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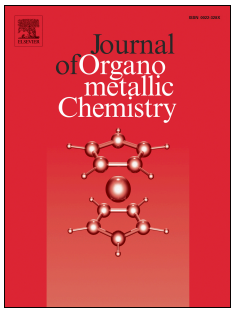

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Reactivity of 2-benzylpyridyl lithium toward benzonitrile derivatives: addition versus elimination

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Abstract

This work investigated the reactivity of 2-benzylpyridyl lithium (2-Pyr)C(Ph)(R)Li (R = $SiMe_3$, **Li1**; R = H, **Li2**) toward benzonitrile derivatives. Based on the different products, the reaction between lithium salts and nitriles might involve in addition, elimination and bimolecular coupling pathways, respectively. Treatment of **Li1** with ArCN (Ar = Ph, *p*-Tolyl, *o*-Tolyl, *p*-OMePh) yielded an addition intermediate pyridyl-1-aza-allyl-lithium $[\{(2\text{-Pyr})C(Ph)C(Ar)N(SiMe_3)\}Li]_2$ (**1,** Ar = Ph) and its corresponding hydrolysis product 2-benzylpyridyl-ketone **2**–**5**, respectively, in which the reaction involved in a 1,3-shift of $-SiMe_3$ group to form a dimeric pyridyl-1-aza-allyl-lithium then followed by acidic hydrolysis. The MeOLi elimination reaction between **Li2** and *p*-$MeO(C_6H_4)CN$ resulted in formation of 4-(2-benzylpyridyl)benzonitrile **6**. The reaction of **Li2** with *p*-$Me(C_6H_4)CN$ in the presence of TMEDA generated a 1:2 hydrolysis adduct 2-benzylpyridyl-enaminone **7**, however, in the absence of TMEDA it afforded a coupling product of bimolecular nitriles, 1-(4-methylphenyl)-2-cyanophenyl-ethanone **8**. We speculated the reaction mechanisms in sequence. The crystal structures of **1** and **5**–**8** were analyzed.

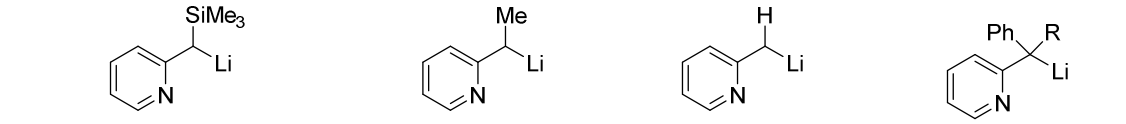
Keywords: 2-benzylpyridyl lithium; nitriles; addition; elimination; bimolecular coupling; silyl group migration.

1. Introduction

The insertion reaction of α-H-free aromatic nitriles into Li-C has been reported for its superiority of forming 1-azaallyls [1,2] and β-diketiminates [3,4]. Pyridyl-substituted azaallyls and β-diketiminates have attracted much more attention for the rigidity of N-heterocycle [5,6,7]. Berth-Jan Deelman and his co-workers have obtained trimethylsilyl-substituted [N,N] bidentate pyridyl-azaallyl ligands [7] and their zirconium complexes [8], which have good π-donating properties than the β-diketiminates [7]. In further studies, they synthesized a series of [N,N] bidentate chelating lithium complexes by the reaction of $-SiMe_3$ substituted pyridyl-alkyl lithium with different α-H free nitriles [6,7], the product existed as a dimeric structure. Zsuzsa Majer and co-workers have prepared a range of [N,O] bidentate nitrogen ligands, and further synthesized β-diketiminates [9]. Thomas C.W. Mak has afforded several group 14 metal-pyridyl-1-azaallyls as dimmers by the reaction of lithium pyridyl-1-azaallyl complex $[Li\{N(SiMe_3)C(Ph)C(R)(C_5H_4N\text{-}2)\}]_2$ [R = $SiMe_3$ or H] with group 14 metal halides, such as $[Ge\{C(C_5H_4N\text{-}2)C(Ph)N(SiMe_3)\}Cl_2]_2$, $[Sn\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2]$, $[Pb\{N(SiMe_3)C(Ph)C(SiMe_3)(C5H4N\text{-}2)\}_2]$ and $[\{(C_5H_4N\text{-}2)C(SiMe_3)C(Ph)N\}(\mu\text{-}SiHCl)]_2$ [5].

As mentioned above, $-SiMe_3$ substituted pyridyl-alkyl lithium (**Chart 1**, **A**) is often as the preferred reactant to produce pyridyl-azaallyls. We have also reported the addition of 2-(trimethylsilyl)pyridylmethyl lithium and nitriles to form pyridyl-1-azaallyllithium complexes $[\{2\text{-}(6\text{-}Me\text{-}Pyr)C(H)C(tBu)N(SiMe_3)\}Li]_2$, $[\{2\text{-}(6\text{-}Me\text{-}Pyr)C(H)C(Ph)N(SiMe_3)\}Li]_2$ and $[\{(2\text{-}Pyr)C(H)C(Ph)N(SiMe_3)\}Li]_2$ [10]. It implies that pyridyl-alkyl lithiums containing $-SiMe_3$ substituent may take nucleophilic addition reaction with nitriles more easily than those of lithium compounds without $-SiMe_3$ substituent, probably due to the $-SiMe_3$ group migrating easier than other alkyl or H atom.

Very recently, we investigated the reactions of 2-ethylpyridyl or 2-methylpyridyl lithium (**Chart 1**, **B** and **C**) without $-SiMe_3$ substituent reacts with nitriles, *in situ*, followed by acid hydrolysis to give β-pyridyl ketones 1-(2-pyridinyl)-2-propanone, 1-phenyl-2-(2-pyridinyl)-1-propanone and 1-(2-methylphenyl)-2-(2-pyridinyl)-1-propanone, *etc* [11], in which the reaction pathway involves in the intermediate adducts pyridyl-1-aza-allyl-lithiums.



(trimethylsilyl)methylpyridyl lithium[10] | ethylpyridyl lithium[11] | methylpyridyl lithium[11] | benzylpyridyl lithiums (R = H, $SiMe_3$) this work

A **B** **C** **D**

Chart 1. Different substituted pyridyl lithiums.

Now, we are interested in 2-benzylpyridyl lithiums (**Chart 1**, **D**) and their reactivity with nitriles. According to reports in the literature, 2-benzylpyridine has been widely studied due to the activity of C(sp^3)-H bonds between the two aromatic rings, such as α-methylenation of benzylpyridines [12], Oxidative Carbonylation [13], N,C-metallization [14], nucleophilic addition of 2-benzylpyridyl lithium and ketones [15]. Nevertheless, influenced by different properties of substituents and external conditions, the reaction of 2-benzylpyridyl lithium and ArCN usually exerts various mechanisms except addition. The diverse substituents of nitriles and less optimum conditions may give rise to elimination or bimolecular coupling outcomes [16] instead of addition products, especially when the electron-donating group is absent in the benzylpyridyl lithium.

