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Synthesis and X-ray Structures of Dilithium, Dipotassium, and Lithium−Potassium 2,6-Pyridyl-Bridged Bis-azaallyl Complexes

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Treatment of dilithium dialkyl complex $[\{(CHSiMe_3)_2C_5H_3N\text{-}2,6\}\{Li(TMEDA)\}_2]$ (**1**) with organonitriles Bu^tCN and Bu^tNC afforded 2,6-pyridyl-bridged bis-azaallyl complexes $[\{\{N(SiMe_3)C(Bu^t)CH\}_2C_5H_3N\text{-}2,6\}\{Li_2(THF)_2\}]$ (**2**) and $[\{\{N(Bu^t)C(SiMe_3)CH\}_2C_5H_3N\text{-}2,6\}\text{-}\{Li_2(TMEDA)\}]$ (**3**). Similar reaction with PhCN afforded a solvent-separated ion complex $[Li(TMEDA)_2][Li\{\{N(SiMe_3)C(Ph)CH\}_2C_5H_3N\text{-}2,6\}]$ (**4**). In situ reaction of $(CH_2SiMe_3)_2C_5H_3N$-2,6 with Bu^nLi/Bu^tOK in the presence of TMEDA, followed by the addition of PhCN, afforded a mixed lithium−potassium complex $[\{\{N(SiMe_3)C(Ph)CH\}_2C_5H_3N\text{-}2,6\}\{Li(Et_2O)\}\{K(TMEDA)\}]$ (**5**), dipotassium complex $[\{\{N(SiMe_3)C(Ph)CH\}_2C_5H_3N\text{-}2,6\}\{\{K(TMEDA)\}_2]$ (**6**), and **4**. Furthermore, sequential addition of the reagents in the order Bu^nLi, Bu^tCN, and Bu^tOK to $(CH_2SiMe_3)_2C_5H_3N$-2,6 afforded a dimeric dipotassium compound $[\{\{N(SiMe_3)C(Bu^t)\text{-}CH\}_2C_5H_3N\text{-}2,6\}\{K_2(Bu^tCN)(TMEDA)\}]_2$ (**7**). X-ray structures of **2**−**7** showed that one of the metals is bonded to the ligand in $[N^-,N,N^-]$ tridentate-chelate fashion, while the other metal interacts with the π-orbitals of the azaallyl arm.

Introduction

Organo alkali-metal complexes are generally used as transfer reagents in preparative main-group and transition metal chemistry. In recent years, structures of this class of complexes and related compounds have attracted much attention. There have been several reviews on the synthesis and structures of organo alkali-metal compounds.[1] The preparation of organolithium compounds can be accomplished by deprotonation of alkane derivatives using reagents such as *n*-butyllithium. However, it was found that mixed organo alkali-metal bases containing lithium and sodium or potassium have stronger deprotonating power over organolithium reagent alone. Wittig,[2] Lochmann,[3] and Schlosser[4] have reported the use of mixed alkali-metal bases in some metalation reactions and the structures of mixed alkali-metal compounds formed in these reactions.

In our earlier studies, we have prepared the pyridine-functionalized azaallyllithium, silaallyllithium, or potassium compounds by reaction of a lithium alkyl with organonitriles.[5] Recently, we reported the synthesis and structures of some phenyl-bridged dianionic 1-bis-azaallyl dilithium complexes resulting from addition of the Li−C bond of $[\{o/m/p\text{-}(CHSiMe_3)_2C_6H_4\}\{Li_2(TMEDA)_2\}]$ to a nitrile RCN (R = Bu^t or Ph) followed by a 1,3-shift of the $SiMe_3$ group. The dipotassium analogues were prepared by the exchange reaction of the dilithium compounds with Bu^tOK.[6] Our study has been extended further to the reaction of the dialkyl derivative of 2,6-bis(trimethylsilyl)lutidine with organonitriles. The derived ligand $[\{N(R^1)C(R^2)CH\}_2C_5H_3N\text{-}2,6]^{2-}$ ($R^1 = SiMe_3$, $R^2 = Bu^t$ or Ph; $R^1 = Bu^t$, $R^2 = SiMe_3$) (**I**) is structurally similar to the reported bis-azaallyl ligand $[m\text{-}\{N(SiMe_3)C(Bu^t)CH\}_2C_6H_4]^{2-}$ (**II**). It is anticipated that the extra coordination from the bridged-pyridyl nitrogen will change the structural features in this class of compounds. Ligand **I** also provides more flexibility in forming a six-member heterocyclic ring by virtue of the twisting of the metallacyclic ring. The metal complex formed will be less strained when compared with the related ligand **III**.[7]

Results and Discussion

Dilithium dialkyl $[\{(CHSiMe_3)_2C_5H_3N\text{-}2,6\}\{Li(TMEDA)\}_2]$ [8] (**1**) derived from dilithiation of 2,6-bis(trimethylsilyl)lutidine was used as the starting compound in the reactions with organonitriles RCN (R = Ph or Bu^t) and isonitrile Bu^tNC. Compound **1** reacts with 2 equiv

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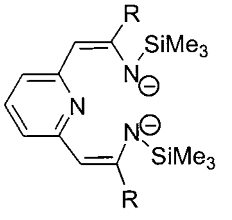
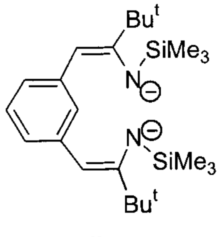
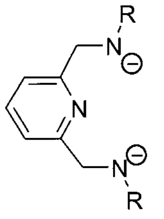


I

R = Ph or Bu^t



II



III

R =2,6-Pr$^i_2$-C$_6$H$_3$, 2,6-Et$_2$-C$_6$H$_3$
or 2,6-Me$_2$-C$_6$H$_3$

of Bu^{t}CN or Bu^{t}NC to afford the 2,6-pyridyl-bridged dilithium bis-azaallyl complexes [{{N(SiMe$_3$)C(Bu^t)-CH}$_2$C$_5$H$_3$N-2,6}{Li$_2$(THF)$_2$}] (**2**) and [{{N(Bu^t)C(SiMe$_3$)-CH}$_2$C$_5$H$_3$N-2,6}{Li$_2$(TMEDA)}] (**3**) (Scheme 1). Both reactions involve the addition of the Li−C bond in [(CHSiMe$_3$)$_2$C$_5$H$_3$N-2,6}{Li$_2$(TMEDA)$_2$}] to the nitriles Bu^{t}CN or Bu^{t}NC followed by a 1,3- or 1,2-shift of the SiMe$_3$ group. Similar lithium derivatives of monoanionic di-*N*,*N*′-pyridyl-1-azaallyl ligand [Li{N(SiMe$_3$)C(R^1)C-(R^2)C$_5$H$_4$N-2}]$_2$ (R^1 = Ph or Bu^t; R^2 = H or SiMe$_3$) and quinolyl-1-azaallyl ligand [Li{N(SiMe$_3$)C(Ph)C(R)C$_9$H$_6$N-2}]$_2$ (R = H or SiMe$_3$) have been prepared in a similar way in our previous work.[5] Other examples of nitrile insertion into metal−carbon bonds to form N,N′-bidentate monoanionic ligands such as 1-azaallyls,[9] *β*-diketiminates,[10] and amidinates [{N(R)}$_2$CR′]$^-$ have been reported in the literature.[11]

In contrast, compound **1** reacts with PhCN in Et$_2$O to afford the solvent-separated ion-pair complex [Li-(TMEDA)$_2$]$^+$[Li{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}]$^-$ (**4**), and its structure has been confirmed by single-crystal X-ray structure analysis. The reason for the formation of an ionic complex is unknown. Lithium azaallyl complexes comprised of a separated ion-pair are scarcely found. There have been three other compounds with similar nature.[12−14] For example, solvent-separated ion-pair types of lithium compounds such as [Li(TMEDA)$_2$]-[Li{C(SiMe$_3$)$_3$}$_2$][15] and [Li([12]crown-4)$_2$][Li{HC(C$_5$H$_4$N-2)$_2$}][16] and some bridged fluorenyllithium compounds [Me$_2$Si(fluorenyl)$_2$Li(THF)$_2$][Li(THF)$_4$],[17] [{(Me$_2$N)B}$_2$-(fluorenyl)$_2$Li(THF)][Li(THF)$_4$],[18] and [(CH$_2$)$_n$(fluorenyl)$_2$]-[Li(THF)$_4$]$_2$[19] have been reported.

