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Improved Synthesis of Unsymmetrical *N*-aryl-*N'*-alkylpyridyl ß-Diketimines using Molecular Sieves and their Lithium Complexes

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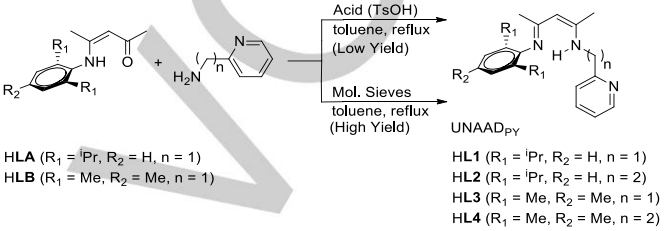
Abstract: The synthesis of unsymmetrical β-diketimines with *N*-aryl-*N'*-alkyl substitution require at least two condensation steps and tedious purification procedures. An improvement for the preparation of four unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketimine ligands (H**L1**-H**L4**) using 5 Å molecular sieves was reported. Synthesis of four Li complexes (Li**L1**, Li**L2**, Li**L3**, and Li**L4**) containing *N*-aryl-*N'*-alkylpyridyl β-diketimines ligands is also presented. All four Li complexes were fully characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. X-ray structure analysis and spectroscopic results indicate that the Li β-diketimine structures and ligand binding modes are governed by the bulkiness of the *N*-aryl substituent and the length of pyridyl arm of the *N*-aryl-*N'*-alkyl β-diketiminate ligand.

Introduction

During past several decades, β-diketimines have been widely used as chelating and sterically crowded spectator ligands.[1-7] Introducing hemilabile pendant pyridyl donors in unsymmetrical *N*-aryl-*N'*-alkyl β-diketimines (UNAAD) in the preparation of unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketimines (UNAADpy) may introduce new electronic and steric binding features which can aid in the stabilization and to the ability to modulate the reactivity of unsaturated metallated complexes.[8-11] In order to understand the coordination abilities of pendant donor of UNAADpy, we recently reported several UNAADpy ligands and their corresponding Zn(II) and Cu(I) complexes.[11-12] However the isolated yields of UNAADpy were low (~50%) and required several purification steps.[9-10] β-diketimines are usually prepared by the condensation of acetylacetone with two equivalents of primary amine in the presence of acid.[13-18] It is worthwhile to mention that most β-diketimines have symmetrical *N*, *N'*-aryl or *N*, *N'*-alkyl substituents,[13, 17, 19-22] but only a few unsymmetrical *N*-aryl-*N'*-alkyl β-diketimines (UNAAD)[23-26] have been reported due to their tedious synthetic procedures.[8-11, 27] Symmetric β-diketimines can be synthesized under several conditions with or without the azeotropic removal of water or with stoichiometric or catalytic amounts of acid.[4, 17, 28] Another approach for the synthesis of symmetrical β-diketimines is the use of molecular sieves that may serve as a catalysts.[29-30] In light of the above, a simple procedure is needed to synthesize unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketimines (UNAADpy). Herein, we report a straightforward procedure for the synthesis of UNAADpy using 5 Å molecular sieves (Scheme 1) in high yield without further purification. This high yield preparation may lead to an increase in the application of unsymmetrical complexes such as UNAADpy.



Scheme 1. Synthesis of the *N*-aryl-*N'*-alkylpyridyl β-diketiminato ligand sets.

β-diketiminato Li complexes are often used as ligand transfer reagents in the preparation of transition metal coordination complexes due to their high yield lithiation and transmetalation activities.[6, 31-45] For example, metal β-diketiminate complexes with rare-earth or d-block transition metals can be synthesized by reaction of β-diketiminato Li complexes with their corresponding metal halides.[1, 5, 46-51] Indeed, there are few studies describing the preparation of Li complexes bearing unsymmetrical *N*-aryl-*N'*-alkyl β-diketimines (UNAAD).[52-53] In order to explore the lithiation chemistry of UNAADpy, we synthesized four UNAADpy Li complexes (LiL1, LiL2, LiL3, and LiL4) and investigated their binding modes in solution as well as in the solid state.

Results and Discussion

Ligand synthesis.