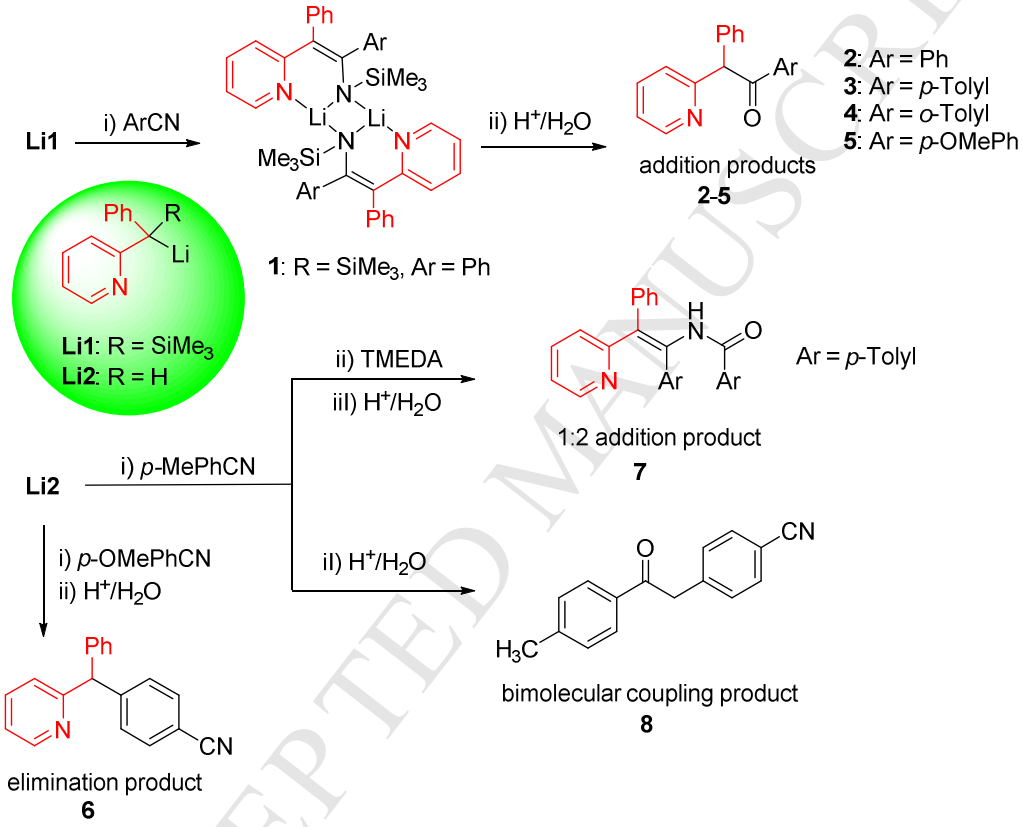
Herein, the present work complements the previous 2-(2-Pyr)C$(R)_2$Li/nitrile insertion investigations by extending the system to include reactions of the carbon anion prepared by the in situ lithiation of the hitherto unknown 2-benzylpyridyl ligand, (2-Pyr)C(Ph)(R)Li (R = $SiMe_3$, **Li1**; R = H, **Li2**) (**Chart 1**, **D**), with ArCN (Ar = Ph, *p*-Tolyl, *o*-Tolyl, *p*-OMePh). Full details on the synthesis and characterization of insertion, elimination and bimolecular coupling compounds are provided.

2. Results and discussion

2.1. Reactions of (2-Pyr)C(Ph)(R)(Li) with ArCN

The general synthesis route for compounds **1**–**8** are illustrated in **Scheme 1**. The starting lithium compounds (2-Pyr)C(Ph)(R)(Li) (R = $SiMe_3$, **Li1**; R = H, **Li2**) were prepared by lithiation of 2-[(2-trimethylsilyl)-benzyl]pyridine [17] and 2-benzylpyridine with ^{n}BuLi, respectively. The dimeric pyridyl-1-aza-allyllithiums were prepared by the addition of **Li1** with ArCN (Ar = Ph, *p*-Tolyl, *o*-Tolyl, *p*-OMePh), respectively, but only [{(2-Pyr)C(Ph)C(Ph)N($SiMe_3$)}Li]$_2$ (**1**) was

isolated. However, their corresponding hydrolysis products 2-benzylpyridyl-ketones (2-Pyr)C(H)(Ph)(CO)Ph (**2**), (2-Pyr)C(H)(Ph)(CO)(4-Me-Ph) (**3**), (2-Pyr)C(H)(Ph)(CO)(2-Me-Ph) (**4**) and (2-Pyr)C(H)(Ph)(CO)(4-OMe-Ph) (**5**) were obtained in high yields. The elimination product (2-Pyr)C(H)(Ph)(4-CNPh) (**6**) was synthesized by the reaction of **Li2** with ArCN (Ar = *p*-OMePh) *via* the intermolecular elimination of MeOLi. (2-Pyr)-C(Ph)C(4-Me-Ph)N(H)(CO)(4-Me-Ph) (**7**) was given by 1:2 addition of **Li2** with ArCN (Ar = *p*-Tolyl). Bimolecular coupling of *p*-MePhCN generated (4-Me-Ph)(CO)C(H)(H)(4-CN-Ph) (**8**).

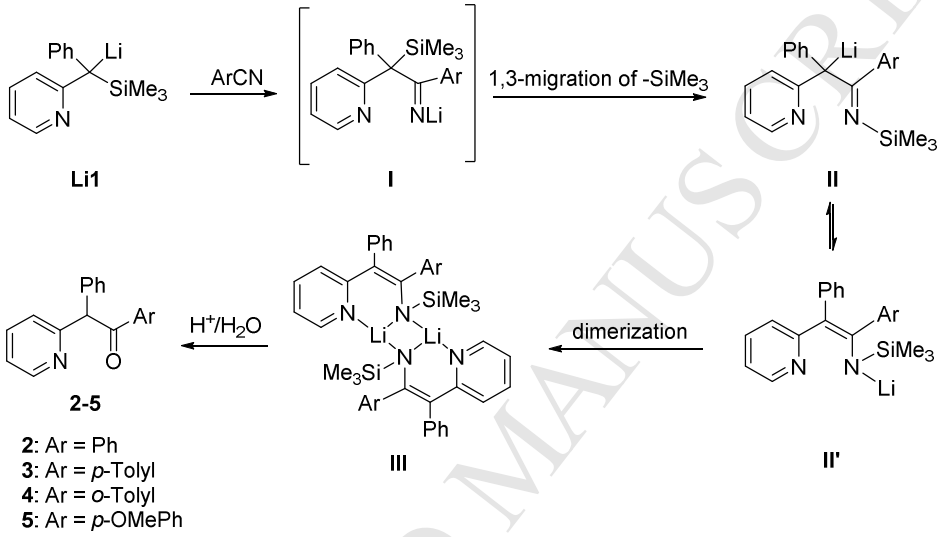


Scheme 1. Synthesis of the compounds **1**–**8**.