In another experiment, we have carried out separate "in situ" reactions of (CH$_2$SiMe$_3$)$_2$C$_5$H$_3$N-2,6 with 1 or 2 equiv of Bu^{n}Li, Bu^{t}OK, and TMEDA, the reagent known as Lochmann's reagent. The deprotonation reaction in diethyl ether at −78 °C was then followed by the addition of same equivalents of PhCN. The reaction of Lochmann's reagent with (CH$_2$SiMe$_3$)$_2$C$_5$H$_3$N-2,6 in 2:1 ratio gave the mixed lithium−potassium complex [{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}{Li(Et$_2$O)}{K(TMEDA)}] (**5**) as the first fraction of crystalline solids and [{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}{K(TMEDA)}$_2$] (**6**) as the second fraction of solids. The other fraction of crystalline solids isolated was found to be compound **4**. The mechanism for the formation of these compounds is shown in Scheme 2. Each of compounds **5** and **6** has been isolated and confirmed by single-crystal X-ray structure determination. On the contrary, the reaction ratio of a 1:1 equivalent of Lochmann's reagent to (CH$_2$-SiMe$_3$)$_2$C$_5$H$_3$N-2,6 gave **6** as the first fraction of product. These results suggest that the reaction products are dependent on the amount of Lochmann's reagent used for deprotonation. On the basis of statistical distribution of products from the reaction, 2 equiv of Lochmann's reagent will give the mixed lithium−potassium complex **5** in higher proportion and which dropped out from the reaction mixture more readily. In the other reaction, the products are presumably in equal proportions, and the dipotassium complex **6** is the most ionic and least soluble among them, so it crystallized out from the reaction mixture first (Scheme 2). The ratio of mixed-metal and dimetallic compounds in the product depends on the ratio of Lochmann's reagent to the starting compound. Similar results have been reported by Lochmann and co-workers.[3] The reaction pathway for the formation of **4**, **5**, and **6** presumably proceeds via the mixed lithium−potassium dialkyl intermediate compound, the addition of the nitrile to the Li−C and K−C bonds, and then the 1,3-SiMe$_3$ migration. Solid-state structures of some mixed alkali-metal complexes have been reported. For example, [Ph$_4$Li{Na(TMEDA)}$_3$],[20] [(PhCH$_2$)$_4$Li$_{2-x}$Na$_{2+x}$(TMEDA)$_4$],[21] [{N=C(NMe$_2$)$_2$}$_6$Li$_4$-Na$_2$],[22] [{N=C(Ph)Bu^t}$_6$Li$_4$Na$_2$],[23] [{N=C(NMe$_2$)$_2$}$_4$Li-{Na(HMPA)}$_3$] (HMPA = O=P(NMe$_2$)$_3$),[24] [{CH$_2$=C(Bu^t)O}$_4$(Bu^{t}O)$_4$Li$_4${K(THF)}$_4$KOH(THF)],[25][(PhNH)$_2$(Bu^{t}O)Li{Na-(TMEDA)}{K(TMEDA)}]$_2$,[26]and[{N(SiMe$_3$)$_2$}$_2$M^1(THF)M^2(THF)$_2$]

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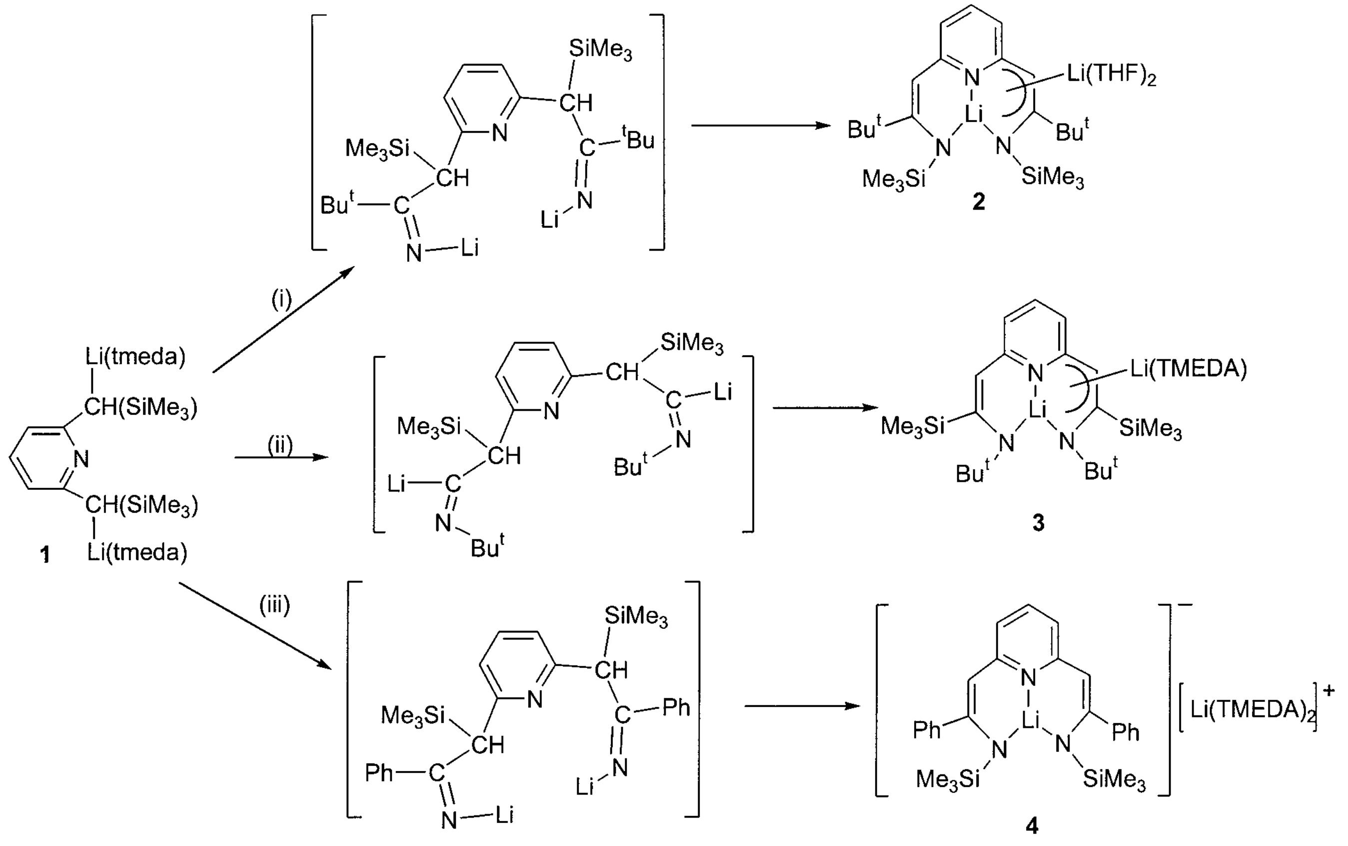
Scheme 1



Reagents: (i) 2 Bu^tCN, THF; (ii) 2 Bu^tNC, Et_2O; (iii) PhCN, Et_2O

(M^1 = Li, M^2 = Na or K; M^1 = Na, M^2 = K) are known.[27] Among these compounds, the difference in the cationic sizes between Li^+ and Na^+ or K^+ has led to the pronounced effect of aggregation state and the number of coordination contacts with the carbanion.

In a similar in situ reaction, sequential addition of 2 equiv of reagents in the order ^nBuLi/TMEDA, Bu^tCN at 0 °C to $(CH_2SiMe_3)_2C_5H_3N$-2,6, followed by 2 equiv of Bu^tOK at −78 °C afforded the dimeric dipotassium compound $[\{\{N(SiMe_3)C(Bu^t)CH\}_2C_5H_3N\text{-}2,6\}\{K_2(TMEDA)(NCBu^t)\}]_2$ (**7**). The reaction probably proceeds also through an intermediate compound similar to that of **2** (Scheme 1) followed by the metal exchange reaction with Bu^tOK.

Compounds **2**−**7** are yellowish orange or red crystalline solids soluble in solvents such as Et_2O, THF, and toluene. The ^1H and ^{13}C NMR spectra of these displayed one set of resonances corresponding to the ligand at ambient temperature. This could be due to the fact that structures of these compounds in solution are fluxional; the π-bonded metal atoms are hopping from one arm to the other due to a low energy barrier.

The molecular structures of each of the crystalline complexes **2**−**7** have been established by X-ray crystallography, and they are illustrated in Figures 1−6, respectively; selected structural data are listed in Tables 1−6.

Compound **2** comprises three independent molecules, one of which is shown in Figure 1. It is a contact-ion-pair type of complex. The coordination spheres of the two lithium atoms within the complex are different, and they are bonded to the two NCCCN skeletons of the bis-azaallyl ligand $[\{N(SiMe_3)C(Bu^t)CH\}_2C_5H_3N\text{-}2,6]^{2-}$ in different modes. The coordination sphere of lithium(1) is three-coordinate, being chelated by two amido-nitrogen atoms of the dianionic ligand at distances of 1.907(5) and 2.098(5) Å and the neutral pyridyl nitrogen atom at 1.908(4) Å. The Li(1)−N(pyridyl) distance is comparatively short for a neutral N-donor bound to lithium, being more akin to Li−N(anionic) distances, such as $[Li\{N(SiMe_3)C_9H_6N\text{-}8\}]_2$ (Li−N(aromatic), 2.011(11) Å);[28] $[Li\{C(SiMe_3)_2C_5H_4N\text{-}2\}]_2$ (Li−N(pyridyl), 1.936(6) Å);[29] $[Li\{CH(C_5H_4N\text{-}2)_2\}\{C_5H_4N\text{-}2)_2CH_2\}]$(Li−N(shorter), 1.960(9) Å); $[Li\{N(SiMe_3)C_9H_6N\text{-}8\}(TMEDA)]$ (Li−N(aromatic), 2.05(2) Å; Li−N(amido), 1.94(1) Å);[28] and $[Li(NHC_6H_2Bu^t_3\text{-}2,4,6)(TMEDA)]$ (Li−N(amido), 1.895(8) Å).[30] The shorter Li(1)−N(pyridyl) distance is presumably a consequence of twisting of the chelating arms, which forces the lithium to the pyridyl nitrogen. The azaallyl arms of the ligand are twisted. The deviations of Li(1), N(1), and N(2) from the pyridine plane are 0.2963, 1.0626, and −0.7083 Å, respectively. Lithium(2) is bonded sideways to N(3), C(14), C(15),

