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Syntheses, Structures, and Reactivities of 2,3-Pyrazyl-Linked Bis(1-aza-allyl) Alkali-Metal Complexes

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The dilithium compound $[Li_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_2]_2$ (**2**) has been obtained by dilithiation of 2,3-bis(trimethylsilylmethyl)pyrazine, $(CH_2SiMe_3)_2C_4H_2N_2\text{-}2,3$ (**1**), using Bu^nLi followed by the reaction with Bu^tCN. Compounds of the heavier congeners $[Na_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_2]_2$ (**3**) and $[K_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_3]_2$ (**4**) have been obtained by treating **2** with Bu^tONa or Bu^tOK, respectively. Treatment of **2** with 4 equiv of $MgBr_2(Et_2O)$ yielded the binuclear magnesium complex $[Mg_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}Br_2(THF)_4]$ (**5**). Similar metathesis reaction of **2** with 4 equiv of $ZnCl_2$ gave the zwitterionic lithium zincate complex $[Zn_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}Cl_2(\mu\text{-}Cl)_2Li_2(THF)_6]$ (**6**). However, the reaction of **2** with 4 equiv of $CdCl_2$ afforded a heterocyclic compound, $[\{Me_2\overline{Si\{NC(Bu^t)C(H)\}\}_2C_4H_2N}_2\text{-}2,3]$ (**7**). X-ray structures of compounds **2**−**7** have been determined.

Introduction

It has been found that 1-aza-allyl ligands can play the role of spectator ligands, by virtue of their strong binding ability to metals, their exceptional and tunable steric demands, and their diversity in bonding modes. Metal 1-aza-allyls and β-diketiminates have been studied and reported.[1−4] Thermally stable 1-aza-allyl complexes of the s-, p-, d-, and f-block metals in a variety of metal oxidation states have been prepared and characterized.[5] This is attributed to the kinetic stabilization provided by the bulky substituents at the 1-N and 3-C positions and the presence of the hard nitrogen and soft carbon potential ligating centers.

In our earlier studies, we have synthesized pyridyl-, quinolyl-linked 1-aza-allyl lithium compounds by the reaction of a lithium alkyl with organonitrile.[6] Recently, the syntheses and structures of the 2,6-pyridyl-linked bis(1-aza-allyl) alkali-metal compounds have been reported.[7] These β-diketiminate-based ligands possess a nitrogen heterocycle as part of the ligand backbone and are thus expected to possess both good σ- and π-donating properties. It is believed that coordination from the heterocylic nitrogen contributes to the stability of the metal compounds found. Moreover, the phenyl-linked bis(1-aza-allyl) alkali-metal compounds show that the electrons within the 1-aza-allyl side chains are delocalized along the phenyl ring, indicating these ligands carry similar features of an open heteropentadienyl ligand.[8] In this work, we report the synthesis of a β-diketiminate-based 2,3-pyrazyl-linked bis(1-aza-allyl) ligand and show the anticipated charge delocalization within the two 1-aza-allyl sidearms through the pyrazyl ring. This might provide the potential of this ligand to be a bulky spectator ligand to influence the coordination environment of the metal similar to the cyclopentadienyl or fulvalene ligands. This series of alkali-metal compounds for the 2,3-pyrazyl-linked bis(1-aza-allyl) ligand were prepared and used as the ligand transfer reagents to synthesize group 2 and 12 metal compounds, and their structures and reactivities are reported.

Results and Discussion

2,3-Bis(trimethylsilylmethyl)pyrazine (**1**) was prepared by the reaction of 2,3-dimethylpyrazine with 2 equiv of Bu^nLi followed by the addition of 100% excess Me_3SiCl (Scheme 1). Dilithiation of **1** with Bu^nLi in THF followed by the reaction with Bu^tCN afforded the 2,3-pyrazyl-linked bis(1-aza-allyl) dilithium complex $[Li_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_2]_2$ (**2**) as dark red crystals in 90.4% yield. Metal-exchange reactions between **2** and 4 equiv of Bu^tONa or Bu^tOK in hexane at 0 °C led to the formation of the dark red crystalline disodium complex $[Na_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_2]_2$ (**3**) and dipotassium complex $[K_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_3]_2$ (**4**) in 62.9 and 53.9% yields, respectively.