*2.2. Synthesis and reaction pathways of compounds **1**–**5***

Li1 reacts with an equiv. of ArCN to yield the adduct compounds **1**–**5**. Dimeric pyridyl-1-aza-allyl-lithiums **1** was prepared by insertion reaction of **Li1** with PhCN in a 1:1 molar ratio in Et_2O for 48 h, and was isolated as orange red crystalline solids **1**·toluene in a high yield of 96% at room temperature, then followed by acidic hydrolysis to give 2-benzylpyridyl-ketone **2** in 83.6% yield (**Scheme 1**). Similarly, 2-benzylpyridyl-ketones **3**–**5** were derived from **Li1** and *p*-(Me)PhCN, *o*-(Me)PhCN and *p*-(OMe)PhCN as yellow solids in 82.4%, 66.6% and 29.1% yield, respectively. Such a reaction involved a 1,2-insertion of the ArCN into the Li-C bond to generate

an intermediate **I** as well as a 1,3-trimethylsilyl migration to form a tautomeric azaallyls **II** and **II'**, **III** was obtained by dimerization of **II'**, followed by acidic hydrolysis to afford **2**–**5** (**Scheme 2**). This method was related to that previously employed in synthesis of other pyridyl azaalyl complexes, *e.g.* pyridyl-1-azaallyllithium complexes [{2-(6-Me-Pyr)C(H)C(R)N($SiMe_3$)}Li]$_2$ [R = *t*Bu or Ph] or [{(2-Pyr)C(H)C(Ph)N($SiMe_3$)}Li]$_2$ [10], 2,6-pyridyl-linked bis(1-azaallyl) and 2,3-pyrazyl-linked bis(1-azaallyl)alkalimetal compounds [18,19]. Furthermore, a series of derived pyridyl-1-azaallyl low-valent group 14 compounds were described [5,20,21].



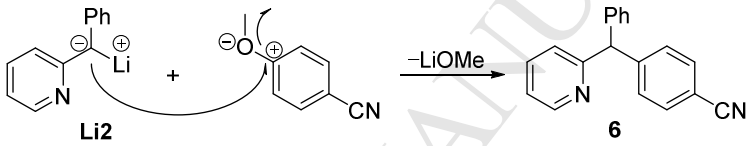
Scheme 2. Proposed pathway for the formation of **2**–**5**.

Compound **1** is extremely air- and moisture-sensitive. It is soluble in THF and Et_2O, but poor solubility in toluene and hexane. It was isolated as an orange crystalline suitable for X-ray diffraction study in toluene at – 30 ºC for three days. Compounds **2**–**5** were obtained as yellow solids after purification by a flash chromatography, and **5** was crystallized as yellow crystals from mixture of Et_2O and hexane at room temperature. Compounds **2**–**5** are slightly air-sensitive or stable. Most commonly, these compounds exist in two tautomers: enol and ketone, depending on the substituent in the molecule [11]. However, the ^{1}H NMR spectra of **2**–**5** show no resonance signals of enol protons O*H* appearing in the range of 14–15 ppm, which confirmed they exist as the ketone form alone.

*2.3. Synthesis and reaction pathways of compounds **6**–**8***

In contrast, **Li2** reacts with ArCN to provide a variety of products **6**–**8**, depending on the reaction substrates and the presence or absence of TMEDA (**Scheme 1**). An elimination product **6**

towards the reaction of **Li2** with *p*-(OMe)PhCN was synthesized accidentally. When an equiv. of *p*-(OMe)PhCN was added to the solution of **Li2** in THF, *in situ* the mixture was suffered to acid hydrolysis and purified by column chromatography, a white solid **6** was obtained in 33.5% yield. The possible mechanism for the formation of **6** was shown in **Scheme 3**. It depicts that Li atom was more electropositive while −OMe group was to the contrary, the carbanion on benzylpyridyl lithium attacked electropositive aromatic-C and an intermolecular elimination reaction between **Li2** and *p*-(OMe)PhCN was apt to come up to form **6** via elimination of LiOMe, which may be due to the –OMe group more likely to leave when existence of a electron-withdrawing group. This is consistent with the reaction of ortho-methoxy group in 1- and 2- naphthoic acids with organolithium to produce a substitution product concomitantly with elimination of methoxyl lithium [22].

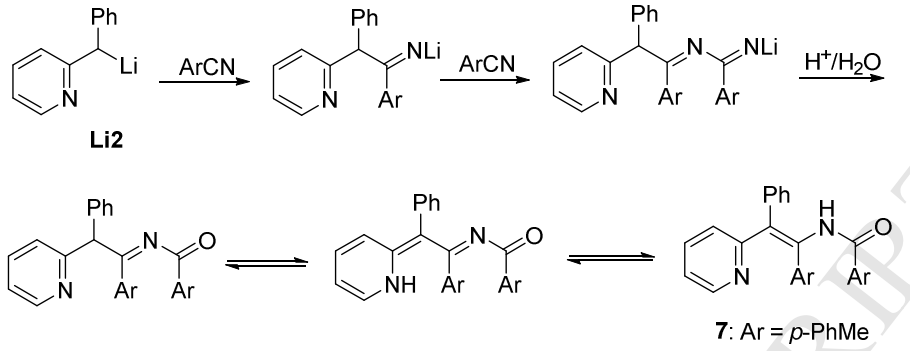


Scheme 3. Possible mechanism for the formation of **6**.

When the reaction of **Li2** with *p*-(Me)PhCN was carried out in the presence of TMEDA, followed by acid hydrolysis, adduct compound **7** was given as a yellow solid in 26% yield; but the same reaction in the absent of TMEDA, coupling product **8** was obtained as a white solid in 64.2% yield. Crystals of **7** and **8** suitable for X-ray diffraction study were grown from a concentrated CH_2Cl_2 solution at room temperature for 3 days, respectively.

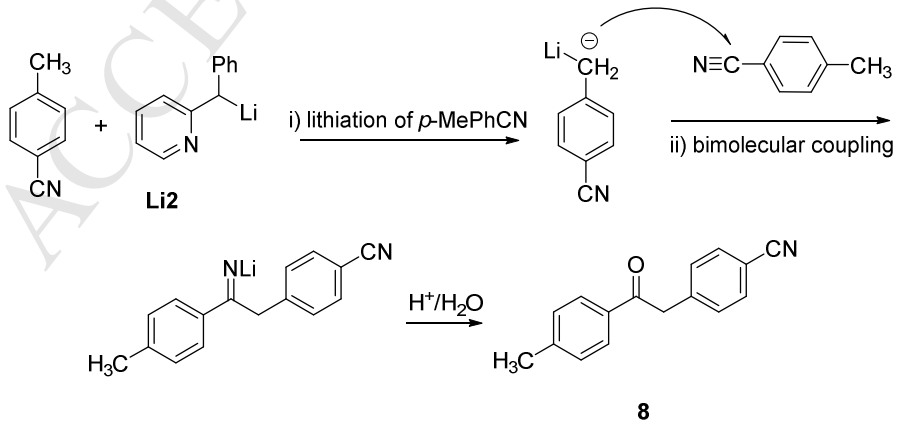
By analyzing the structure of **7**, it is a 1:2 adduct which bearing a large conjugated structure instead of the 1-azaallyllithiums as anticipated. As it reported in the literature, TMEDA as an amine component reagent [23] can effectively preclude secondary oligomerizing interactions and produce monomeric or dimeric lithium complex, which increases the carbanionic reactivity distinctly. Therefore, nucleophilic carbanion of 2-benzylpyridyl-lithium is an attack on ArCN to yield an intermediate 1-azaallyl lithium, a second attack ArCN to give another intermidiate 1,3-diazaallyl lithium, undergoing hydrolysis to afford a conjugated product which exists as three tautomers: pyridyl-imino ketone, 1,2-(dihydropyridyl)-imino ketone and pyridyl-enaminone (**Scheme 4**). X-ray crystallography and the ^{1}H NMR spectra (resonance signal of N*H* proton appearing at δ 14.54 ppm) demonstrated that compound **7** presented in the form of

pyridyl-enaminone. The pathway is comparable to the previousely reported reaction of $LiCH(SiMe_3)_2$ with PhCN in a 1:2 M ratio to yield the 1,3-diazaallyl lithium [24,25].



