerization of isocyanate in excellent yield under mild conditions.

Introduction

Bidentate 2-imino/aminopyrrole ligand precursors (Chart 1), making possible the introduction of several kinds of exceptional tunable steric and electronic features required for compensating coordinative unsaturation of metal centers, have attracted considerable attention in the areas of organometallic and coordination chemistry in the recent year.[1] The synthesis and characterization of several classes of metal complexes containing 2-imino/aminopyrrolyl ligands, such as Ca(II),[2] Mg(II),[3] Al(III),[4] Ni(II),[5] Cu(II),[6] Zr(IV),[7] Hf(IV),[7a,8] Ti(IV),[9] W(V),[9a] Ta(V)[10] and rare-earth metals,[11] have been particularly studied, being mainly used as polymerization catalysts and molecular catalysts.

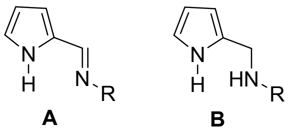

Chart 1 2-Iminopyrrole (**A**) and 2-aminopyrrole (**B**) ligand precursors

However, their alkali metal complexes are generally prepared and employed in *situ*,[12] they have rarely been isolated from reaction solution and are poorly characterized in the solid state, let alone the characterization of their structural features. Thus, full realization of the utilization potential of these elements still requires substantial advances in understanding their basic coordination and organometallic chemistry.

Driven by the lack of structural information on 2-imino/aminopyrrolyl potassium complexes, and in light of our recent studies on alkali metal complexes incorporating 2-aminopyrrolyl ligands,[13] we decided to isolate and characterize the potassium complexes with bidentate pyrrolyl ligand $[C_4H_3NH(2\text{-}CH{=}N^tBu)]$ and $[C_4H_3NH(2\text{-}CH_2NH^tBu)]$, respectively. More remarkable, their structural characterizations have uncovered a surprisingly diverse range of novel structures from 1D coordination polymer to 2D supramolecular network, and these potassium complexes exhibited highly catalytic activities for the cyclotrimerization of aryl isocyanate to the corresponding 1,3,5-triaryl isocyanurate under mild conditions.

Results and discussion

Synthesis and characterization of potassium complexes

Treatment of KH with one equiv. of the iminopyrrolyl ligand $[C_4H_3NH(2\text{-}CH{=}N^tBu)]$ in THF solution resulted in the one-dimensional chain potassium complex of the molecular formula $[C_4H_3N(2\text{-}CH{=}N^tBu)K(THF)]_n$ **(1)**. Similarly, treatment of one equiv. of KH with $[C_4H_3NH(2\text{-}CH_2NH^tBu)]$ in THF resulted in the corresponding two-dimensional plane potassium complex $[C_4H_3N(2\text{-}CH_2NH^tBu)K]_n$ **(2)** with good yield (see Scheme 1). Each of **1** and **2** were fully characterized by satisfactory C, H and N microanalysis, ^1H, ^{13}CNMR spectra at ambient temperature, and their solid-state structures were established using single-crystal X-ray diffraction analysis. The ^1H NMR spectra of **1** exhibits two doublets for $C(CH_3)_3$ and $CH{=}N$ at δ 1.25 and 8.06, respectively,

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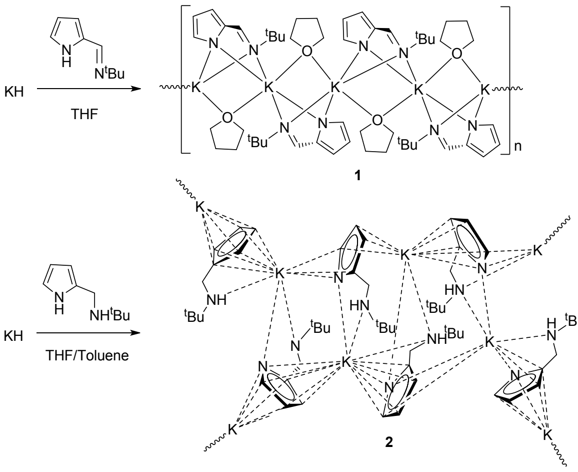

Scheme 1 Synthetic routes to complex **1** and **2**.

representing the manner of molecular structure **1** in a solution maintain the solid ones at room temperature. The protons of complex **2** were downfield shifted and exhibited similar spectral feature of the corresponding lithium complex in the ^{1}H NMR spectrum[13b]. In addition, the pyrrole ring protons and other protons showed resonance signals in each complex at expected regions. The NMR spectra also supported the presence of the carbon atom in each complex, which are consistent with the structure of X-ray analysis.