β-diketimines exist as symmetrical and unsymmetrical ligands due to the variability of the substitutions on the backbone or enamine functional groups. Symmetrical β-diketimines can be synthesized in a one pot reaction from acetylacetone and 2 equivalents of amine using acid catalysts such as TsOH/HCl (or mixtures of both) in 80~95% yield.[17] Current preparations of unsymmetrical *N*-aryl-*N'*-alkyl β-diketimines (UNAAD; in 50-60% yield) requires a two-step procedure starting from acetylacetone and arylamine followed by second condensation with another alkylamine.[8, 10] Recently, our group reported the synthesis of UNAADpy ligands H**L1**-H**L4** using catalytic quantities of TsOH. The reaction was monitored for two days using ^{1}H NMR (Table 1).[11-12] We found that using one equivalent of TsOH gave low product yields that required further purification. From a rational synthetic standpoint, UNAAD ligands could be synthesized from aryliminoketone or alkyliminoketone with alkyl- or aryl-amine, respectively. According to literature precedence, the order of aryl- or alkyl-amine addition is important.[10, 17] Reaction between aryliminoketone with alkylamine is usually preferred as compared to reaction of alkyliminoketone with arylamine. As determined by

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Supporting information for this article is available on the *WWW* under htttp://

[1], pyridylalkyliminoketone (alkyliminoketone) with one or two equivalents of aryl amine forms symmetrical *N*,*N'*-diaryl substituted ß-diketimine as the major product with a minor statistical mixture (e.g. *N*-aryl-*N'*-alkyl β-diketimines and *N*,*N'*-dialkyl β-diketimines) and free pyridylalkylamine. Therefore, UNAADpy ligands H**L1**-H**L4** should be synthesized from aryliminoketone H**LA** and H**LB** with a suitable pyridylalkylamine (Scheme 1).

The synthesis of diketimines and enamines are accomplished using condensation reactions.[54-58] It is thought that molecular sieves drive condensation reactions in the forward direction by behaving as activating or dehydrating agents.[29-30, 57, 59] Another benefit of using molecular sieves that they are easily removed after filtration.[59] According to ^{1}H NMR monitoring, preparation of UNAADpy (H**L1**-H**L4**) is achieved in 48 hrs using 5 Å molecular sieves (Table 1; Scheme 1). Confirmation of the desired H**L1**-H**L4** products was accomplished using ^{1}H NMR spectroscopy (see the supporting information) The purity (>98%) was determined by comparison to our previous data.[11]

Table 1. Influence of molecular sieves in the preparation of *N*-aryl-*N'*-alkylpyridyl ß-diketimines (UNAADpy)

Ligands	Yield using 5 Å Molecular Sieves (%)[a]	Yield using T_SOH (%) [b]	Reaction time (h)
H**L1**	96	57	48
H**L2**	95	55	48
H**L3**	98	56	48
H**L4**	95	66	48

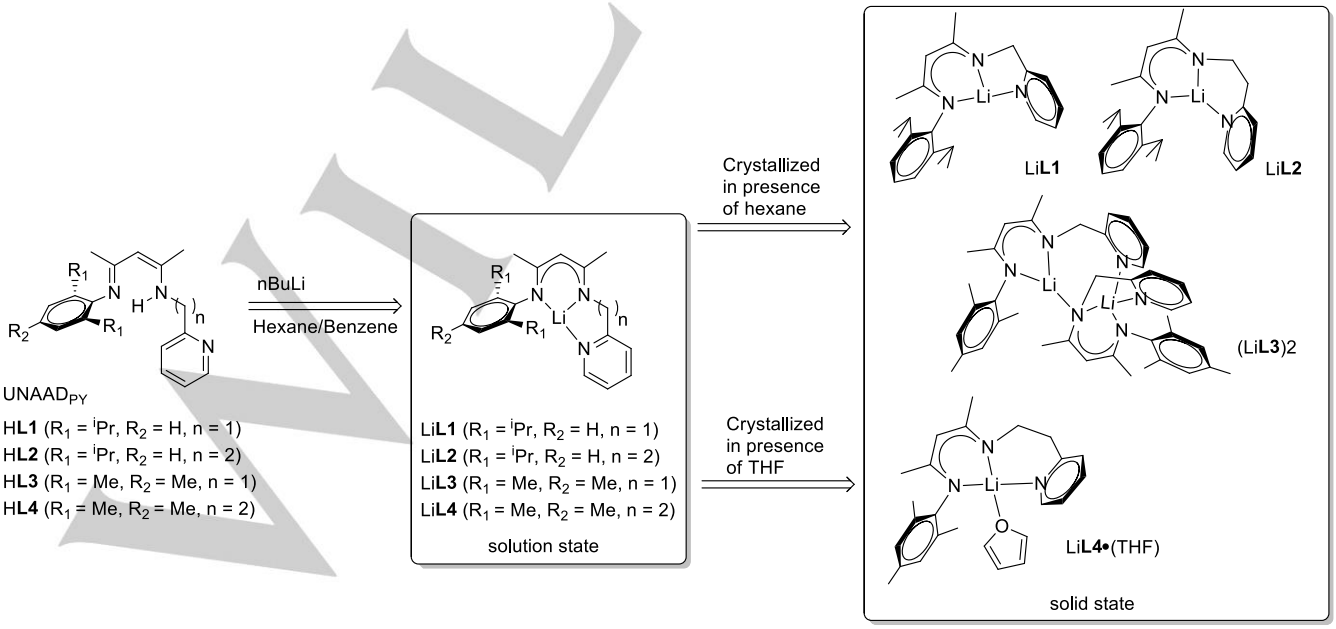
[a] Isolated yield of final product in presence of molecular sieves 5 Å. [b] Isolated yields of final product in presence of TsOH.