Scheme 4. Reaction pathways for the formation of **7**.

Unexpectedly, compound **8** is the hydrolyzate of bimolecular ArCN coupling product. We suggest the formation of **8** as shown in **Scheme 5**. i) Lithiation of *p*-(Me)PhCN occurred by **Li2** firstly to yield [(4-cyanophenyl)methyl]-lithium, ii) a C-centered nucleophile adds to ArCN proceeding C-C coupling to give an intermediate lithioimine, followed by acidic hydrolysis to yield **8**. It illustrates that with the nonparticipation of TMEDA, the insertion reaction of **Li2** with ArCN (Ar = *p*-Tolyl) was difficult to occur. It may be owing to **Li2** existence as an oligomer, which reduced its nucleophilic reactivity, by contrast, the lithiation of alkyl-substituted arenes is come up quickly [23]. Meanwhile, it may be that α-hydrogen of alkyl-substituted arenes is active enough to react with organolithium under the strong electron-withdrawing effect of –CN, and form the constitutionally stable carbanion which is effective to couple another *p*-tolunitrile molecular.



Scheme 5. Possible mechanism for the formation of **8**.

*2.4. Crystal structures of compounds **1**, **5**, **6**, **7** and **8***

The molecular structure of **1** (the molecule of toluene has been omitted) is illustrated in **Fig. 1**, the selected bond distances and bond angles are shown in **Table 1**.

The lithium compound **1** exists as the centrosymmetric dimer. Each Li atom is three-coordinated with N [2.029(3) Å, 2.068(4) Å, 1.993(3) Å (Li1-N1^{i}, Li1-N2^{i}, Li1-N2)]. The diatance of Li1-N2 is shorter than that of Li1-N1^{i} and Li1-N2^{i}, and is also shorter than that found in the pyridyl-substituted 1-azaallyl [{2-(6-Me-Pyr)C(H)C(tBu)N(SiMe$_3$)}Li]$_2$ [Li-N=2.207(4) Å] [10]. The distance of Li1 atom to pyridine nitrogen N1^{i}[Li1-N1^{i} =2.029(3) Å] is slight longer than that found in the lithium β-diketiminate [Li{N(SiMe$_3$)C(Bu^{t})C(H)C(Ph)N(SiMe$_3$)}]$_2$[1.970(2) Å] [26]. The distance of Li1 atom to enamine nitrogen N2^{i}[Li1-N2^{i} =2.068(4) Å] is longer than that found in the 1,3-diazaallyllithium complexes [Li{N(R)C(Ph)NC(Ph)=C(H)R}(thf)]$_2$[Li-N=1.990(1)] [26]. The atoms of Li1, N2^{i}, Li1^{i}, N2 form a four-membered ring and they are coplanar. Steric-hindrance effect results from the aryl groups of **1** generates a distorted six-membered ring Li1^{i}N1C5C6C13N2, which is similar to the structure of pyridyl-1-azaallyllithium [{2-(6-Me-Pyr)C(H)C(tBu)N(SiMe$_3$)}Li]$_2$ [10]. Li1^{i}N2C13 is planar, and forming a dihedral angle of 62.83(0.12)° to the planar Li1^{i}N1C5C13. The distance of C6 to the planar Li1^{i}N1C5C13 is 0.3600 (0.0028) Å.

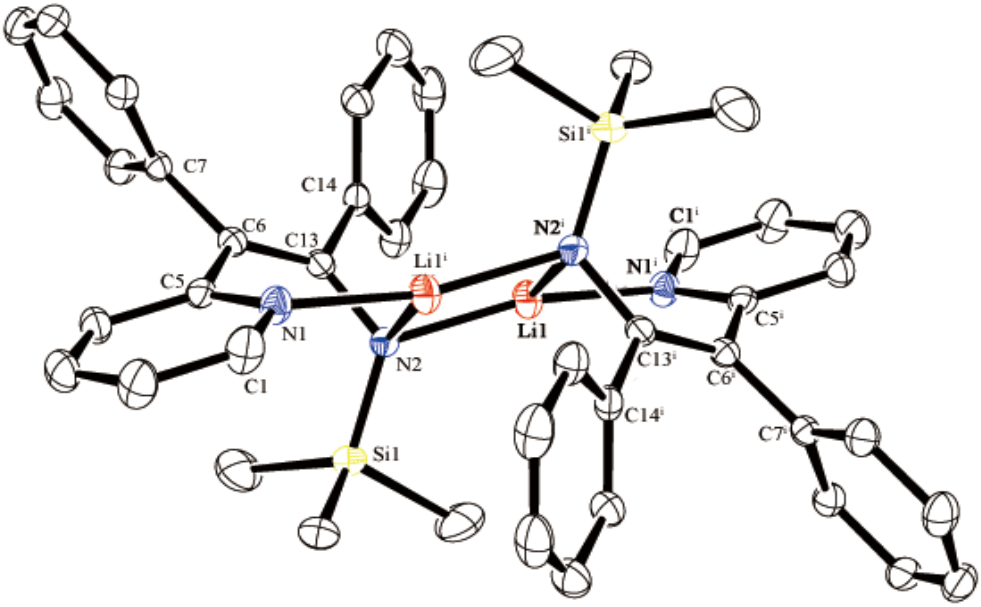


Fig. 1. Molecular structure of compound **1**.

Table 1

Selected bond lengths (Å) and angles (°) for complex **1**.