X-ray single crystal structures of 1 and 2.

Complex **1** crystallizes in the orthorhombic space group Pnma with two formula units in the unit cell. The asymmetric unit contains one potassium ion K$^+$, one pyrrolyl ligand L$^-$, and one solvent molecular THF (Figure 1). In the crystal structure of **1**, it presents a one-dimensional coordination polymer, the connection of potassium ion by bridging iminopyrrolyl ligand and O atom of THF to give 1D coordination chains running along the *y* axis. As a result, the center metal ion K$^+$ of complex **1** was hexa-coordinated by two *O* atoms from two THF molecular and four *N* atoms from two ligand molecules. Therefore, the geometry around the potassium ion in **1** can be best described as a distorted octahedral. The K1–N1$_{\text{pyrrolyl}}$ and K1–N2$_{\text{imino}}$ bond distances, 2.806(3) and 2.893(3) Å respectively, are much shorter than the corresponding K–N distances observed in iminopyrrolyl potassium complex [{2-(Ph$_3$CN=CH)C$_4$H$_3$N}K(THF)$_{0.5}$]$_4$ (2.971(3) and 3.005(3) Å respectively).[14] The K1–O1 bond distances of 2.820(3) Å are within the range of K–O bond distances reported in the literature. The bite angle of 61.93(12)° for N(1)-K(1)-N(2) was observed for the iminopyrrolyl chelated to the potassium atom.

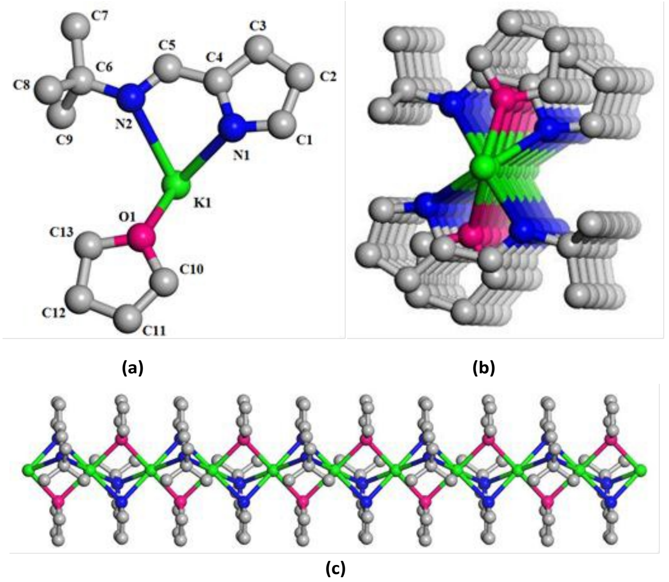

Fig. 1 (**a**) Asymmetric unit of complex **1**, with atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level; (**b**) and (**c**) fragment of polymeric coordination chain, running along the y axis from a different perspective, in the crystal structure of complex **1**. Hydrogen atoms are omitted for clarity.

In contrast to complex **1**, the potassium complex **2** crystallizes in a mixed solvent of THF and toluene. It shows in the orthorhombic space group Pccn with four molecules in the unit cell. The asymmetric unit of potassium complex **2** contains two aminopyrrolyl ligand and two potassium ions (Figure 2). It is noted that the coordination spheres of the two potassium ions are different. The ion K1 is coordinated by two nitrogens from an aminopyrrolyl ligand in a bidentate fashion and π interaction (η^5-mode) from one pyrrole ring of the adjacent aminopyrrolyl ligand while the second ion, K2, is coordinated by K-π interaction (η^2-mode) from pyrrole ring of aminopyrrolyl ligand, and chelated by nitrogen atom of the adjacent pyrrole ring in a κ^1 fashion. In the grown structure, the potassium ion K1 is observed as a sandwich structure between two pyrrolyl ring π-electron densities in a η^5-fashion and further chelated by two nitrogen atoms of one aminopyrrolyl ligand. The other potassium ion K2 are surrounded by three aminopyrrolyl