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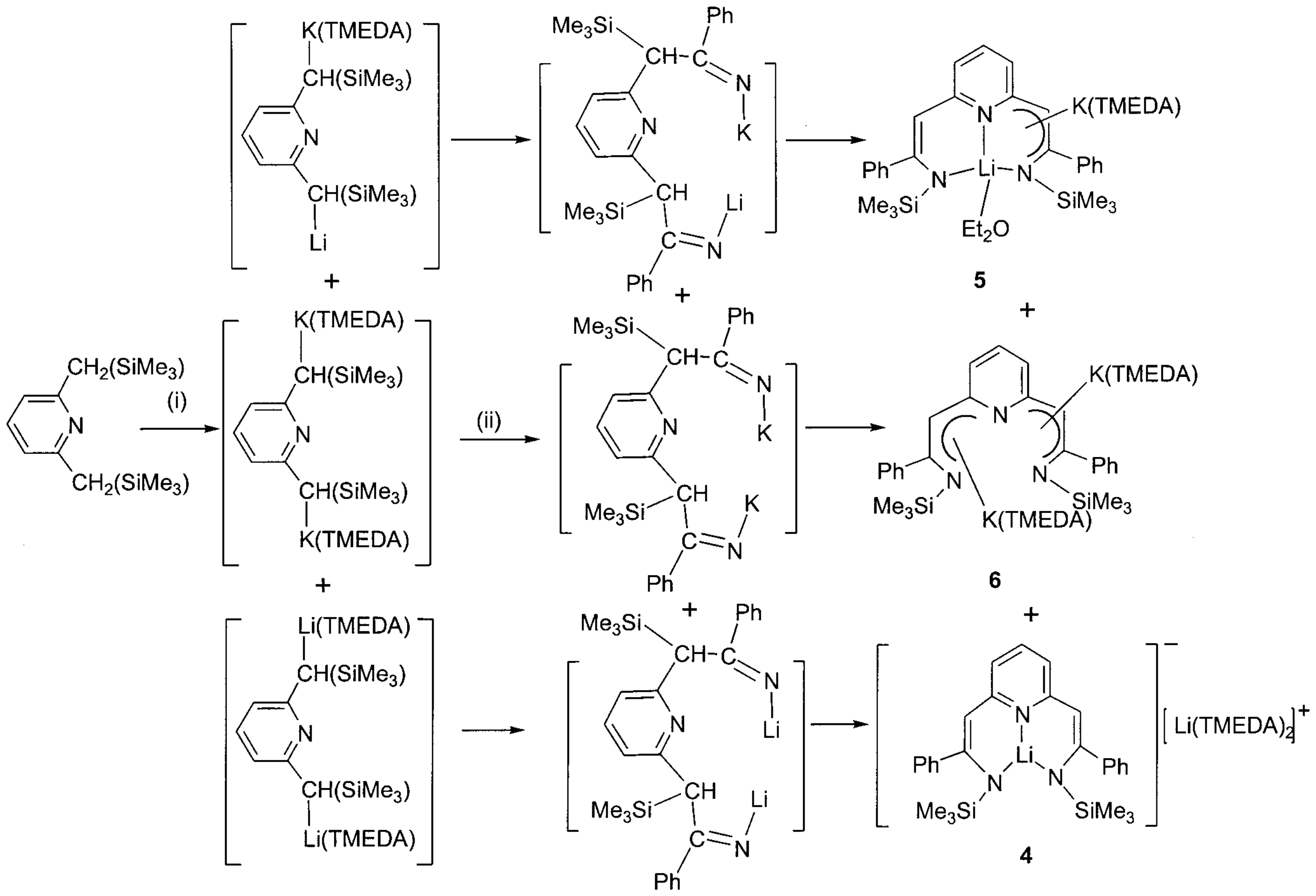
Scheme 2



Reagentsand conditions: (i) KOBu^t, LiBu^n, TMEDA, Et$_2$O, -78°C; (ii) PhCN, Et$_2$O

C(16), and N(2) at distances of 2.548(4), 2.538(4), 2.500(4), 2.411(4), and 2.081(4) Å, respectively. This suggests some extent of π-interaction between Li(2) and the NCCCN skeleton with some delocalization in the ligand backbone. Li(2) is also coordinated to two THF molecules.

Similarly, compound **3** also forms a contact-ion-pair in the solid state and has a ligand backbone similar to **2**. Li(1) in **3** is bonded to the three nitrogen atoms of the tridentate ligand. Li(2) is located above the pyridyl plane and has contacts with N(3), C(14), C(15), C(16), and N(2) at distances of 2.374(4), 2.525(4), 2.583(4), 2.533(4), and 2.075(4) Å. The Li(2) atom is further coordinated to one TMEDA molecule. The structures of **2** and **3** contrast with the related phenyl-bridged bis(1-azaallyl) compound [{m-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}],[6] which showed that both lithium metals are bonded to both azaallyl arms of the dianionic ligand with π-interaction. In contrast, the structures of the pyridyl-bridged compounds **2** and **3** showed π-bonding interaction of the metal to one azaallyl arm and the other being a tridendate chelate.

In the mixed lithium−potassium compound **5**, the Li(1) atom lies 0.7907 Å from the pyridyl plane and is ligated to the three nitrogen atoms of the azaallyl ligand and one Et$_2$O molecule. On the contrary, the K(1) atom lies on the side opposite the lithium atom with a deviation of 2.1646 Å from the plane. Considering the orientation of the pyridyl plane and the bond angles around the N(2) and N(3) atoms, it appears that the Li−N bonds mainly arise from the interaction of Li with the nitrogen sp^2 lone pair, whereas those involving K arise from interaction with the nitrogen p lone pair. The lithium metal is preferably bonded to the three nitrogen atoms in chelate fashion and is probably due to the smaller size of lithium. In contrast with compounds **2** and **3**, the potassium atom has significant contacts with the three nitrogen atoms with slightly longer K(1)−N(2) (3.0093(14) Å) and K(1)−N(3) (3.0283(13) Å) bond distances. These distances can be compared with the K−N(amido) bond distances found in [(PhNH)$_2$(Bu^{t}O)Li{Na(TMEDA)}{K(TMEDA)}]$_2$ (2.955(4) and 2.882(3) Å)[26] and the 2-azaallyl potassium compound [(PhCHNCHPh)K(PMDETA)]$_n$ (PMDETA = N,N,N,N'',N''-pentamethyldiethylenetriamine (2.868(5), 2.930(6) Å)[31] and the K−N(neutral) bond distances (K(1)−N(4) 2.8512(17) Å and K(1)−N(5) 2.9287(18) Å) in the same molecule. In the K(1)N(2)C(7)C(6)C(5)N(1) backbone, the K(1)−C bond distances are in the range 3.0964(15)−3.1578(18) Å, comparable with the K−C bond distances in [(Me$_2$C$_5$H$_5$-2,4)K(TMEDA)]$_n$ (3.069(7), (3.276(7) Å)[32] and [(Ph$_3$C)K(PMDETA)]$_n$ (3.146(6)−3.483(7) Å).[33] In the K(1)N(2)C(7)C(6)C(5)N(1) backbone, the K(1)−C bond distances of 3.585−3.969 Å are too long to be

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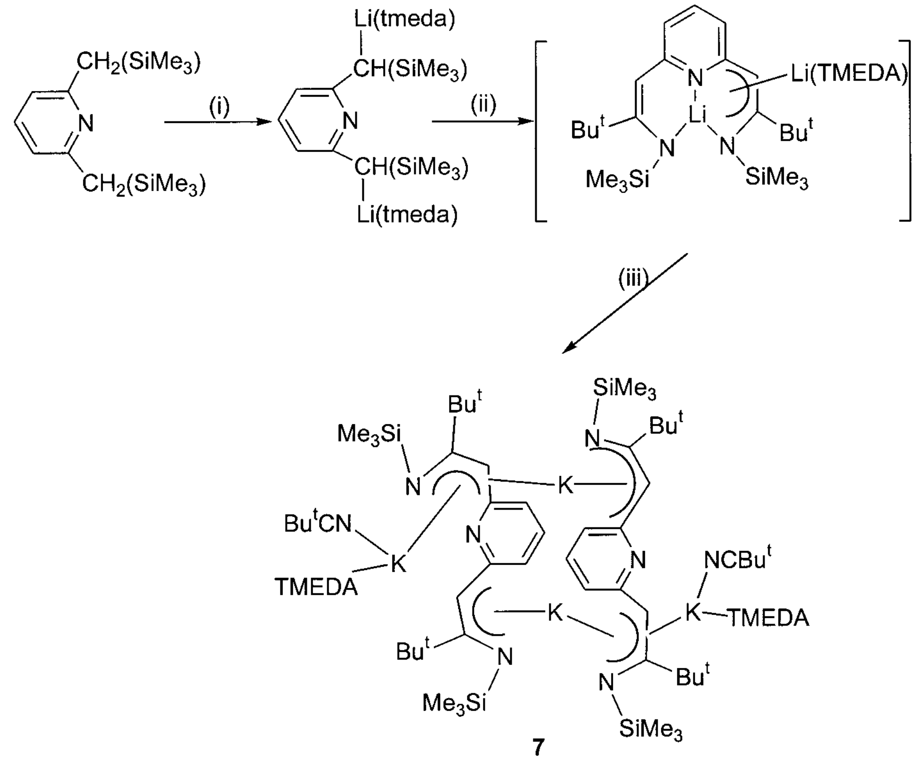
Scheme 3