Synthesis and Characterization of Li Complexes.

UNAADpy (H**L1**, H**L2**, H**L3**, and H**L4**) were treated with an equimolar amount of *n*-butyllithium providing the desired Li complexes Li**L1**, Li**L2**, Li**L3**, and Li**L4**, respectively (Scheme 2). The fact that *n*-butyllithium can deprotonate the β-diketimine ligands gives clues regarding the coordination ability of Li within these metal complexes. The absence of downfield N-H resonances in the ^{1}H NMR spectrum of the Li complexes suggests that the β-diketimines are deprotonated to their anionic form. The ^{1}H NMR spectra of the four Li complexes (**L1**-**L4**) show a single type of resonance associated with the β-diketiminato backbone and the chelated pyridyl arm, indicating that the solution structures of Li**L1**, Li**L2**, Li**L3**, and Li**L4** are rather similar. All Li complexes were characterized by ^{1}H NMR, ^{13}C NMR, X-ray diffraction, and elemental analysis. X-ray diffraction quality crystals of complexes Li**L1**, Li**L2**, and Li**L3** were obtained from saturated hexane solutions (Table S1). The crystallographic results of Li**L1** and Li**L2** show that the Li cation is chelated by the β-diketiminato ligand **L1**$^-$ or **L2**$^-$. On the other hand, the Li**L3** ligand has a binuclear structure with an unusual Li coordination mode. Attempts to grow crystals of Li**L4** from a saturated hexane solution were unsuccessful (results not shown). Vapour diffusion of pentane into a solution of Li**L4** in THF gave X-ray quality crystals yellow crystals that revealed a THF solvated Li**L4·(**THF) product. During our investigation of Li**L1**-Li**L4** complexes, we found that LiL1-LiL4 are quite soluble in non-polar solvents such as hexane, pentane, and benzene. These complexes are stable in dry air but decompose in the presence of moisture. The synthetic procedure and crystallization conditions for the four Li complexes are shown in Scheme 2.

Molecular Structures of Li Complexes.

The molecular structures of all four Li complexes are shown in Figure 1. Li**L1** crystallized with two crystallographically independent but structurally similar molecules in the asymmetric unit. Figure 1a shows only one Li**L1** molecule in the asymmetric unit due to identical coordination geometries, bond lengths, and bond angles for the 2nd molecule in the unit cell. The anionic tridentate ligand **L1**$^-$ displays a slightly distorted T-shaped coordination geometry with a slight dislocation of Li (0.086 Å) from the least-squares-plane (LSP) derived from the three nitrogen atoms. The pyridylmethyl arm of the Li**L1** forms a nearly planar five-member ring about the Li centre, and connects with the planar six-membered diazapentadienyl bidentate chelate ring by a Li



Scheme 2. Preparation and recrystallization of lithium complexes.

bridge. In contrast to Li**L1**, the Li centre of Li**L2** (Figure 1b) exhibits a non-planar distorted Y-shaped coordination geometry and is positioned below the LSP derived from the three nitrogen atoms by approximately 0.379 Å. This distortion may be due to the longer pyridylethyl arm that is chelated to the Li center. Indeed, the pyridylethyl arm of the Li**L2** forms a six-member ring in the twist boat conformation that is connected to the planar six-membered diazapentadienyl bidentate chelate ring by a Li bridge.