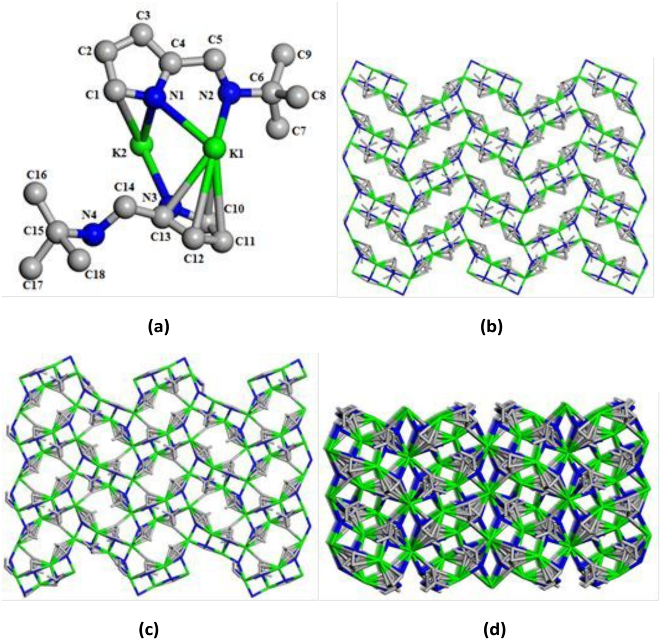

Fig. 2 **(a)** Asymmetric unit of complex 2, with atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level; (**b**) and **(c)** Section of the extended framework structure showing K-C or K-N atom connectivity; **(d)** the resulting two-dimensional layer packing. Hydrogen atoms are omitted for clarity.

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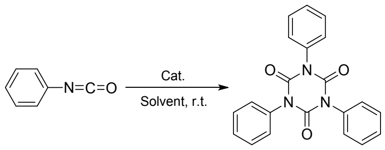
moieties, three pyrrolyl rings bind to potassium ion through its central *N*-atom or ring *C*-atoms into μ_3-(η^1-η^2-η^4)-mode to form a 2D supramolecular network structure formed. The K1–N1$_{pyrrolyl}$, K1–N3$_{pyrrolyl}$, K2–N1 $_{pyrrolyl}$ and K2–N3$_{pyrrolyl}$ bond distances, 2.747(3), 2.968(3), 2.898(3) and 2.765(4) Å respectively, are in good agreement with K–N distances observed in complex **1**. The K1–N2$_{amino}$ bond distance (2.969(3) Å) fits well with the corresponding K–N distances observed in iminopyrrolyl potassium complex [{2-($Ph_3CN{=}CH)C_4H_3N$}K(THF)$_{0.5}$]$_4$ 3.005(3) Å.[14] The distances between the potassium ion K1 and the pyrrole ring atoms (C10, C11, C12, C13 and N3) were found to be 3.124(4), 3.248(5), 3.125(4), 2.932(4) and 2.968(3) Å, respectively. These distances are within the range of K-pyrrolyl centroid distances found in the polymeric potassium compound of the sandwiched type reported in the literature.[13f] To the best of our knowledge, this is the first example of a μ_3-(η^1-η^2-η^4)-mode developed by a pyrrole ring towards potassium atoms.

The cyclotrimerization of isocyanate catalysed by potassium complexes

Over the past few years, the industrial and commercial application of isocyanurates have attracted much attention because it could enhance the physical properties of polyurethanes, copolymer resins and coating materials[15], such as increased thermal and chemical resistance, water-resistance, transparency, and impact resistance[16]. And the cyclotrimerization of isocyanate has been studied thoroughly and many types of catalysts have been developed to obtain the isocyanurates in high yields. For example, metal-based catalytic systems including inexpensive transition metals such as Zn[17], Sn[18], Cu[19], Ni[19], Ti[20], noble metal Pd[21], rare earth metals[22] and so on. Organic and inorganic molecular catalysts including N-heterocyclic carbenes,[23] phosphines,[24] amines,[25] fluoride anions,[26] p-toluenesulfinate[27]and carbamate anions.[28] Our group also have reported utilizing various type pyrrolyl lithium complexes as catalysts for cyclotrimerization of isocyanates.[13b,c,g] For further exploiting new reaction systems based on alkali metal complexes with functionalized pyrrole ligands, the above potassium complexes as catalysts for cyclotrimerization of aryl isocyanats were studied, and the results are listed in Table 1.