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Reagents and conditions: (i)$LiBu^n$, TMEDA, -78°C; (ii) Bu^tCN, Et_2O; (iii) $KOBu^t$, Bu^tCN

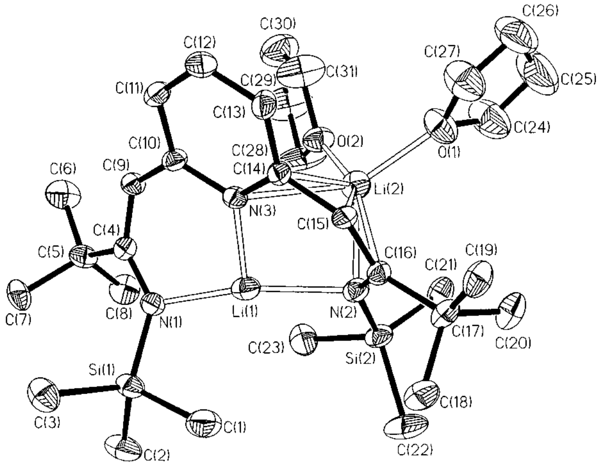

Figure 1. Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity.

considered any significant interaction between the K(1) and these carbon atoms. The Li−N bond distances (2.026, 2.090, and 2.117 Å) are longer than the corresponding distances in compounds **2** and **3**, due to the deviation of the lithium atom from the pyridyl plane.

Compound **4** is composed of a separated-ion-pair type of complex. The structure of the anion $[Li\{\{N(SiMe_3)C(Ph)CH\}_2C_5H_3N\text{-}2,6\}]^-$ as shown in Figure 4 is centrosymmetric and comprised of a three-coordinate lithium bonded to the two amido-nitrogens at 1.995(2) Å and the pyridyl nitrogen at 1.907(6) Å. Li(1) is coplanar with the pyridyl ring, and the two amido nitrogen atoms slightly deviate from the pyridyl plane with a deviation of 0.2435 Å. The average Li(1)−N distance of 1.966 Å is 0.11 Å shorter than the similar distances in **5**. This is probably because the additional coordination of Et_2O molecules creates a more crowded environment around the lithium atom. Also, the Li−N distances in **5** are longer than those in **2** and **3**. In the structure of the counterion $[Li(TMEDA)_2]^+$, the coordination sphere of of lithium(2) is tetrahedral, being coordinated to the four nitrogen atoms of the TMEDA molecules at distances of 2.169(3) and 2.176(3) Å, respectively.

Table 1. Selected Bond Distances [Å] and Angles [deg] for 2

Li(1)−N(3)	1.908(4)	Li(2)−N(3)	2.548(4)
Li(1)−N(1)	1.907(5)	N(1)−C(4)	1.342(2)
Li(1)−N(2)	2.098(5)	C(4)−C(9)	1.366(3)
Li(1)−C(4)	2.723(5)	C(9)−C(10)	1.429(3)
Li(1)−Li(2)	2.931(6)	C(10)−C(11)	1.393(3)
Li(2)−O(1)	1.971(5)	C(11)−C(12)	1.372(4)
Li(2)−O(2)	1.971(4)	C(12)−C(13)	1.379(3)
Li(2)−N(2)	2.081(4)	C(13)−C(14)	1.396(3)
Li(2)−C(16)	2.411(4)	C(14)−C(15)	1.459(2)
Li(2)−C(15)	2.500(4)	C(15)−C(16)	1.396(2)
Li(2)−C(14)	2.538(4)	N(2)−C(16)	1.354(3)

N(3)−Li(1)−N(1)	100.3(2)	C(14)−Li(2)−N(3)	30.6(1)
N(3)−Li(1)−N(2)	94.6(2)	C(16)−N(2)−Li(1)	108.5(2)
O(2)−Li(2)−O(1)	95.6(2)	Li(2)−N(2)−Li(1)	89.1(2)
N(2)−Li(2)−C(16)	34.1(2)	Li(1)−N(3)−Li(2)	80.9(2)
N(2)−Li(2)−C(15)	62.6 (1)	C(16)−C(15)−Li(2)	70.0(1)
N(2)−Li(2)−C(14)	83.2(1)	N(2)−C(16)−Li(2)	59.5(1)
N(2)−Li(2)−N(3)	78.4(1)	N(1)−C(4)−C(9)	124.4(2)
C(16)−Li(2)−C(15)	33.0(1)	C(4)−C(9)−C(10)	127.3(2)
C(16)−Li(2)−C(14)	63.4(1)	C(16)−C(15)−C(14)	131.5(2)
C(16)−Li(2)−N(3)	75.8(1)	N(2)−C(16)−C(15)	122.1(2)
C(15)−Li(2)−C(14)	33.7(1)		
C(15)−Li(2)−N(3)	57.1(1)		

The molecular structure of $[\{\{N(SiMe_3)C(Ph)CH\}_2C_5H_3N\text{-}2,6\}\{\{K(TMEDA)\}_2]$ (**6**) is somewhat similar to that of the mixed lithium−potassium compound **5**. The potassium atoms lie on both sides of the trigonal plane

Table 2. Selected Bond Distances [Å] and Angles [deg] for 3

N(1)−Li(1)	1.938(4)	N(3)−C(16)	1.373(2)
N(3)−Li(1)	2.028(4)	N(1)−C(1)	1.356(2)
N(2)−Li(1)	1.942(4)	C(1)−C(2)	1.413(3)
N(1)−Li(2)	2.374(4)	C(1)−C(15)	1.430(3)
N(3)−Li(2)	2.074(4)	C(2)−C(3)	1.380(3)
N(5)−Li(2)	2.180(4)	C(3)−C(4)	1.344(3)
N(4)−Li(2)	2.153(4)	C(4)−C(5)	1.416(3)
C(1)−Li(2)	2.525(4)	C(5)−C(6)	1.399(3)
N(2)−C(11)	1.487(2)	C(6)−C(7)	1.422(3)
N(1)−C(5)	1.359(2)		

N(1)−Li(1)−N (2)	100.43(17)	N(5)−Li(2)−C(1)	105.05(16)
N(1)−Li(1)−N(3)	95.08(17)	N(1)−Li(2)−C(1)	31.94(7)
N(2)−Li(1)−N(3)	161.1(2)	N(3)−Li(2)−Li(1)	48.05(12)
N(1)−Li(1)−Li(2)	58.86(12)	N(4)−Li(2)−Li(1)	105.91(18)
N(2)−Li(1)−Li(2)	132.43(18)	N(5)−Li(2)−Li(1)	169.61(19)
N(3)−Li(1)−Li(2)	49.59(12)	N(1)−Li(2)−Li(1)	44.32(10)
N(3)−Li(1)−Li(2)	132.06(19)	C(1)−Li(2)−Li(1)	66.08(12)
N(3)−Li(2)−N(4)	127.6(2)	N(1)−C(5)−C(6)	123.39(16)
N(4)−Li(2)−N(5)	83.75(14)	C(5)−C(6)−C(7)	131.32(18)
N(3)−Li(2)−N(5)	81.93(13)	N(2)−C(7)−C(6)	120.87(18)
N(4)−Li(2)−N(1)	105.83(17)	N(1)−C(1)−C(15)	121.01(16)
N(5)−Li(2)−N(1)	130.05(17)	C(16)−C(15)−C(1)	132.30(19)
N(3)−Li(2)−C(1)	82.25(12)	N(3)−C(16)−C(15)	119.25(18)
N(4)−Li(2)−C(1)	128.50(18)		

Table 3. Selected Bond Distances [Å] and Angles [deg] for 4

Li(1)−N(1)	1.907(6)	C(2)−C(3)	1.359(3)
Li(1)−N(2)	1.995(2)	C(1)−C(4)	1.420(3)
Li(2)−N(3)	2.169(3)	C(4)−C(5)	1.400(3)
Li(2)−N(4)	2.176(3)	C(5)−N(2)	1.362(3)
C(1)−N(1)	1.362(2)	C(5)−C(6)	1.545(3)
C(1)−C(2)	1.373(3)		

N(1)−Li(1)−N(2)	103.9(2)	N(2)−C(5)−C(4)	127.9(2)
N(2)−Li(1)−N(2a)	152.1(3)	N(2)−C(5)−C(6)	116.6(2)
N(1)−C(1)−C(2)	121.7(2)	C(5)−C(4)−C(1)	132.4(2)
N(1)−C(1)−C(4)	120.3(2)	C(5)−N(2)−Si(1)	126.7(1)
C(2)−C(1)−C(4)	118.0(2)	C(5)−N(2)−Li(1)	112.5(2)
C(3)−C(2)−C(1)	119.0(2)	Si(1)−N(2)−Li(1)	120.2(2)
C(2)−C(3)−C(2a)	120.7(3)	N(3a)−Li(2)−N(3)	129.3(3)
C(1a)−N(1)−C(1)	117.8(2)	N(3)−Li(2)−N(4a)	117.13(8)
C(1)−N(1)−Li(1)	121.1(1)	N(3)−Li(2)−N(4)	86.02(8)
C(4)−C(5)−C(6)	115.5(2)	N(4a)−Li(2)−N(4)	126.3(3)

described by the three ligating nitrogens. Each of the potassium centers lie closer to one of the azaallyl arms, showing π-interaction.