The molecular structure of LiL3, in contrast to LiL1, is binuclear with an unusual Li coordination mode (Figure 1c). The unusual dinuclear structure of LiL3, as compared to LiL1, may due to the decreased steric influence of the ortho position of N-aryl substituent (2,4,6-trimethylphenyl) of the β-diketiminato ligand $L3^-$. One of the Li's in the dinuclear LiL3 complex displays a distorted tetrahedral environment that is coordinated by a bidentate diazapentadienyl chelate ring and two pyridyl moieties. The other Li atom in LiL3 is coordinated by three nitrogen atoms giving rise to a trigonal pyramidal coordination mode. The trigonal pyramidal coordination mode involves a bidentate diazapentadienyl chelate ring and a bridged amide group from another diazapentadienyl chelate ring. The three coordinate Li ion sits 0.512 Å below the LSP of three nitrogen atoms. Using THF as a crystallization solvent gave a THF solvated product LiL4·(THF) (Figure 1d). The anionic tridentate ligand $L4^-$ exhibits distorted tetrahedral coordination geometry with a coordinated THF molecule. The pyridylethyl arm of the LiL4·(THF) forms a six-membered ring in the twist boat conformation that connects to the planar six-membered diazapentadienyl bidentate chelate ring by a Li bridge. In contrast to LiL2, the Li of LiL4·(THF) sits out of the LSP of three nitrogen atoms by 0.706 Å.

In common with all known structures of *N,N'*-aryl substituent β-diketiminato Li complexes,[2, 60] the NCCCN backbone atoms are coplanar, indicating a delocalized electronic structure. The pyridyl group of the LiL1-LiL4 complexes coordinates to the Li ion with Li-N_{py} bond lengths of 2.061~2.170 Å. These bonds are longer than the Li-N_{amide} bond lengths of 1.864~2.008 Å of the NCCCN backbones. For comparison of Li**L1**-Li**L4** to the free ligand H**L1**, selected bond distances and angles, are listed in Table 2. Considering the crystallographic results of all of the Li complexes discussed above, there are two factors that apparently affect the structure of the Li complexes containing the UNAADpy ligand. First, the bulky 2,6-bisisopropylphenyl substituent of $\mathbf{L1}^-$ and $\mathbf{L2}^-$ may encourage the Li**L1** and Li**L2** complexes to form tridentate three coordinated mononuclear compounds. On the other hand, the less bulky 2,4,6-trimethylphenyl substituents of H**L3** and H**L4** may lead to an increase in vacancy around the metal center allowing for increased coordination. Indeed, Li**L3** and Li**L4**·(THF) both display four coordinate environments about the Li center. Second, the length of pyridyl arm in UNAADpy ligands, may also affect the metal center geometry and the behaviour of the tridentate chelation or bridged dimerization binding modes. In general, the chelating pyridylmethyl arms form five-membered rings with anionic β-diketiminato moieties $\mathbf{L1}^-$ and $\mathbf{L3}^-$, and the pyridylethyl arms form six-membered rings with the anionic β-diketiminato moieties $\mathbf{L2}^-$ and $\mathbf{L4}^-$. In a chelating ring stability study of corresponding Zn(II) and Cu(I) complexes,[11-12] we found that the five-membered chelating ring (pyridylmethyl arm) have stronger tendency to becomes a pendent arm than the six-membered chelating ring (pyridylethyl arm) in solution. Therefore, the unusual dinuclear structure formation of Li**L3** may

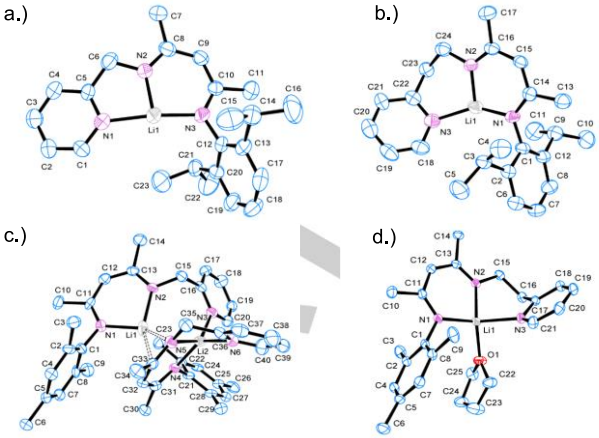


Figure1. ORTEP of Li**L1** (a), Li**L2** (b), Li**L3** (c), and Li**L4**·(THF) (d) at the 50% probability level**.** Hydrogen atoms were not shown for clarity**.**

due to the hemilabile nature of the pyridylmethyl arm during the crystallization packing process.

Complexation of LiL3 and LiL4 with THF.