Li(1)-N(2)	1.993(3)	Li(1)^{i}-N(2)^{i}	1.993(3)
Li(1)-N(1)^{i}	2.029(3)	Li(1)^{i}-N(1)	2.029(3)
Li(1)-N(2)^{i}	2.068(4)	Li(1)^{i}-N(2)	2.068(4)
N(1)-C(5)	1.355(2)	N(2) -Si(1)	1.7071(15)
N(1)-C(1)	1.347(2)	N(2)-C(13)	1.388(2)
C(5)-C(6)	1.485(2)	C(6)-C(13)	1.374(2)
N(2)-Li(1)-N(2)^{i}	100.91(14)	N(1)^{i}-Li(1)-N(2)^{i}	96.67(14)
N(2)-Li(1)-N(1)^{i}	160.74 (19)	C(6)-C(13)-N(2)	125.91(15)
N(1)-C(5)-C(6)	118.17(14)	C(5)-N(1)-Li(1)^{i}	111.99(14)
C(13)-C(6)-C(5)	122.45(15)	N(2)-C(13)-C(14)	113.80(14)
C(13)-N(2)-Si(1)	124.40(12)	C(13)-N(2)-Li(1)	108.88(14)
C(13)-N(2)-Li(1)^{i}	92.64(13)	C(1)-N(1)-Li(1)^{i}	127.29(16)
Si(1)-N(2)-Li(1)	121.73(12)	Si(1)-N(2)-Li(1)^{i}	116.85(12)
Li(1)-N(2)-Li(1)^{i}	79.09(14)		

The molecular structure of **5** is illustrated in **Fig. 2**, the selected bond distances and bond angles are shown in **Table 2**.

Compound **5** consists of three six-membered rings. The bond length of C13-O2 [1.219(3) Å] is confirmed as C=O bond. The distance of C17-O1[1.361(3) Å] is shorter than that of C20-O1[1.442(4) Å], it may due to the p-π conjugation between O1 and benzene. The angle of C17-O1-C20 is 117.3(2)°. The atoms of C20, O1, C13, O2 and benzene with C14, C17 in it are coplanar, and respectively, forming a dihedral angle of 58.29(0.07)°, 78.57(0.08)° with the benzene contains C6 in it and the pyridine ring.

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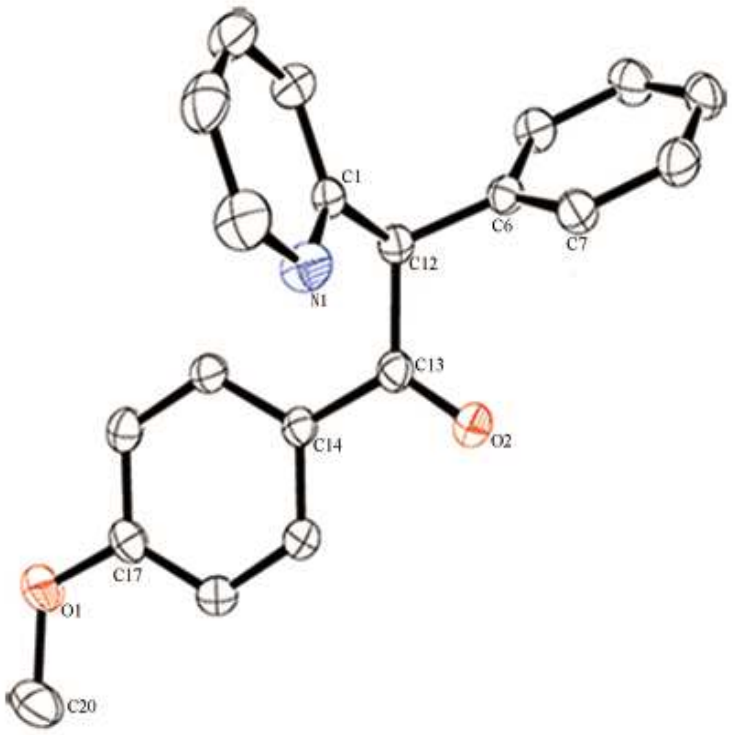

Fig. 2. Molecular structure of compound **5**.

Table 2

Selected bond lengths (Å) and angles (°) for complex **5**.

N(1)-C(1)	1.330(3)	C(12)-C(1)	1.523(3)
C(12)-C(6)	1.523(3)	C(6)-C(7)	1.382(3)
C(13)-C(12)	1.538(3)	C(14)-C(13)	1.488(3)
O(2)-C(13)	1.219(3)	O(1)-C(17)	1.361(3)
O(1)-C(20)	1.442(4)		
N(1)-C(1)-C(12)	118.0(2)	C(6)-C(12)-C(1)	110.15(19)
C(6)-C(12)-C(13)	113.54(19)	O(2)-C(13)-C(12)	120.8(2)
O(2)-C(13)-C(14)	120.4(2)	C(14)-C(13)-C(12)	118.8(2)
C(17)-O(1)-C(20)	117.3(2)		

The molecular structure of **6** is illustrated in **Fig. 3**, the selected bond distances and bond angles are shown in **Table 3**.

Compound **6** consists of three six-membered rings. The bond angle of C16-C19-N2 is almost close to linear [179.1(3)°]. The cyclobenzene with C16 in it and the atoms of C6, C19, N2 are in

the same plane, and respectively, forming a dihedral angle of 76.82(0.09)°, 77.53(0.10)° with the benzene contains C7 in it and the pyridine ring. The distance between C19 and N2 is 1.136(3) Å, which is demonstrated as C≡N bond.

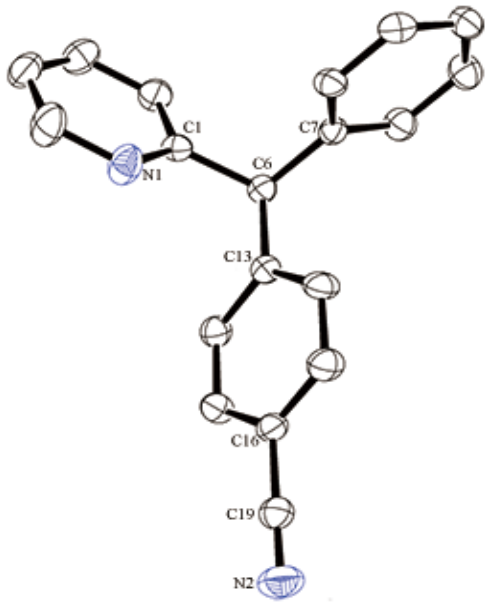

Fig. 3. Molecular structure of compound **6**.

Table 3

Selected bond lengths (Å) and angles (°) for complex **6**.

N(1)-C(1)	1.335(3)	C(6)-C(1)	1.525(4)
C(6)-C(7)	1.529(4)	C(13)-C(6)	1.524(3)
C(19)-C(16)	1.449(4)	N(2)-C(19)	1.136(3)
C(1)-C(6)-C(7)	110.4(2)	C(13)-C(6)-C(7)	113.8(2)
N(2)-C(19)-C(16)	179.1(3)		

The molecular structure of **7** is illustrated in **Fig. 4**, the selected bond distances and bond angles are shown in **Table 4**.

Compound **7** contains four six-membered rings. Respectively, the bond lengths of C21-O1 [1.218(2) Å], N(2)-C(21) [1.366(2) Å], C21-C22 [1.496(2) Å], C7-N2 [1.395(2) Å], C6-C7 [1.368(2) Å], C1-C6 [1.485(2) Å], C1-N1 [1.345(2) Å], indicating that a *p*,π-electron conjugation among the structure framework N1=C1−C6=C7−N2−(C21=O1)−C22. The pyridine ring and C6, C7, N2 are coplanar. The atom of C21 is with a deviation of 0.5061 (0.0033) Å to the planar. The

structure of **7** is distorted because of the steric hinerance from four six-membered rings. The dihedral angle of pyridine ring and cyclobenzene with C8 in it is 73.21(0.08)°.