The molecular structure of compound **7** as shown in Figure 5 is a dimer. There are two kind of potassium environments in the structure of **7**. K(1) and K(1A) are π-bonded to one of the azaallyl arms of each of the two ligands and coordinate to the nitrogen atoms of the TMEDA and Bu^tCN molecules. K(2) and K(2A) are sandwiched between two ligands, being π-bonded to the azaallyl arms, and share the azaallyl arms with K(1) and K(1A), respectively.

By comparing the relevant structural data in **2**−**4** with the closely related lithium complexes derived from monoionic β-diketiminate ligands,[11] it was found that the bondings within the NCCCN ligand backbone in the sidearms are mainly localized with RC═C double bonds and leaving the aromaticity of the pyridyl ring unaffected. Some of the Li−N distances in **2**−**4** are comparatively shorter. Similar to the lithium azaallyl compounds, the LiNCCCN six-membered metallacyclic rings are also puckered.

Table 4. Selected Bond Distances [Å] and Angles [deg] for 5

K(1)−N(1)	2.7554(14)	C(14)−C(15)	1.3742(18)
K(1)−N(4)	2.8512(17)	N(5)−C(31)	1.529(3)
K(1)−N(5)	2.9287(18)	N(1)−C(1)	1.3553(19)
K(1)−N(2)	3.0093(14)	N(1)−C(5)	1.3746(15)
K(1)−N(3)	3.0283(13)	N(2)−C(7)	1.3595(15)
K(1)−Li(1)	3.072(3)	N(3)−C(15)	1.3596(18)
K(1)−C(7)	3.0964(15)	C(1)−C(2)	1.402(2)
K(1)−C(6)	3.1420(17)	C(1)−C(14)	1.4396(18)
K(1)−C(5)	3.1578(18)	C(2)−C(3)	1.378(2)
Li(1)−N(1)	2.026(2)	C(3)−C(4)	1.366(3)
Li(1)−O(1)	2.089(3)	C(4)−C(5)	1.412(2)
Li(1)−N(2)	2.090(3)	C(5)−C(6)	1.438(2)
Li(1)− N(3)	2.117(3)	C(6)−C(7)	1.376(2)

N(1)−K(1)−N(4)	94.88(4)	N(3)−K(1)−C(6)	102.43(4)
N(1)−K(1)−N(5)	149.49(4)	Li(1)−K(1)−C(6)	63.54(5)
N(4)−K(1)−N(5)	62.38(5)	C(7)−K(1)−C(6)	25.47(4)
N(1)−K(1)−N(2)	63.71(4)	N(1)−K(1)−C(5)	25.75(3)
N(4)−K(1)−N(2)	155.77(4)	N(4)−K(1)−C(5)	94.10(4)
N(4)−K(1)−N(2)	131.59(4)	N(5)−K(1)−C(5)	129.26(4)
N(1)−K(1)−N(3)	62.40(4)	N(2)−K(1)−C(5)	61.67(4)
N(4)−K(1)−N(3)	104.97(4)	N(3)−K(1)−C(5)	87.52(4)
N(5)−K(1)−N(3)	139.80(4)	C(7)−K(1)−C(5)	48.33(4)
N(2)−K(1)−N(3)	76.15(3)	C(6)−K(1)−C(5)	26.39(4)
N(1)−K(1)−Li(1)	40.22(5)	N(1)−Li(1)−O(1)	103.50(12)
N(4)−K(1)−Li(1)	128.16(6)	N(1)−Li(1)−N(2)	95.63(10)
N(5)−K(1)−Li(1)	169.00(6)	O(1)−Li(1)−N(2)	118.81(13)
N(2)−K(1)−Li(1)	40.19(5)	N(1)−Li(1)−N(3)	92.99(11)
N(3)−K(1)−Li(1)	40.59(5)	O(1)−Li(1)−N(3)	111.97(11)
N(1)−K(1)−C(7)	62.40(4)	N(2)−Li(1)−N(3)	124.51(14)
N(4)−K(1)−C(7)	135.13(4)	Li(1)−N(1)−K(1)	78.33(9)
N(5)−K(1)−C(7)	118.25(4)	Li(1)−N(3)−K(1)	71.53(8)
N(2)−K(1)−C(7)	25.68(3)	C(15)−N(3)−Li(1)	105.34(11)
N(3)−K(1)−C(7)	97.71(4)	Li(1)−N(3)−K(1)	70.82(7)
Li(1)−K(1)−C(7)	57.63(5)	C(7)−C(6)−C(5)	131.01(11)
N(1)−K(1)−C(6)	48.26(4)	N(2)−C(7)−C(6)	128.39(13)
N(2)−K(1)−C(6)	47.14(3)		

Conclusion

We have shown that the novel pyridyl-bridged bis(1-azaallyl) ligands $[\{\{N(R^1)C(R^2)CH\}_2C_5H_3N\text{-}2,6]^{2-}$ (R^1 = Bu^t or $SiMe_3$, R^2 = Bu^t or Ph) are prepared by the reaction of the dilithium compound derived from 2,6-bis(trimethylsilylmethyl)lutidine with organonitriles or isonitriles followed by 1,3- or 1,2-trimethylsilyl migration. The dilthium bis-azaallyl compound can be converted to the dipotassium analogues by the reaction with Bu^tOK. The mixed lithium−potassium compound was prepared by mixed metalation with Lochmann's reagent, followed by reaction with PhCN. The X-ray structures of the compounds had shown that the dianionic pyridyl-bridged bis-azaalyl ligand behaves as both a σ- and π-donor.

Experimental Section

General Consideration. All manipulations were carried out either in a nitrogen-filled drybox or under nitrogen using standard Schlenk techniques. Solvents were dried over and distilled from sodium/benzophenone (diethyl ether and tetrahydrofuran) or sodium/potassium alloy (pentane). Benzonitrile and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were purchased from Aldrich and distilled from KOH prior to use. Trimethylacetonitrile, *tert*-butyl isocyanide, *n*-butyllithium, and potassium *tert*-butoxide were purchased form Aldrich and used without further purification. 2,6-Bis(trimethylsilylmethyl)pyridine was prepared as described in the literature.[8] ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, using a Bruker DPX-300 spectrometer in sealed tubes at ambient probe temperature. The ^{1}H chemical shifts were referenced to internal C_6D_5H (δ 7.15 ppm), ^{13}C chemical