Table1. Optimization of cyclotrimerization of isocyanate catalyzed by potassium complex [a]

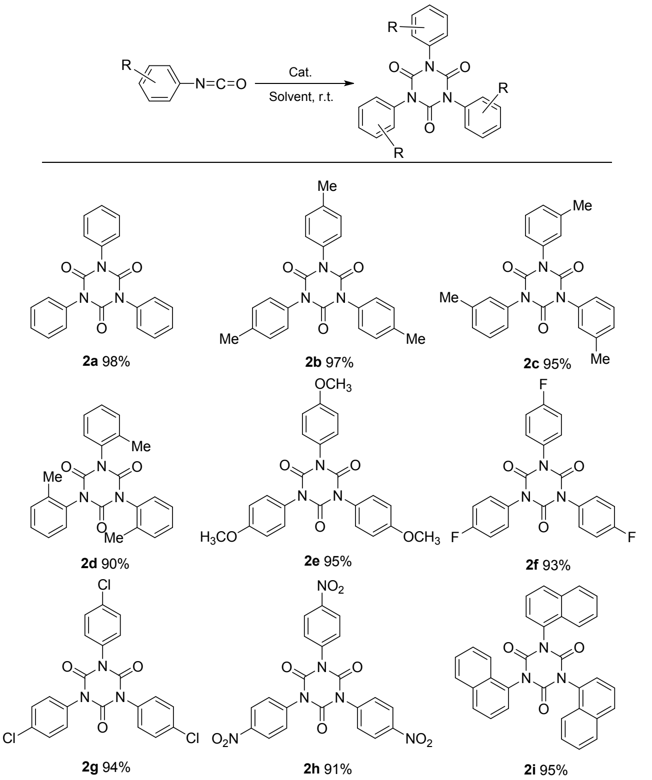


1a 2a

Entry	Catalyst loading (mol %)	Solvent	Time (h)	Yield (%)[b]
1	1.0	Et_2O	0.5	99
2	1.0	THF	0.5	>99
3	1.0	PhMe	0.5	97
4	1.0	None	0.5	98
5	0.5	THF	0.5	>99
6	0.25	THF	0.5	>99
7	0.1	THF	0.5	96
8	0.1	THF	3	99
9	0.05	THF	3	98
10	0.025	THF	3	95
11[c]	0.05	THF	3	92

[a]Reaction conditions: isocyanate (30 mmol), room temperature, complex **1** as catalyst. [b]Isolated yield. [c]Complex **2** as catalyst.

Scheme 2 Substrate scope for cyclotrimerization of isocyanates[a]



2a 98% **2b** 97% **2c** 95%

2d 90% **2e** 95% **2f** 93%

2g 94% **2h** 91% **2i** 95%

[a]Reaction conditions: isocyanate (30 mmol), room temperature, 3 h, complex **1** as catalyst with 0.05% mol. [b]Isolated yield.

The cyclotrimerization of phenyl isocyanate to 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione worked well in various solvents at room temperature for 0.5 h in the presence of 1 mol% of the complex **1** (Table 1, entries 1-4), indicating the solvent compatibility of the catalysts though the best result was obtained when tetrahydrofuran was employed as solvent. Pleasingly, the title complexes could promote this reaction almost quantitatively at the 0.1 to 1.0 mol% loadings (Table 1, entries 5-8). It is worth noting that the cyclotrimerization reaction also can afford 95% isolated yield after 3h when the loading of catalyst is decreased to 0.025% (Table 1, entry 10). We also evaluated the catalytic behavior of complex **2** for cyclotrimerization of isocyanates. it also exhibited good activity

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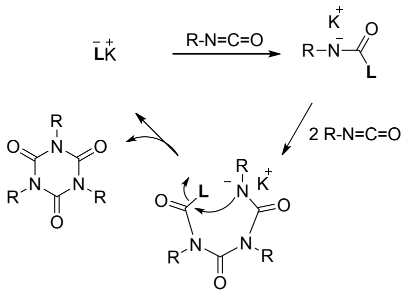
for catalytic reaction (Table 1, entry 11), giving the product yields over 90%.