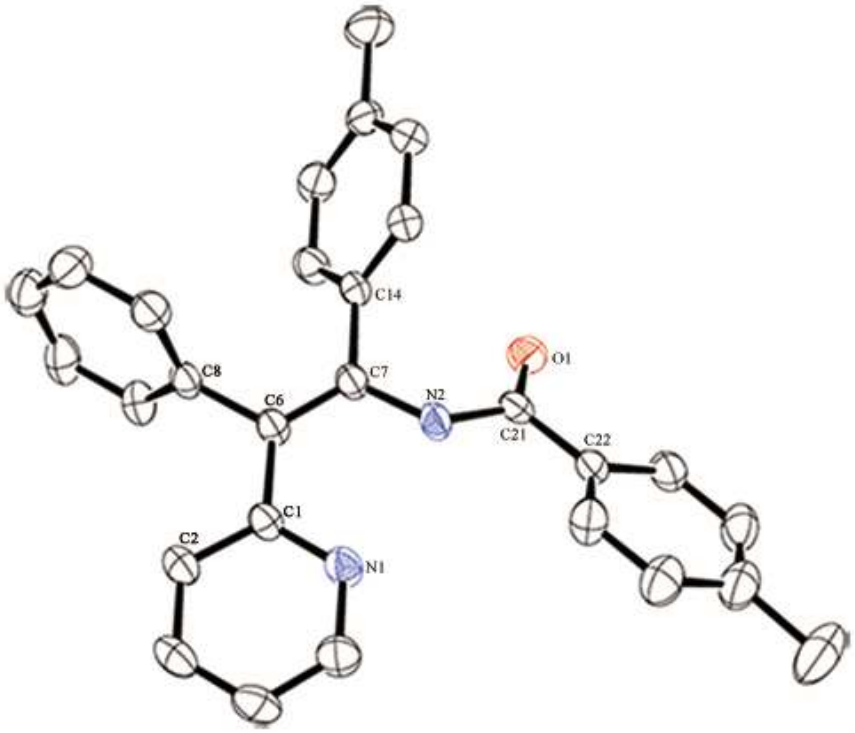

Fig. 4. Molecular structure of compound **7**.

Table 4

Selected bond lengths (Å) and angles (°) for complex **7**.

N(1)-C(1)	1.345(2)	C(1)-C(6)	1.485(2)
C(6)-C(8)	1.495(2)	C(6)-C(7)	1.368(2)
N(2)-C(7)	1.395(2)	N(2)-C(21)	1.366(2)
O(1)-C(21)	1.218(2)	C(21)-C(22)	1.496(2)
C(14)-C(7)	1.485(2)		
N(1)-C(1)-C(6)	118.78(14)	C(1)-C(6)-C(8)	116.01(13)
C(7)-C(6)-C(1)	124.94(15)	N(2)-C(7)-C(14)	116.44(13)
C(21)-N(2)-C(7)	129.29(15)	O(1)-C(21)-N(2)	123.80(17)
N(2)-C(21)-C(22)	114.11(15)	O(1)-C(21)-C(22)	122.08(16)

The molecular structure of **8** is illustrated in **Fig. 5**, the selected bond distances and bond angles are shown in **Table 5**.

Compound **8** is composed of two cyclobenzenes. The distance of C9-O1 is 1.214(2) Å, which is comparable to the bond lengths of C=O bond. C9-O1 and the cyclobenzene which contain C10 in it are in the same plane, it is suggested that they are conjugated. The bond length of C1-N1[1.141(2) Å] is confirmed as C≡N bond. The dihedral angle of two cyclobenzenes is 58.66 (0.05)°.

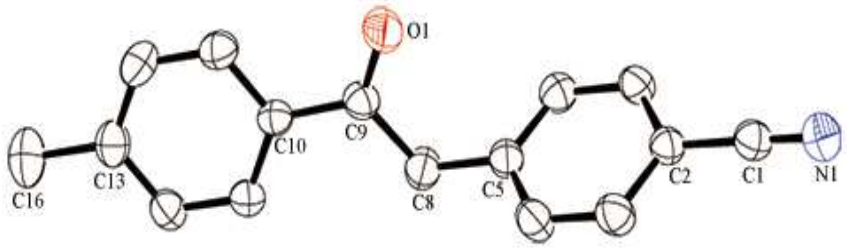

Fig. 5. Molecular structure of compound **8**.

Table 5

Selected bond lengths (Å) and angles (°) for complex **8**.

N(1)-C(1)	1.141(2)	C(1)-C(2)	1.442(3)
C(5)-C(8)	1.500(3)	C(9)-C(8)	1.510(3)
C(10)-C(9)	1.483(3)	C(9)-O(1)	1.214(2)
N(1)-C(1)-C(2)	177.8(2)	C(5)-C(8)-C(9)	115.37(16)
O(1)-C(9)-C(8)	120.64(18)	O(1)-C(9)-C(10)	120.81(17)

3. Conclusions

To summarize, reactivity of 2-benzylpyridyl lithium toward benzonitrile derivatives have been investigated and discussed. Very different from the 2-alkylpyridyl lithiums, when 2-benzylpyridyl lithium reacts with nitriles, it could give addition, elimination and bimolecular coupling products based on the substituent of carbanion. The reaction of 2-[(2-trimethylsilyl)-benzyl]pyridyl-lithiums and ArCN gave the addition products. Reaction between 2-benzylpyridyl-lithiums and ArCN may give rise to three different kinds of products: when TMEDA was added into the system, a 1:2 adduct was generated, but in the absence of TMEDA, a coupling product of bimolecular nitriles was obtained, and an elimination product was came up when methoxyl nitrile *p*-MeO(C_6H_4)CN reacts with 2-benzylpyridyl-lithium.

4. Experimental

4.1. General

All manipulations were performed under nitrogen atmosphere by standard Schlenk techniques. Solvents were dried with sodium, and distilled from sodium, and stored over molecular sieves (4 Å). Deuterated solvents were dried with sodium/potassium alloy (C_6D_6) and molecular sieves (4 Å) ($CDCl_3$). All chemicals were purified by distillation. 2-Benzylpyridine, trimethylchlorosilane, benzonitrile, *o*-tolunitrile, *p*-tolunitrile, 4-methoxybenzonitrile and n-butyllithium in hexane (2.5 M) were purchased from energy chemical. ^{1}H and ^{13}C NMR spectra were performed with a Bruker DRX−300 MHz spectrometer. Elemental analyses were performed with a Vario EL−III instrument.