Table 5. Bond Lengths [A] and Angles [deg] for 6

K(1)−N(1)	2.667(4)	K(1)−N(3)	2.831(5)
K(1)−N(2)	2.835(5)	K(1)−N(5)	2.898(6)
K(1)−N(4)	2.961(6)	K(1)−C(1)	3.273(6)
K(1)−C(15)	3.247(6)	K(2)−N(2)	2.796(4)
K(1)−C(14)	3.339(6)	K(2)−N(6)	2.847(5)
K(2)−C(5)	3.520(6)	K(2)−C(7)	3.170(6)
K(2)−N(1)	2.696(4)	K(2)−C(6)	3.309(6)
K(2)−N(3)	2.836(5)	N(2)−C(7)	1.345(6)
K(2)−C(5)	3.301(6)	C(1)−C(14)	1.417(7)
K(2)−N(7)	2.936(5)	C(5)−C(6)	1.439(7)
C(14)−C(15)	1.374(7)	N(3)−C(15)	1.344(7)
C(6)−C(7)	1.378(7)		
N(1)−K(1)−N(3)	70.48(14)	N(2)−K(1)−C(5)	59.85(13)
N(1)−K(1)−N(2)	70.83(13)	C(15)−K(1)−C(5)	82.39(15)
N(3)−K(1)−N(2)	95.75(13)	C(14)−K(1)−C(5)	64.23(14)
N(3)−K(1)−N(5)	161.51(19)	N(1)−K(2)−N(3)	70.02(14)
N(1)−K(1)−N(4)	140.91(17)	N(1)−K(2)−N(6)	89.93(14)
N(2)−K(1)−N(4)	135.57(18)	N(3)−K(2)−N(6)	103.09(15)
N(2)−K(1)−C(14)	110.78(14)	N(3)−K(2)−N(7)	133.17(16)
N(1)−K(2)−N(2)	71.04(13)	N(1)−K(2)−C(7)	63.82(14)
N(2)−K(2)−N(3)	96.54(13)	N(3)−K(2)−C(7)	113.53(14)
N(2)−K(2)−N(6)	146.07(15)	N(2)−K(2)−C(5)	63.24(13)
N(1)−K(2)−N(7)	145.30(15)	C(7)−K(2)−C(5)	47.29(14)
N(1)−K(1)−N(5)	96.01(18)	N(2)−K(2)−C(6)	46.44(13)
N(2)−K(1)−N(5)	91.36(17)	C(7)−K(2)−C(6)	24.44(12)
N(3)−K(1)−N(4)	121.27(19)	N(2)−K(2)−K(1)	49.77(10)
N(5)−K(1)−N(4)	61.6(2)	C(7)−K(2)−K(1)	63.98(11)
N(1)−K(1)−C(15)	62.52(15)	C(6)−K(2)−K(1)	67.06(10)
N(2)−K(1)−C(15)	111.91(14)	C(5)−N(1)−C(1)	119.6(5)
N(1)−K(1)−C(1)	23.78(13)	C(1)−N(1)−K(1)	104.0(3)
N(2)−K(1)−C(1)	94.37(14)	C(1)−N(1)−K(2)	120.5(3)
C(15)−K(1)−C(1)	46.81(15)	N(1)−C(5)−C(6)	121.0(5)
N(3)−K(1)−C(14)	45.75(14)	N(1)−C(5)−K(2)	52.4(3)
C(1)−K(1)−C(14)	24.72(13)	C(6)−C(5)−K(2)	77.7(3)
K(2)−C(5)−K(1)	65.05(11)	N(3)−K(2)−C(5)	93.28(14)
C(7)−C(6)−K(2)	72.1(3)	N(1)−K(2)−C(6)	46.46(13)
N(2)−C(7)−C(6)	128.5(5)	N(3)−K(2)−C(6)	111.45(14)
C(6)−C(7)−K(2)	83.4(3)	C(5)−K(2)−C(6)	25.14(12)
C(15)−C(14)−C(1)	136.2(6)	K(1)−N(1)−K(2)	86.42(13)
C(1)−C(14)−K(1)	75.1(3)	K(2)−N(2)−K(1)	81.39(12)
N(2)−K(2)−N(7)	120.46(16)	N(1)−C(1)−C(14)	120.2(5)
N(6)−K(2)−N(7)	62.25(16)	C(7)−C(6)−C(5)	134.6(5)
N(2)−K(2)−C(7)	25.05(12)	N(3)−C(15)−C(14)	128.1(5)
N(1)−K(2)−C(5)	23.53(12)		

shifts were referenced to C_6D_6 (δ 128.0 ppm) and ^7Li chemical shifts to $LiNO_3$ in $CDCl_3$. Mass spectral data were recorded on a 5989-In mass spectrometer. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, Oxbridge, U.K.

[{N(SiMe$_3$)C(Bu^t)CH}$_2$C$_5$H$_3$N-2,6}{Li$_2$(THF)$_2$}] (2). [{(CHSiMe$_3$)$_2$C$_5$H$_3$N-2,6}{Li(TMEDA)}$_2$] (**1**) was prepared by addition of Bu^{n}Li (8.6 mL, 13.76 mmol, 1.6 M in hexane) dropwise via syringe to a chilled (0 °C) solution of $(CH_2SiMe_3)_2C_5H_3N$-2,6 (1.73 g, 6.89 mmol) and TMEDA (2.1 mL, 13.94 mmol) in Et_2O (40 mL). After stirring for 8 h at room temperature, Bu^{t}CN (1.6 mL, 14.47 mmol) was added gradually to the resulting orange solution at 0 °C. The mixture was allowed to warm to room temperature and then stirred for a further 12 h to afford an orange slurry. Volatiles were removed under reduced pressure, and the resulting orange residue was dissolved in THF and filtered. Evaporation of the solvent and recrystallization from THF/hexane at room temperature yielded yellow crystals of **2**, which were washed with pentane (2 × 5 mL) and dried in vacuo (3.43 g, 87%). Anal. Calcd for $C_{23}H_{41}N_3Si_2Li_2$ (**1** − 2 THF): C, 64.15; H, 9.83; N, 9.76. Found: C, 62.80; H, 9.66; N, 10.95. ^1H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): δ 0.51 (s, 18 H, Si*Me*$_3$), 1.41 (m, 8 H, THF), 1.45 (s, 18 H, C*Me*$_3$), 3.52 (m, 8 H, THF), 5.60 (s, 2 H, C*H*), 6.25 (d, *J* = 7.8 Hz, 2 H, *m*-C$_5$*H*$_3$N), 6.88 (t, *J* = 7.8 Hz, 1 H, *p*-C$_5$*H*$_3$N). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_5N (2:1)): δ 5.56 (Si*Me*$_3$), 25.72 (THF), 31.70 (C*Me*$_3$), 40.98 (*C*Me$_3$), 67.74 (THF), 97.00 (*C*H), 112.23, 159.24 (*C*$_5$H$_3$N), 171.96 (*C*(Bu^t)). MS (EI, 70 ev): *m*/*z* 423 (27, [M − Li − 2 THF + 1]$^+$), 417 (5.7, [M − 2 Li − 2 THF + 2]$^+$), 366 (88, [M − Li −2 THF − CMe$_3$]$^+$).

Table 6. Selected Bond Distances [Å] and Angles [deg] for 7

K(1)−N(1)	2.699(2)	C(3)−C(4A)	1.354(4)
K(1)−N(5)	2.833(3)	C(4)−C(3A)	1.354(4)
K(1)−N(2)	2.882(2)	C(4)−C(5)	1.432(5)
K(1)−N(6)	2.901(5)	C(5)−C(6)	1.440(4)
K(1)−N(4)	2.924(3)	C(1)−N(1A)	1.362(3)
K(1)−C(5)	3.175(3)	C(1)−C(2)	1.393(4)
K(1)−C(7)	3.294(3)	C(1)−C(15)	1.455(4)
K(1)−C(1A)	3.428(3)	C(6)−C(7)	1.406(5)
K(2)−N(1)	2.746(2)	C(7)−C(8)	1.582(4)
K(2)−N(2)	2.776(3)	C(15)−C(16)	1.389(3)
K(2)−N(3)	2.819(2)	N(1)−C(5)	1.340(4)
K(2)−C(16)	3.031(3)	N(1)−C(1A)	1.362(3)
K(2)−C(1)	3.276(3)	N(2)−C(7)	1.325(4)
C(1)−K(1A)	3.428(3)	N(3)−C(16)	1.343(4)
C(2)−C(3)	1.396(4)		
N(5)−K(1)−N(2)	157.41(9)	N(1)−K(2)−C(16)	118.80(8)
N(1)−K(1)−N(6)	125.88(10)	N(2)−K(2)−C(16)	145.35(8)
N(5)−K(1)−N(6)	87.27(10)	N(3)−K(2)−C(16)	26.23(7)
N(2)−K(1)−N(6)	114.85(10)	N(1)−K(2)−C(1)	106.42(7)
N(1)−K(1)−N(4)	139.94(10)	N(2)−K(2)−C(1)	166.60(8)
N(5)−K(1)−N(4)	63.06(8)	N(3)−K(2)−C(1)	59.52(7)
N(2)−K(1)−N(4)	118.60(8)	C(16)−K(2)−C(1)	47.95(7)
N(6)−K(1)−N(4)	89.84(11)	N(1)−K(2)−K(1)	33.38(5)
N(1)−K(1)-C(5)	24.72(7)	N(2)−K(2)-K(1)	37.62(5)
N(5)−K(1)-C(5)	96.62(8)	N(1)−K(1)-N(5)	97.63(8)
N(2)−K(1)-C(5)	61.99(7)	N(1)−K(1)-N(2)	66.29(7)
N(6)−K(1)-C(5)	150.58(10)	N(4)−K(1)-C(7)	105.99(9)
N(4)−K(1)-C(5)	117.95(10)	C(5)−K(1)-C(7)	47.51(7)
N(1)−K(1)-C(7)	61.66(7)	N(1)−K(1)-C(1A)	21.81(6)
N(5)−K(1)-C(7)	135.06(10)	N(5)−K(1)-C(1A)	80.62(7)
N(2)−K(1)-C(7)	23.58(8)	N(2)−K(1)-C(1A)	86.62(7)
N(6)−K(1)-C(7)	137.60(10)	N(6)−K(1)-C(1A)	111.31(10)
N(1)−K(2)-N(2)	67.19(7)	N(4)−K(1)-C(1A)	137.21(9)
N(1)−K(2)-N(3)	144.04(8)	C(5)−K(1)-C(1A)	41.66(7)
N(2)−K(2)-N(3)	132.61(7)	C(7)−K(1)-C(1A)	83.45(8)
K(1)−N(1)-K(2)	112.58(8)	C(15)−C(1)-K(1A)	88.61(17)
K(2)−N(2)-K(1)	106.36(8)	K(2)−C(1)-K(1A)	158.04(11)
C(16)−N(3)-K(2)	87.73(14)	C(7)−C(6)-C(5)	132.7(3)
C(2)−C(1)-C(15)	125.4(2)	N(2)−C(7)-C(6)	60.49(13)
N(1A)-C(1)−K(1A)	47.41(13)	C(16)−C(15)-C(1)	129.5(3)
C(2)−C(1)−K(1A)	127.41(18)	N(3)−C(16)−C(15)	123.0(3)

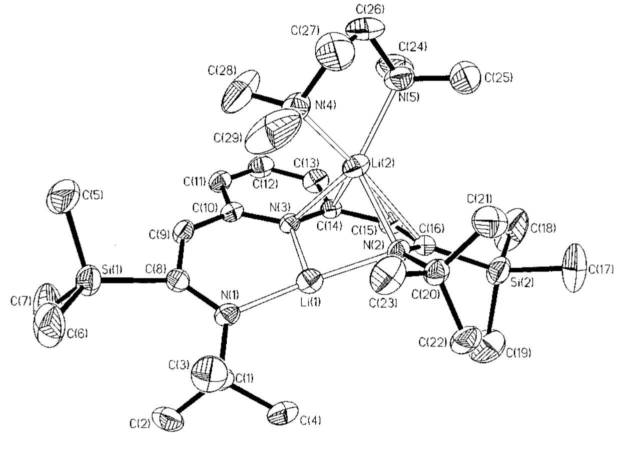

Figure 2. Molecular structure of complex **3**. Hydrogen atoms have been omitted for clarity.