Under the optimized reactions, the representative isocyanates were also examined using above complex **1** as a catalyst at 0.05 mol% loading (Scheme 2). The *para*-substituted isocyanates with electron-donating groups exhibited higher reactivity, and the corresponding isocyanurates were obtained over 95% yields (**2b, 2e**). Comparatively, the *para*-substituted isocyanates with electron-withdrawing groups are relatively inert, giving the desired products in 91-94% yield because of weak nuclephilicity (**2f**-**2g**). And the substrate with stronger electron-withdrawing group such as 4-nitrophenyl isocyanate also gave the corresponding product **2h**. In addition, the substituent groups at the *meta* or *ortho* positions of aromatic ring, as well as 1-naphthyl isocyanate, were well tolerated, the desired isocyanurates **2c**-**2d** and **2i** were isolated in moderate to excellent yields (90-95%), indicating that the electronic effects were not evident in this process.

General, this kind of potassium complex shows the higher activities in the cyclotrimerization of isocyanates. Their catalytic effects are superior to that of the corresponding lithium complex [Li{C_4H_3N(2-CH_2NH^tBu)}$_2$Li(THF)$_2$] (TON=980)[13b] and lanthanide complexes (TON=392)[22]. A proposed mechanism for the cyclotrimerization of isocyanates catalyzed by this complex would be similar to the reaction catalyzed by Lewis base (Scheme 3).[13b]



Scheme 3 Proposed mechanism for the cyclotrimerization of isocyanates.

Experimental

General

Unless otherwise noted, all syntheses and manipulations of air-sensitive materials were performed under a purified nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone under nitrogen. Hexane and toluene were dried using sodium potassium alloy and distilled under nitrogen prior to use. KH (30% dispersion in mineral oil) was purchased from Aldrich and washed with hexane (2x10 mL) in a Schlenk tube before used. All chemicals were sublimed, recrystallized or distilled before use. ^{1}H NMR (600 MHz), ^{13}C NMR (150.9 MHz) spectra of the compounds were recorded on a BRUKER AVANCE III 600MHz instrument at 298 K. Elemental analyses were performed on a Vario EL-III instrument. The ligand [C_4H_3NH(2-CH=N^{t}Bu)] and [C_4H_3NH(2-CH_2NH^tBu)] were synthesized according to the literature procedure.[13a]

Preparation of the Potassium complexes

Synthesis of [C_4H_3N(2-CH=N^{t}Bu)K(THF)]$_n$ (1).

A solution of [C_4H_3NH(2-CH=N^{t}Bu)] (0.450 g, 3.0 mmol) in THF (15 mL) was added slowly to a suspension of KH (0.12 g, 3.0 mmol) in THF (15 mL) at -78 °C, the reaction was warmed to room temperature and stirred overnight. The resulting solution was filtered and concentrated, followed by overnight storage at -10 °C afforded colorless, block-like X-ray quality crystals (0.478 g, 61%). Mp: 51 ^{o}C (dec). ^{1}H NMR (*d*-THF): 8.06 (d, J = 3.9 Hz, 1H, C*H*=N*tBu*), 6.86 (s, 1H, C_4H_3N), 6.33 (m, 1H, C_4H_3N), 6.02 (m, 1H, C_4H_3N), 3.58(s, 4H, THF), 1.73(s, 4H, THF), 1.25 (d, *J*= 3.8 Hz, 9H, N*Bu^t*); ^{13}C NMR (*d*-THF): 149.4 (*C*H=N^{t}Bu), 129.6 (C_4H_3N), 128.0(C_4H_3N), 114.5 (C_4H_3N), 107.7 (C_4H_3N), 67.1 (THF), 54.9 (*C*(CH_3)$_3$), 29.6(C(CH_3)$_3$), 25.2 (THF); Anal. Calcd for $C_{13}H_{22}KN_2O$: C, 59.73; H, 8. 48; N, 10.72. Found: C, 59.51; H, 8.13; N, 10.44.