*4.2. Synthesis of **1***

^{n}BuLi (4.02 mL, 2.5 M, 10.00 mmol) was added to the solution of 2-[(2-trimethylsilyl)-benzyl]pyridine (2.48 mL, 10.00 mmol) in Et_2O (30 mL) at 0 ℃, the orange-red solution was restored upto room temperature and stirred for 24 h. Benzonitrile (1.02 mL, 10.00 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red solution mixture. The solvents of residue were removed in vacuo to give a dark red solid, and recrystallized as orange crystals in toluene at −30℃ for three days. Yield: 3.36 g (96%). ^{1}H NMR (C_6D_6, TMS, 300MHz): δ(ppm) 8.63(d, 2H, Py−H), 7.83(d, 4H, Ar−H), 7.41−7.57(m, 18H, Py−H and Ar−H), 7.24-7.30(m, 4H, Py−H and Ar−H), 0.08[s, 9H, $Si(CH_3)_3$]. ^{13}C NMR(C_6D_6, TMS, 75MHz): δ(ppm) 155.7, 149.6, 137.0, 122.7, 120.9 (Py−C), 140.0, 134.2, 128.6, 128.3, 127.9 (Ar−C), 140.5, 112.8 (C=C), 17.7 (−CH_3). Anal. Calcd for $C_{44}H_{46}Li_2N_4Si_2 \cdot C_7H_8$: C, 77.24; H, 6.86; N, 7.06. Found: C, 77.21; H, 6.88; N, 7.03.

*4.3. Synthesis of **2***

Enough distilled water was added to the solution of **1** (2.12 g, 3.02 mmol) in Et_2O (30 mL) at 0 ℃ and stirred for 24 h, followed by extraction with dichloromethane (50 mL×3). The yellow subnatant was collected and dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a yellow solid was purified by column chromatography. Yield: 1.38 g (83.6%). M.p.

132 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300MHz): δ(ppm) 8.44 (d, 1H, Py−H), 8.00(d, 2H, Ar−H), 7.55−7.68(m, 4H, Py−H and Ar−H), 7.37−7.38 (m, 4H, Py−H and Ar−H), 7.11(t, 1H, Py−H), 7.21 (m, 2H, Ar−H), 5.56 (s, 1H, −CH−). ^{13}C NMR ($CDCl_3$, TMS, 75MHz): δ(ppm) 162.25 (C=O), 150.12, 147.41, 137.21, 136.23, 133.11, 130.38, 128.33, 128.12, 126.29, 125.57, 122.28, 118.09 (Ar−C and Py−C), 54.32 (−CH−). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.45; H, 5.62; N, 5.09.

*4.4. Synthesis of **3***

^{n}BuLi (4.25 mL, 2.5 M, 10.48 mmol) was added to the solution of 2-[(2-trimethylsilyl)-benzyl]pyridine (2.60 mL, 10.48 mmol) in Et_2O (30 mL) at 0 ℃, the orange-red solution was restored upto room temperature and stirred for 24 h. *p*-Tolunitrile (2.38 g, 10.48 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red solution mixture. Just enough distilled water was added to hydrolyze the above product, followed by extraction with dichloromethane (50 mL×3). The yellow subnatant was collected and dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a yellow solid was purified by column chromatography. Yield: 2.48 g (82.4%). M.p. 162.6 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300MHz): δ(ppm) 8.45 (d, 1H, Py−H), 7.17−7.33 (m, 2H, Py−H), 7.07−6.89 (m, 9H, Py−H and Ar−H), 6.78−6.82 (t, 1H, Ar−H), 6.59 (d, 1H, −CH−), 2.24 (s, 3H, Ar−CH_3). ^{13}C NMR ($CDCl_3$, TMS, 75MHz): δ(ppm) 162.29 (C=O), 150.09, 147.45, 137.15, 136.27, 133.03, 130.42, 128.38, 128.16, 126.33, 125.63, 122.31, 118.12 (Ar−C and Py−C), 30.38 (−CH−), 20.16 (−CH_3). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.55; H, 5.98; N, 4.91.

*4.5. Synthesis of **4***

^{n}BuLi (4.01 mL, 2.5 M, 10.00 mmol) was added to the solution of 2-[(2-trimethylsilyl)-benzyl]pyridine (2.48 mL, 10.00 mmol) in Et_2O (30 mL) at 0 ℃, the orange-red solution was restored upto room temperature and stirred for 24 h. *o*-Tolunitrile (1.18 mL, 10.00 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red solution mixture. Just enough distilled water was added to hydrolyze the above product, followed by extraction with dichloromethane (50 mL×3). The

yellow subnatant was collected and dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a light yellow solid was purified by column chromatography. Yield: 1.91 g (66.6%). M.p. 145~149 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 8.52 (d, 1H, Py–H), 7.35 (t, 1H, Pyr−H), 7.24 (s, 1H, Py–H), 7.01 (m, 9H, Pyr−H and Ar−H), 6.86 (t, 1H, Ar−H), 6.66 (d, 1H, −CH−), 2.31 (s, 3H, Ar−CH_3). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ(ppm) 162.27 (C=O), 150.11, 147.44, 141.35, 140.50, 136.24, 133.02, 130.40, 128.38, 126.34, 125.65, 122.32, 118.14, 108.04 (Ph−C and Py−C), 30.39 (−CH−), 20.21 (−CH_3). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.56; H, 5.93; N, 4.93.

*4.6. Synthesis of **5***

^{n}BuLi (7.01 mL, 2.5 M, 15.75 mmol) was added to the solution of 2-[(2-trimethylsilyl)-benzyl]pyridine (3.80 mL, 15.75 mmol) in Et_2O (30 mL) at 0 ℃, the orange-red solution was restored upto room temperature and stirred for 24 h. 4-Methoxybenzonitrile (3.83 g, 15.75 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red solution mixture. Just enough distilled water was added to hydrolyze the above solution, followed by extraction with dichloromethane (50 mL×3). The yellow subnatant was collected and dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a yellow solid was purified by column chromatography. The product was crystallized as yellow crystals from mixture of Et_2O and n-hexane at room temperature. Yield: 1.38 g (29.1%). M.p. 195.4 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 8.42 (d, 1H, Py-H), 7.12−7.25 (m, 2H, Py−H), 7.02−6.78 (m, 9H, Py−H and Ar−H), 6.65−6.74 (t, 1H, Ar−H), 6.56(d, 1H, −CH−), 2.21 (s, 3H, Ar−CH_3). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ(ppm) 162.22 (C=O), 150.03, 147.42, 137.11, 136.23, 133.01, 130.38, 128.35, 128.13, 126.32, 125.61, 122.29, 118.11 (Ar−C and Py−C), 30.32 (−CH−), 20.12 (−CH_3). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.22; H, 5.66; N, 4.57.

*4.7. Synthesis of **6***

^{n}BuLi (23.95 mL, 2.5 M, 59.87 mmol) was added to the solution of 2-benzylpyridine (4.00 mL, 24.95 mmol) in THF (100 mL) at 0 ℃, the red suspension was restored upto room temperature and stirred for 24 h. 4-Methoxybenzonitrile (3.32 g, 24.95 mmol) was added to the

mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red clear solution mixture. After the acid hydrolysis of 60% H_2SO_4 solution under the condition of ice bath until pH=1, neutralized with saturated NaOH until pH=7, amount of solid arised in the process and dissolved by just enough distilled water, followed by extraction with dichloromethane (100 mL×3). The mixture was dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a white solid was purified by column chromatography. The product was crystallized as colorless crystals from mixture of EtOAc and n-hexane at room temperature. Yield: 2.26 g (33.5%). M.p. 87 ℃. ^{1}HNMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 8.57 (s, 1H, Py−H), 7.54 (m, 3H, Ar−H), 7.05 (m, 9H, Py−H and Ar−H), 6.86 (t, 1H, Ar−H), 5.69 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ(ppm) 162.67, 150.59, 149.32, 142.34, 138.20, 133.33, 131.30, 130.37, 129.90, 128.28, 125.08, 123.14, 120.00 (Ar−C and Py−C), 111.62 (−CN), 60.08 (−CH−). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.46; H, 5.20; N, 10.34.