[{{N(Bu^t)C(SiMe$_3$)CH}$_2$C$_5$H$_3$N-2,6}{Li$_2$(TMEDA)$_2$}] (3). To an orange solution of [{(CHSiMe$_3$)$_2$C$_5$H$_3$N-2,6}{Li(TMEDA)}$_2$] (**1**) (10.30 mmol) in Et_2O (40 mL) was added dropwise Bu^{t}NC (1.16 mL, 20.29 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and became deep red. Filtration followed by concentration of the solution and cooling at −30 °C yielded **3** as red crystals. Yield: 5.12 g (91.1%). Anal. Calcd for $C_{29}H_{57}Li_2N_3Si_2$: C, 63.81; H, 10.52; N, 12.82. Found: C, 62.75; H, 9.99; N, 12.80. ^1H NMR (300 MHz,

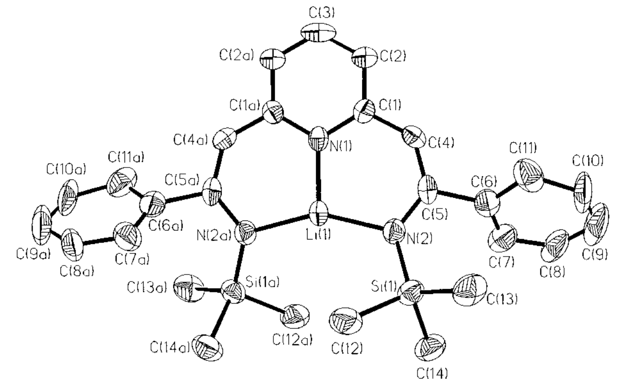

Figure 3. Molecular structure of the anion of complex **4**. Hydrogen atoms have been omitted for clarity.

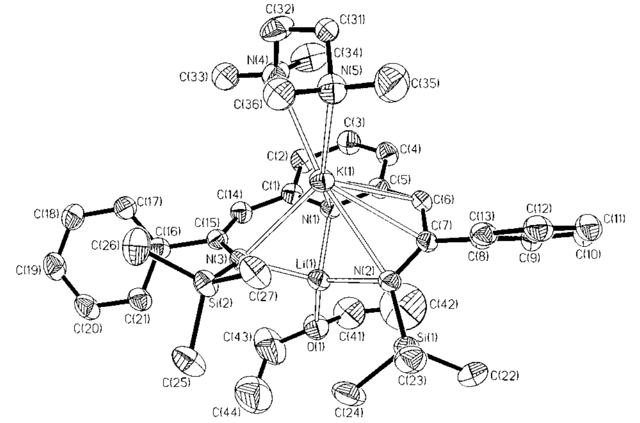

Figure 4. Molecular structure of complex **5**. Hydrogen atoms have been omitted for clarity.

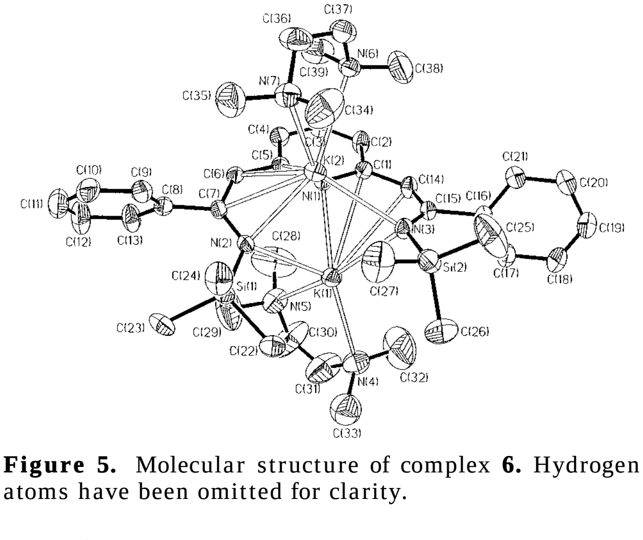

Figure 5. Molecular structure of complex **6.** Hydrogen atoms have been omitted for clarity.

C_6D_6): *δ* 0.56 (s, 18 H, Si*Me*$_3$), 1.47 (s, 18 H, C*Me*$_3$), 1.50 (s, 4 H, C*H*$_2$N), 1.83 (s, 12 H, N*Me*$_2$), 5.37 (s, 2 H, C*H*), 6.15 (d, *J* = 7.5 Hz, 2H, *m*-C_5H_3N), 6.92 (t, *J* = 7.8 Hz, 1H, *p*-C_5H_3N). ^{13}C NMR (75.5 MHz, C_6D_6): *δ* 1.92 (Si*Me*$_3$), 31.57 (C*Me*$_3$), 45.98 (*C*Me$_3$), 52.25 (TMEDA), 58.36 (TMEDA), 112.94 (*C*H), 118.56, 129.02, 135.65 (C_5H_3N), 154.85 (*C*(Bu^t)).

[Li{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}][Li(TMEDA)$_2$] (4). To an orange solution of [{(CHSiMe$_3$)$_2$C$_5$H$_3$N-2,6}{Li(TMEDA)}$_2$] (**1**) (10.30 mmol) in Et$_2$O (60 mL) was added dropwise PhCN (2.1 mL, 20.59 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and became red. Filtration and concentration of the solution yielded **4** as orange crystals (6.57 g, 91%). Anal. Calcd for $C_{39}H_{65}N_7Si_2Li_2$: C, 66.76; H, 9.27; N, 13.98. Found: C, 66.42; H, 9.74; N, 13.51. ^1H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 0.30 (s, 18 H, Si*Me*$_3$), 2.06 (s, 24 H, N*Me*$_2$), 2.30 (s, 8 H, C*H*$_2$N), 5.38 (s, 2 H, C*H*), 6.12 (d, *J* = 7.8 Hz, 2 H, *m*-C_5H_3N), 6.87 (t, *J* = 7.8 Hz, 1 H, *p*-C$_5$*H*$_3$N), 7.13−7.19 (m, 2 H, *p*-C$_6$*H*$_5$), 7.23−7.28 (m, 4 H, *m*-C$_6$*H*$_5$), 7.69−7.73 (m, 4 H, *o*-C$_6$*H*$_5$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 4.72 (Si*Me*$_3$), 45.90 (THF), 58.24 (THF), 102.60 (*C*H), 112.79, 126.87, 128.93, 137.00, 150.31, 158.56 (*C*$_6$H$_5$ and *C*$_5$H$_3$N), 168.76 (*C*(Ph)). MS (EI, 70 ev): *m/z* 457 (100, [M − 2 Li −2 TMEDA + 2]$^+$), 442 (53, [M − 2 Li −2 TMEDA − Me + 2]$^+$).

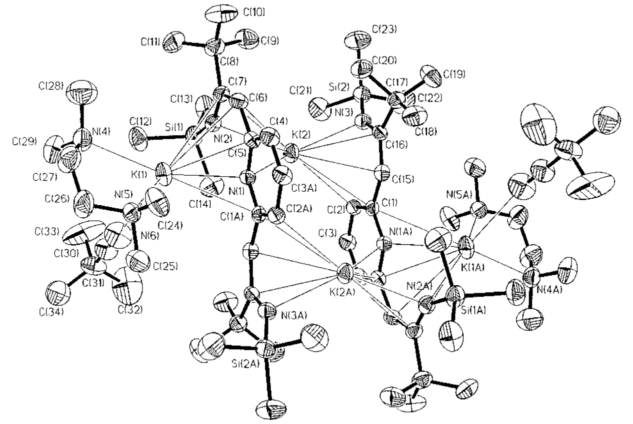

Figure 6. Molecular structure of complex **7**. Hydrogen atoms have been omitted for clarity.