In order to understand the THF binding ability of LiL3 and LiL4, an ^{1}H NMR titration was performed by the sequential addition of THF to a C_6D_6 solutions of LiL3 and LiL4 (Fig. S9-S10 respectively). The NMR signals assigned to THF increasingly moved to lower-field upon the gradual addition of THF. These titration results are similar to a previous ^{1}H NMR titration study of symmetrical *N, N'*-aryl β-diketiminato Li complexes that suggest a rapid equilibrium at 298K between THF coordination and de-coordination in the NMR time scale.[52] Therefore, a similar behaviour of rapid equilibrium between THF coordination and de-coordination in the ^{1}H NMR time scale for LiL3 and LiL4 is likely. It is reasonable to conclude that THF binds rather weakly to LiL3 and LiL4.

Conclusions

We successfully synthesized a series of unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketimines (UNAAD$_{py}$; H**L1**-H**L4**) using molecular sieves 5 Å as a catalyst with improved yield compared to using acid (TsOH) catalysts. The lithiation products of Li**L1**-Li**L4** were obtained by treatment of H**L1**-H**L4** with ^{n}BuLi, respectively. X-ray structure analysis and spectroscopic results reveals three types binding modes, monomer (Li**L1**, Li**L2**), dimer (Li**L3**), and THF adduct (Li**L4**·THF). Li**L3** exists as dimer due to the less bulky *N*-aryl substituent and shorter pyridylmethyl arm, while **LiL4** exists as a THF-adduct due to the bulkier *N*-aryl substituent and longer pyridylethyl arm. In summary, we obtained high yields of ligands H**L1**-H**L4** and the observed variable binding modes in Li**L1**-Li**L4** due to the bulkiness of the *N*-aryl substituent and the length of pyridyl arm.

Experimental Section

All manipulations involving Li complexes were carried out in an atmosphere of purified dinitrogen in a dry box, or using standard Schlenk line techniques. Chemical reagents were purchased from Aldrich Chemical Co. Ltd., Lancaster Chemicals Ltd., or Fluka Ltd.

Table 2. Selected bond lengths (Å) and angles (deg) for H**L1**, Li**L1**, Li**L2**, Li**L3** and Li**L4** complexes

	H**L1**	Li**L1**		Li**L2**	Li**L3**	Li**L4**(THF)
		Molecule A	Molecule B			
Li-$N_{amide(aryl)}$		1.940(10)	1.898(10)	1.892(9)	1.968(17)[c]; 1.997(16)[d]	1.992(4)
Li- $N_{amide(alkyl)}$		1.872(10)	1.858(10)	1.874(8)	2.002(19)[c]; 2.011(16)[d]	1.979(4)
Li-N_{py}		2.061(11)	2.074(10)	2.034(9)	2.046(17)[d]; 2.104(16)[d]	2.172(4)
C-$C_{(NCCCN\ backone)}$	1.431(5)	1.393(7)	1.401(7)	1.413(6)	1.404(12)[c]; 1.414(12)[c]	1.407(3)
	1.367(5)	1.410(7)	1.406(7)	1.417(6)	1.407(11)[d]; 1.400(12)[d]	1.413(3)
$\Delta_{C\text{-}C}$[a]	0.064	0.017	0.005	0.004	0.010[c]; 0.007[d]	0.006
C-$N_{(NCCCN\ backone)}$	1.305(4)	1.323(6)	1.334(6)	1.328(5)	1.314(10)[c]; 1.322(10)[c]	1.326(3)
	1.350(4)	1.316(6)	1.314(6)	1.322(5)	1.321(10)[d]; 1.293(10)[d]	1.315(3)
$\Delta_{C\text{-}N}$[a]	0.045	0.007	0.020	0.006	0.008[c]; 0.028[d]	0.011
N_{amide}-Li-N_{amide}		99.2(5)	100.1(5)	102.0(4)	97.8(8)[c]; 89.6(7)[d]	96.38(19)
$N_{amide(aryl)}$-Li-N_{py}		172.6(6)	173.3(6)	142.6(5)	103.1(7)[d]; 140.6(8)[d]	131.7(2)
$N_{amide(alkyl)}$-Li-N_{py}		86.0(4)	84.8(4)	102.5(4)	137.5(8)[d]; 83.4(6)[d]	93.93(17)
∠NCCCN, aryl[b]	81.44	72.8	71.29	77.15	84.90[c]; 88.26[d]	85.09

[a] Bond length difference of NCCCN backbone. [b]∠angle between the NCCCN backbone plane and *N*-aryl ring. [c] Structural parameters around three coordinated Li ion. [d] Structural parameters around four coordinated Li ion.