Synthesis of [C_4H_3N(2-CH_2NH^tBu)K]$_n$ (2).

A solution of [C_4H_3NH(2-CH_2NH^tBu)] (0.457 g, 3.0 mmol) in THF (15 mL) was added slowly to a suspension of KH (0.12 g, 3.0 mmol) in THF (15 mL) at -78 °C, the reaction was warmed to room temperature and stirred overnight. The resulting solution was filtered and concentrated to a small amount and recrystallized to generate colorless, slice-like X-ray quality crystals (0.296 g, 52%). Mp: 73 ^{o}C (dec). ^{1}H NMR (C_6D_6+C_5D_5N): 8.92 (br, 1H, N*H*), 6.59(s, 2H, C_4H_3N), 6.36 (s, 2H, C_4H_3N), 6.19 (s, 2H, C_4H_3N), 3.58 (d, 2H, *J* = 7.5 Hz, C*H*$_2$NBu^t), 0.92 (s, 18H, CH_2N*Bu^t*); ^{13}C NMR (C_6D_6+C_5D_5N): 131.8 (C_4H_3N), 116.4 (C_4H_3N), 108.1 (C_4H_3N), 105.2 (C_4H_3N), 49.7 (*C*(CH_3)$_3$), 40.0 (*C*H$_2$NBu^t), 28.7 (C(CH_3)$_3$); Anal. Calcd for $C_{18}H_{30}K_2N_4$: C, 56.80; H, 7.94; N, 14.72. Found: C, 56.27; H, 7.71; N, 14.59.

Typical procedure for the catalytic reaction of isocyanate to isocyanurate

A 100 mL Schlenk flask was charged with potassium complexes (0.05 mol%) and 20 mL of tetrahydrofuran was added, then phenyl isocyanate (30 mmol) was added dropwise through a syringe with stirring. The solution became cloudy gradually and the white suspension was stirred at room temperature for 3 h after the addition was completed. The resulting suspension was concentrated under reduced pressure and washed with diethyl ether (3 x 10 mL), gave the corresponding isocyanurate as a white solid. All of the products were characterized by NMR techniques.

Conclusions

In summary, we have presented the synthesis and characterization of two potassium complexes incorporating 2-imino/aminopyrrolyl ligand. According to X-ray analysis, the synthesized complexes **1** and **2** are 1D zig-zag coordination polymer and 2D supramolecular network in the solid state,

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respectively. This work also represents rare example of the potassium complex supported by pyrrolide species in various coordination mode (η^1-η^5). Two potassium complexes exhibited very good catalytic activities for the cyclotrimerization of aryl isocyanate to 1,3,5-triaryl-1,3,5-triazinane-2,4,6-trione under mild conditions.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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Graphic Abstract

for

Potassium Complexes Containing Bidentate Pyrrole Ligands: Synthesis, Structures, and Catalytic Activity for the Cyclotrimerization of Isocyanates

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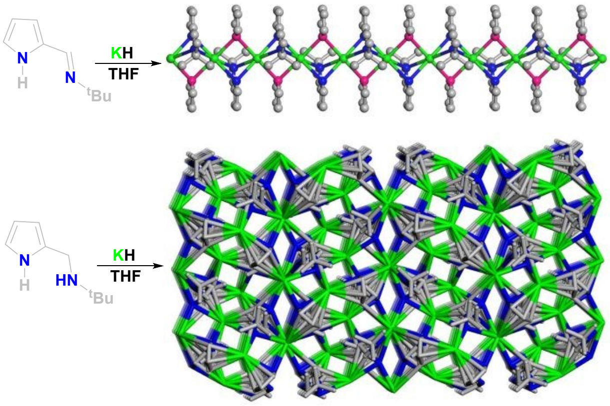

2-(*t*-Butyliminomethyl)pyrrole and 2-(*t*-butylaminomethyl)pyrrole react with KH to give potassium complexes with intriguing 1D zig-zag coordination polymer and 2D supramolecular network structures, respectively. They proved to be an effective class of catalysts for cyclotrimerization of isocyanate in excellent yield under mild conditions.