[{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}{Li(Et$_2$O)}{K(TMEDA)}] (5) and [{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}{K(TMEDA)}$_2$] (6). To a solution of (CH$_2$SiMe$_3$)$_2$C$_5$H$_3$N-2,6 (4.23 g, 16.8 mmol) in hexane (40 mL) was added Lochmann's reagent (a reaction mixture of Bu^{n}Li (21.0 mL, 33.6 mmol, 1.6 M in hexane, Bu^{t}OK, 3.77 g, 33.7 mmol, and TMEDA, 5.1 mL, 33.9 mmol) at −78 °C. The resulting mixture was stirred at −40 °C for 5 h. PhCN (3.44 mL, 33.6 mmol) was then added at −78 °C, and the mixture was stirred at −40 °C for a further 5 h. PhCN (3.44 mL, 33.6 mmol) was then added to the mixture at −78 °C and stirred under −40 °C for a further 5 h. Removal of solvent under vacuum and recrystallizing the red residue from Et$_2$O/hexane afforded reddish-yellow crystals of **5**, 2.50 g (20.3%).^1H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 0.08 (s, 18 H, Si*Me*$_3$), 2.04 (s, 36 H, N*Me*$_2$), 2.27 (s, 4 H, C*H*$_2$N), 5.17 (s, 2 H, C*H*), 6.28 (d, *J* = 7.8 Hz, 2 H, *m*-C$_5$*H*$_3$N), 7.00 (t, *J* = 7.8 Hz, 1 H, *p*-C$_5$*H*$_3$N), 7.06−7.09 (m, 4 H, C$_6$*H*$_5$), 7.17−7.20 (m, 2 H, C$_6$*H*$_5$), 7.3−7.37 (m, 4H, *o*−*C*$_6$*H*$_5$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 4.79 (Si*Me*$_3$), 45.84 (TMEDA), 45.65 (TMEDA), 57.89 (TMEDA), 98.21 (*C*H), 112.87, 125.94, 135.77, 152.74, 159.03 (*C*$_6$H$_5$ and *C*$_5$H$_3$N), 166.59 (*C*(Ph)). ^7Li NMR (155.5 MHz, C_6D_6/C_5D_5N (2:1)): *δ* −1.10. Concentrating the remaining solution and cooling at −30 °C yielded 4.4 g (23.5%) of **6**. ^1H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 0.11 (s, 18H, Si*Me*$_3$), 2.02 (s, 60H, N*Me*$_2$), 2.14 (s, 20H, C*H*$_2$N), 5.17 (s, 2H, C*H*), 6.33 (d, *J* = 7.8 Hz, 2H, *m*-C$_5$*H*$_3$N), 7.08 (t, *J* = 7.8 Hz, 1H, *p*-C$_5$*H*$_3$N), 7.17−7.20 (m, 4H, *m*-C$_6$*H*$_5$), 7.29−7.31 (m, 2H, *p*-C$_6$*H*$_5$), 7.50−7.53 (m, 4H, *o*-C$_6$*H*$_5$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_5N (2:1)): *δ* 4.84 (Si*Me*$_3$), 45.65 (TMEDA), 57.89 (TMEDA), 98.21 (*C*H), 112.87, 125.94, 135.77, 152.74, 159.03 (*C*$_6$H$_5$ and *C*$_5$H$_3$N), 166.59 (*C*(Ph)). Keeping the remaining mother liquor at −30 °C for 7 days yielded 1.5 g of **4** (12.7%).

[{{N(Bu^t)C(SiMe$_3$)C(H)}$_2$C$_5$H$_3$N-2,6}{K(TMEDA)K-(NCBu^t)}]$_2$ (7). To a colorless solution of [{(SiMe$_3$)CH$_2$}$_2$C$_5$H$_3$N-2,6] (4.92 g, 19.55 mmol) with TMEDA (5.90 mL, 39.10 mmol) in Et$_2$O (40 mL) was added slowly LiBu^n (24.44 mL, 39.10 mmol, 1.6 M) at −78 °C. After stirring at room temperature for 8 h, 4.50 mL (40.70 mmol) of Bu^{t}CN was added dropwise to the reaction mixture at −78 °C. It was allowed to stir at 25 °C for 12 h, and a red suspension was formed. KOBu^t (4.48 g, 39.92 mmol) in Et$_2$O (20 mL) was added slowly at −78 °C. The reaction mixture was stirred at −40 °C for 4 h. The mixture

Table 7. Summary of Crystallographic Data for Compounds 2−7

	2	3	4	5	6	7
formula	$C_{31}H_{58}Li_2N_3O_2Si_2$	$C_{29}H_{57}Li_2N_5Si_2$	$C_{39}H_{65}Li_2N_7Si_2$	$C_{37}H_{58}KLiN_5OSi_2$	$C_{39}H_{65}K_2N_7Si_2$	$C_{34}H_{66}K_2N_6Si_2$
fw	574.86	545.86	702.04	691.10	766.36	693.14
color/shape	yellow/blocks	red/needles	yellow/blocks	orange/blocks	yellow/blocks	yellow/blocks
cryst size (mm^3)	0.56 × 0.48 × 0.46	0.30 × 0.25 × 0.22	0.52 × 0.37 × 0.25	0.90 × 0.70 × 0.50	0.59 × 0.54 × 0.52	0.40 × 0.35 × 0.30
cryst system	trigonal	orthorhombic	orthorhombic	monoclinic	triclinic	triclinic
space group	$P3_1$	*Pbca*	$C222_1$	*P*2(1)/*c*	*P*1	$P\bar{1}$
a (Å)	32.449(5)	15.856(6)	17.328(4)	16.725(3)	11.130(8)	11.552(2)
b (Å)	32.449(5)	18.273(1)	22.307(5)	11.815(2)	11.965(9)	14.882(3)
c (Å)	8.795(2)	25.252(2)	14.091(3)	22.686(5)	17.925(12)	15.279(3)
α (deg)	90	90	90	90	101.884(18)	63.67(3)
β (deg)	90	90	90	105.39(3)	94.267 (18)	80.83(3)
γ (deg)	120	90	90	90	96.676(17)	73.29(3)
V (Å^3)	8020(3)	7316.4(8)	5446.9(19)	4322(1)	2308(3)	2253.3(8)
Z	9	8	4	4	2	2
density (Mg/m^3)	1.357	0.991	0.856	1.062	1.103	0.721
abs coeff (mm^{-1})	0.150	0.119	0.092	0.210	0.290	0.273
F(000)	2835	2400	1528	1492	828	552
θ range for data collecn (deg)	1.26−25.52	1.88−24.00	2.89−24.00	1.86−24.00	1.76−24.00	1.65−24.00
no. of reflns collected	13 809	4030	3178	4419	11 605	4332
no. of indep reflns (R_{int})	13 809 (0.0000)	4030 (0.0000)	3083 (0.0763)	4419(0.0000)	7246(0.0630)	4332(0.0000)
no. of obsd reflns [$I > 2\sigma(I)$]	8502	2833	2175	2877	7246	2651
goodness of fit on *F*	0.933	1.175	1.069	1.092	0.850	1.127
R [$I > 2\sigma(I)$]	0.0699	0.0935	0.0843	0.0695	0.0638	0.0707
R_w [$I > 2\sigma(I)$]	0.1736	0.1462	0.1884	0.1975	0.1774	0.2050
extinction coeff	0.00009(6)	0.00017(5)	0.0000(3)	0.0000(9)	0.0001(8)	0.0000(14)
largest diff peak and hole (e Å^{-3})	0.217 and −0.235	0.151 and −0.120	0.159 and −0.132	0.275 and −0.191	0.261 and −0.235	0.580 and −0.205

was then left to stir for another 4 h at room temperature. Filtration followed by concentration of the solution and cooling at −30 °C yielded **7** as red crystals. Yield: 7.51 g (55.4%). Mp: 157−159 °C. Anal. Calcd for $C_{29}H_{57}K_2N_5Si_2$: C, 57.09; H, 9.42; N, 11.48. Found: C, 56.64; H, 9.31; N, 11.68. ^{1}H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): δ 0.53 (s, 18H, $SiMe_3$), 0.84 (s, 9H, (Me_3)CCN)), 1.35 (s, 18H, CMe_3), 2.04 (s, 12H, NMe_2), 2.26 (s, 4H, CH_2N), 5.44 (s, 2H, C*H*), 7.21 (d, J = 17.4 Hz, 2H, *m*-C_5H_3N) 7.71 (br. s, 1H, *p*-C_5H_3N). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_5N (2:1)): δ 4.84 ($SiMe_3$), 45.65 (TMEDA), 57.89 (TMEDA), 98.21 (*C*H), 112.87, 125.94, 135.77, 152.74, 159.03 (C_6H_5 and C_5H_3N), 166.59 (*C*(Ph)).

Crystallography. Selected single crystals were sealed in Lindemann glass capillaries under dinitrogen. X-ray intensities were measured at 293 K on an MSC/Rigaku RAXIS IIc imaging-plate diffractometer for compounds **2**, **3, 5, 6**, and **7** and at 296 K for compound **4**, using Mo Kα radiation (λ = 0.71073 Å). A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program for **2**−**7**.[34] The crystal structures of compounds **2**−**7** were determined by the direct method, which yielded the positions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure−factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM-compatible personal computer with the SHELXTL-PLUS,[35] SHELXTL-93,[36] or SHELXTL-97 program package.[37] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[38] Crystallographic data collection and structure refinement of all compounds are summarized in Table 7.

Acknowledgment. The work described in this paper was substantially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. CUHK 4265/00P).

Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org. Author: Ref 12 was missing. The remaining refs were numbered consecutively. Please provide missing ref or renumber the following references.

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