All reagents were used without further purification, apart from all solvents, which were dried over Na (Et_2O, THF) or CaH_2 (CH_2Cl_2, CH_3CN) and then thoroughly degassed before use. Molecular sieves (5 Å, 8-12 mesh) were purchased from Acros Ltd. 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one[61] and 2-((2,4,6-trimethylphenyl)imido)-2-penten-4-one[62] were synthesized following published procedures. Molecular sieves (5 Å, 8-12 mesh) dried under vacuum overnight at 250°C prior to use. ^{1}H NMR and ^{13}C NMR spectra were acquired using a Varian Gemini-200 proton/carbon FT NMR, 400 MHz or a Varian Gemini-500 proton/carbon FT NMR spectrometer. ESI mass spectra were collected using a Waters ZQ 4000 mass spectrometer. Elemental analyses were performed using a Heraeus CHN-OS Rapid Elemental Analyzer.

Ligand Synthesis: The syntheses of H**L1**-H**L4** were carried out using similar procedures. As a representative example, the synthesis of H**L1** is given in detail below.

HL1: 2-(2,6-diisopropylphenylimido)-2-pentene-4-one (4.2 g, 0.39 mmol) and 2-(aminomethyl) pyridine (2.0 mL, 0.39 mmol) were refluxed in toluene (50 mL) for 2 days in presence of 5 Å molecular sieves (30 g). The resultant mixture was filtered and evaporated under reduced pressure. The filtrate was extracted with hexane to obtain a yellow solid (5.4 g, 96%). The ^{1}H NMR data (details in supporting information) regarding N*H*, Py-*H*, backbone-C*H* protons, and ESI-MS *m/z* data are in agreement as discussed in our previous literature data reports.[11]

HL2-HL4: Following a similar procedure as described for H**L1**, H**L2**-H**L4** were obtained as reddish brown, dark brown, and glittering yellow oil in yield 95-98% respectively. The ^{1}H NMR data (details in supporting information) regarding N*H*, Py-*H*, backbone-C*H* protons, and ESI-MS *m/z* data are in agreement as discussed in our previous literature data reports.[11]

Lithiation: Li**L1**, Li**L2**, Li**L3**, and Li**L4** were synthesized using similar procedures. The ^{1}H NMR and ^{13}C NMR spectra of compounds Li**L1**-Li**L4** in C_6D_6 solution are shown in Fig. S7-S14 respectively. As a representative example the synthesis of Li**L1** is given in detail below.

LiL1: In an inert atmosphere, ^{n}BuLi (1.01 mL, 1.05 equiv, 1.60 M in hexanes) was added dropwise to a stirred solution of H**L1** (0.527 g, 1.51 mmol) in benzene (0.898 mL). The solution was stirred for approximately 60 min producing a yellow precipitate. The reaction was reduced in volume and placed at -20 °C overnight. The solution was filtered under vacuum to give a cream yellow solid (0.415 g, 77%). Single crystals of Li**L1** suitable for X-ray diffraction were obtained from several recrystallizations from hexane solutions at -20°C. ^{1}H NMR (C_6D_6, 200 MHz, 298K): δ 7.30 (d, *J* = 5.3 Hz,1H, $Py1_{l1}$), 7.21-7.15 (m, 3H, Ar-$H_{j1,\ k1}$), 6.85 (td, *J* = 7.6 Hz, 1H, $Py3_{i1}$), 6.53 (d, *J* = 8 Hz, 1H, $Py4_{h1}$), 6.32 (t, *J* = 6.4 Hz, 1H, $Py2_{g1}$), 5.09 (s, 1H, backone-CH_{f1}), 4.51 (s, 2H, CH_2Py_{e1}), 3.53 (septet, 2H, *J* = 7 Hz, $ArCH(CH_3)_{2,\ d1}$), 2.02 (s, 3H, backone-$CH_{3,\ c1}$), 1.98 (s, 3H, backone-$CH_{3,\ b1}$), 1.30 (d, 6H, *J* = 7 Hz, $ArCH(CH_3)_{2,\ a1}$), 1.18 (d, 6H, *J* = 7 Hz, $ArCH(CH_3)_{2,\ a1}$). ^{13}C NMR (C_6D_6, 100 MHz, 298K): δ 165.11, 164.73, 162.79, 150.09,

148.16, 141.07, 136.41, 123.26, 122.92, 122.21, 120.95, 93.92, 55.03, 28.06, 25.18, 23.43, 22.88, 21.17. Anal. Calcd for $C_{23}H_{30}LiN_3$: C, 77.72; H, 8.51; N, 11.82. Found: C, 77.69; H, 8.55; N, 11.81.