4.8. Synthesis of ***7***

^{n}BuLi (24.00 mL, 2.5 M, 60.00 mmol) was added to the solution of 2-benzylpyridine (4.85 mL, 30.00 mmol) in THF (100 mL) at 0 ℃, then TMEDA (9.00 mL, 60.00 mmol) was added, the red suspension was restored upto room temperature and stirred for 24 h. *p*-Tolunitrile (3.51 g, 30.00 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red clear solution mixture. After the acid hydrolysis of 60% H_2SO_4 solution under the condition of ice bath until pH=1, neutralized with saturated NaOH until pH=7, amount of solid arised in the process and dissolved by just enough distilled water, followed by extraction with dichloromethane (100 mL×3). The mixture was dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a yellow solid was purified by column chromatography. The product was crystallized as yellow crystals from CH_2Cl_2 at room temperature. Yield: 3.15 g (26%). M.p. 233.5 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 14.54 (s, 1H, NH), 8.64 (d, 1H, Py−H), 8.01 (d, 2H, Py−H), 7.32 (d, 1H, Ar−H), 6.95−7.28 (m, 14H, Py−H and Ar−H), 2.46 (s, 3H, $-CH_3$), 2.24 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ(ppm) 174.4 (C=O), 164.6 (C=N), 144.2, 132.5, 132.3, 129.8, 129.5, 129.4, 129.1, 128.9, 128.6, 127.9 (Ar−C), 134.1, 125.9, 122.8, 101.5 (Py−C), 93.9 (C=C), 21.3 ($-CH_3$). Anal. Calcd for $C_{28}H_{24}N_2O$: C, 83.14; H, 5.98; N, 6.93. Found: C, 83.11; H, 5.92; N, 6.96.

*4.9. Synthesis of **8***

^{n}BuLi (23.95 mL, 2.5 M, 59.87 mmol) was added to the solution of 2-benzylpyridine (4.8 mL, 29.93 mmol) in THF (100 mL) at 0 ℃, the red suspension was restored upto room temperature and stirred for 24 h. *p*-Tolunitrile (3.51 g, 29.93 mmol) was added to the mixture at 0 ℃, warmed to room temperature gradually, and stirred for 48 h to give a dark red clear solution mixture. After the acid hydrolysis of 60% H_2SO_4 solution under the condition of ice bath until pH=1, neutralized with saturated NaOH until pH=7, amount of solid arised in the process and dissolved by just enough distilled water, followed by extraction with dichloromethane (100 mL×3). The mixture was dried with anhydrous $MgSO_4$, the volatile solvent was removed in vacuo, a white solid was purified by column chromatography. The product was crystallized as colorless crystals from CH_2Cl_2 at room temperature. Yield: 2.26 g (64.2%). M.p. 106 ℃. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 7.81−7.84 (d, 1H, Ar−H), 7.53−7.56 (d, 2H, Ar−H), 7.28−7.31 (d, 2H, Ar−H), 7.20−7.22 (d, 2H, Ar−H), 4.26 (s, 2H, −CH_2−), 2.35 (s, 3H, −CH_3). ^{13}C NMR($CDCl_3$, TMS, 75 MHz): δ(ppm) 170.37 (−CN), 145.56, 141.20, 133.24, 131.44, 130.48, 129.55 (Ar−C), 46.05 (−CH_2−), 22.60 (−CH_3). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.62; H, 5.53; N, 6.01.

Table 6. Details of the X-ray structure determination of complexes **1**, **5**, **6**, **7**, **8**

Complex	**1·toluene**	**5**	**6**	**7**	**8**
Formula	$C_{44}H_{46}Li_2N_4Si_2$·C_7H_8	$C_{20}H_{17}NO_2$	$C_{19}H_{14}N_2$	$C_{28}H_{24}N_2O$	$C_{16}H_{13}NO$
M_w(g mol^{-1})	793.04	303.35	270.32	404.49	235.27
T (K)	200(2)K	276(2)K	297(2)K	279(2)K	298(2)K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	*P*-1	*P*-1
a (Å)	13.8654(5)	17.2353(14)	10.910(5)	8.6482(4)	5.6225(8)
b (Å)	9.7373(3)	5.7560(4)	11.857(5)	9.4014(4)	8.7441(13)
c (Å)	17.6892(6)	32.539(3)	12.016(5)	14.6248(7)	14.160(2)
α (°)	90	90	90	87.128(2)	83.361(5)
β (°)	100.0860(10)	99.676(2)	106.596(13)	82.705(2)	79.706(5)
γ (°)	90	90	90	69.5480(10)	71.791(5)
V (Å^3)	2351.34(14)	3182.1(4)	1489.6(11)	1105.08(9)	649.32(17)
Z	2	8	4	2	2
Dcalcd (g cm^{-3})	1.120	1.266	1.205	1.216	1.203
μ (mm^{-1})	0.113	0.082	0.072	0.074	0.075
F (000)	844	1280	568	428	248

Reflections collected	17066	16590	7996	12273	8194
Independent (R_{int}) reflections	4154 (0.0319)	5453 (0.0388)	1732 (0.0543)	3910 (0.0243)	2290 (0.0225)
Goodness of fit on F^2	1.045	1.055	1.067	1.027	1.015
Final R indices [I＞2σ(I)]					
R_1	0.0446	0.0587	0.0479	0.0450	0.0532
wR_2	0.1095	0.1497	0.0978	0.1148	0.1305
R indices (all data)					
R_1	0.0579	0.0959	0.0849	0.0710	0.0806
wR_2	0.1186	0.1740	0.1113	0.1309	0.1551

4.10. X-ray crystallography

Data collection of **1**, **5**, **6**, **7** and **8** was performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were solved by direct methods (SHELXS-2014) and refined against F^2 by full-matrix least squares using SHELXL-2014. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. In the checkCIF report of complex **1**·toluene, calculated moiety formula ($C_{44}H_{46}Li_2N_4Si_2$, C_7H_7) was caused by the absence of a hydrogen atom, the lack of a hydrogen atom resulted from a unordered carbon atom (C26) of $–CH_3$ in toluene. Resolution of data collection of compound **6** was not good enough, which resulted the less value of sine (theta_max)/wavelength (0.5195). Crystal data and experimental details of the structure determinations are listed in Table **6**.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no.1571792 for **1**, no.1571793−1571796 for **5**–**8**, Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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Highlights

- Insertion reaction of 2-benzylpydidyl lithium with nitriles has been investigated
- C-C coupling is proceed via a carbanion attack
- Possible mechanism for the formation of different products is been speculated

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