LiL2: In an inert atmosphere, ^{n}BuLi (1.01 mL, 1.05 equiv, 1.60 M in hexanes) was added dropwise to a stirred solution of H**L2** (0.548 g, 1.51 mmol) in benzene (0.898 mL). LiL2 was isolated from hexane to give orange crystals (0.367 g, 66 %). ^{1}H NMR (C_6D_6, 200 MHz, 298K): δ 7.66 (d, *J* = 5.3 Hz, 1H, $Py1_{n2}$), 7.30-7.15 (m, 3H, Ar-$H_{k2\text{-}m2}$), 6.85 (td, *J*= 7.6 Hz, 1H, $Py3_{j2}$), 6.53 (d, *J*= 8 Hz, 1H, $Py4_{i2}$), 6.32 (t, *J* = 6.4 Hz, 1H, $Py2_{h2}$), 4.95 (s, 1H, backone-CH_{g2}), 3.50 (septet, *J* = 7 Hz, 2H, $ArCH(CH_3)_{2,\ f2}$), 3.66 (t, *J* = 7 Hz, 2H, $CH_2CH_2Py_{e2}$), 2.63 (t, *J* = 7 Hz, 2H, $CH_2CH_2Py_{d2}$), 1.96 (s, 3H, backone-$CH_{3,\ c2}$), 1.93 (s, 3H, backone-$CH_{3,\ b2}$), 1.29 (d, *J* = 7 Hz, 6H, $ArCH(CH_3)_{2,\ a2}$), 1.18 (d, *J* = 7 Hz, 6H, $ArCH(CH_3)_{2,\ a2}$). ^{13}C NMR (C_6D_6, 100 MHz, 298K): δ 165.32, 162.65, 162.18, 150.12, 148.41, 141.25, 137.86, 124.33, 123.11, 122.78, 121.34, 93.35, 49.47, 40.93, 27.98, 25.01, 23.34, 23.07, 21.27. Anal. Calcd for $C_{24}H_{32}LiN_3$: C, 78.02; H, 8.73; N, 11.37. Found: C, 77.99; H, 8.74; N, 11.40.

LiL3: In an inert atmosphere, ^{n}BuLi (1.04 mL, 1.08 equiv, 1.60 M in hexanes) was added dropwise to a stirred solution of H**L3** (0.463 g, 1.51 mmol) in hexane (0.928 mL). This complex was isolated from hexane at to give yellow crystals (0.269 g, 57%).^{1}H NMR (C_6D_6, 400MHz, 298K): δ 7.21 (s, 1H, $Py1_{k3}$), 6.98 (s, 2H, Ar-H_{j3}), 6.85(td, *J* = 7.6 Hz, 1H, $Py3_{i3}$), 6.53 (d, *J* = 8 Hz, 1H, $Py4_{h3}$), 6.32 (t, *J* = 6.4 Hz, 1H, $Py2_{g3}$), 5.00 (s, 1H, backone-CH_{f3}), 4.51 (s, 2H, CH_2Py_{e3}), 2.32 (s, 6H, ortho $PhCH_{3,\ d3}$), 2.29 (s, 3H, para $PhCH_{3,\ c3}$), 2.00 (s, 3H, backone-$CH_{3,\ b3}$), 1.95 (s, 3H, backone-$CH_{3,\ a3}$). ^{13}C NMR (C_6D_6, 100 MHz, 298K): δ165.77, 165.51, 163.72, 151.61, 149.07, 137.10, 131.17, 131.10, 129.75, 122.86, 121.53, 94.77, 56.12, 23.76, 23.70, 22.26, 21.69. Anal. Calcd for $C_{20}H_{24}LiN_3$: C, 76.66; H, 7.72; N, 13.41. Found: C, 76.86; H, 7.67; N, 13.65.

LiL4: In an inert atmosphere, ^{n}BuLi (0.99 mL, 1.03 equiv, 1.60 M in hexanes) was added dropwise to a stirred solution of H**L4** (0.485 g, 1.51 mmol) in hexane (4.83 mL). This complex was isolated from hexane at to give orange crystals (0.365 g, 74%).^{1}H NMR (C_6D_6, 400MHz, 298K): δ 7.75 (d, *J* = 4.4 Hz,1H, $Py1_{l4}$), 7.03 (s, 2H, Ar-H_{k4}), 6.86 (td, *J* = 9.4 Hz, 1H, $Py3_{j4}$), 6.49 (d, *J* = 8.8 Hz1, H, $Py4_{i4}$), 6.33 (t, *J* = 5.4 Hz, 1H, $Py2_{h4}$), 4.92 (s, 1H, backone-CH_{g3}), 3.34 (t, *J* = 5.6 Hz, 2H, $CH_2CH_2Py_{f4}$), 2.55 (t, *J* = 5.6 Hz, 2H, $CH_2CH_2Py_{e4}$), 2.33 (s, 3H, para $PhCH_{3,\ d4}$), 2.31 (s, 6H, ortho $PhCH_{3,\ c4}$),1.95 (s, 3H, backone-$CH_{3,\ b4}$), 1.91 (s, 3H, backone-$CH_{3,\ a4}$). ^{13}C NMR (C_6D_6, 100 MHz, 298K): δ 166.19, 163.16, 162.89,148.89, 138.39, 131.22, 130.97, 129.74, 129.62, 124.88, 122.02, 93.99, 50.34, 41.28, 23.60, 22.05, 21.75, 19.82. Anal. Calcd for $C_{21}H_{26}LiN_3$: C, 77.04; H, 7.72; N, 13.41. Found: C, 76.98; H, 7.75; N, 13.63. Single crystals of Li**L4**(THF) suitable for X-ray diffraction were obtained from the vapor diffusion of pentane into a THF solution of Li**L4**.

X-ray crystal structure determinations.

All single-crystal X-ray diffraction data were measured using a Bruker Nonius Kappa CCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å).The Bruker SMART program package was used to determine the unit cell parameters and to collect data. All structures were solved by direct methods and were refined on F^2 by the full-matrix least-squares method using the SHELXL-2014/7 program.[63] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at the calculated positions and included in the final stage of refinements with fixed parameters. Further details are given in Table S1 in the supporting information. CCDC No. 1814931 (for Li**L1)**, 1814932 (for Li**L2**), 1814933 (for Li**L3**), and 1814934 (for Li**L4**) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: β-Diketiminate ligand • Lithium • Acetylacetone • Chelation

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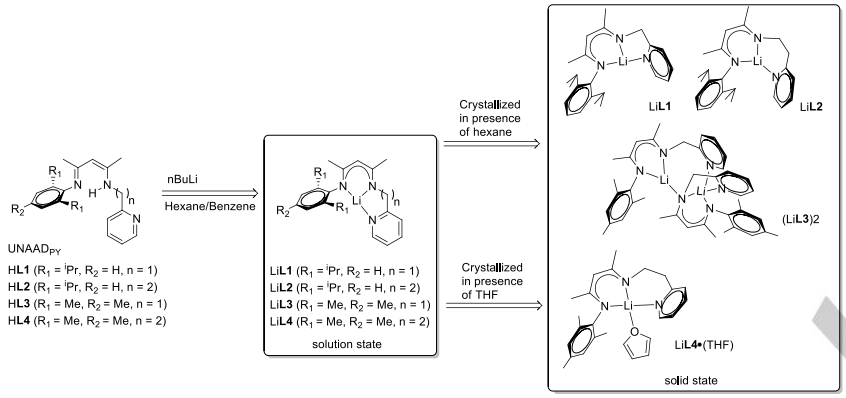

Four unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketiminate ligands H**L1**-H**L4** and were synthesized in the presence of 5 Å molecular sieves in high yield. Deprotonation of unsymmetrical *N*-aryl-*N'*-alkylpyridyl β-diketimines using ^{n}BuLi yields corresponding stable Li complexes. These lithium complexes were characterized using single crystal X-ray diffraction. The observed binding mode differences of Li**L1**, Li**L2**, Li**L3**, and Li**L4** are rationalized by considering the steric interference of the *N*-aryl substituent and the length of pyridyl arm of the *N*-aryl-*N'*-alkyl β-diketiminate ligand.

***Lithiation Chemistry**

ß-Diketiminato Lithium Complexes

Kuldeep Chand, Cheng-Long Tsai, Hsuan-Ying Chen, Wei-Min Ching, Sung-Po Hsu, James R. Carey, Sodio C. N. Hsu

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Improved Synthesis of Unsymmetrical N-aryl-N'-alkylpyridyl ß-Diketimines using Molecular Sieves and their Lithium Complexes