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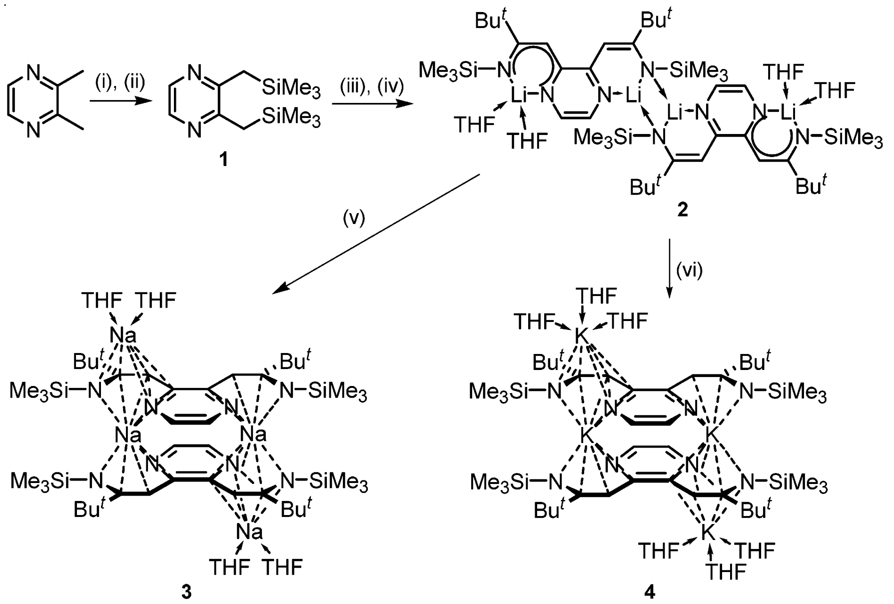
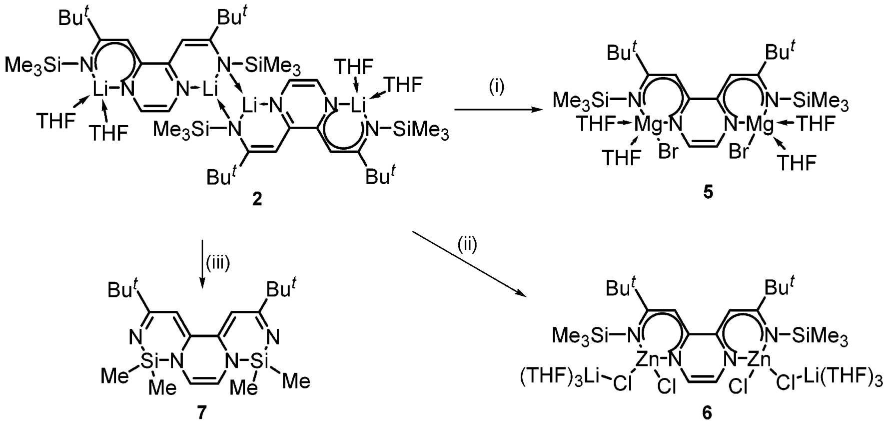
Scheme 1[a]



[a] Reagents: (i) 2 Bu^{n}Li, 2 TMEDA, Et_2O; (ii) excess Me_3SiCl; (iii) 2 Bu^{n}Li, THF; (iv) 2 Bu^{t}CN; (v) 4 Bu^{t}ONa, hexane, recrystallized from THF/toluene; (vi) 4 Bu^{t}OK, hexane, recrystallized from THF.

Scheme 2[a]



[a] Reagents: (i) 4 $MgBr_2(Et_2O)$, Et_2O, recrystallized from THF; (ii) 4 $ZnCl_2$, Et_2O, recrystallized from THF (iii) 4 $CdCl_2$, Et_2O.

The reactivity of **2** as a ligand transfer reagent was studied by treating it with 4 equiv of $MgBr_2(Et_2O)$ or $ZnCl_2$, which afforded the binuclear magnesium complex [Mg_2{{N($SiMe_3$)C(Bu^t)-C(H)}$_2C_4H_2N_2$-2,3}$Br_2(THF)_4$] (**5**) and the zwitterionic lithium zincate complex [Zn_2{{N-($SiMe_3$)C(Bu^t)C(H)}$_2C_4H_2N_2$-2,3}$Cl_2(\mu\text{-}Cl)_2Li_2(THF)_6$] (**6**) as red and reddish orange crystals in 61.4 and 89.8% yield, respectively (Scheme 2). Attempts to eliminate LiCl and THF from **6** by sublimation were not successful, as it decomposed at higher temperature.

Attempts to synthesize the cadmium(II) compound by reacting **2** with 2 or 4 equiv of $CdCl_2$ have not been successful. However, the reaction of **2** with 4 equiv of $CdCl_2$ afforded the unexpected cyclized product [{Me_2-Si{NC(Bu^t)C(H)}}$_2C_4H_2N_2$-2,3] (**7**) in moderately high yield (86.7%). After standing the reaction mixture for about 30 days, some black solids were precipitated out, which was presumably the side products of the reaction. The formation of the silicon heterocyclic compound **7** resulted from the formation of a new Si−N bond and the cleavage of a Si−C bond. It was also found that the aromaticity of the pyrazyl ring was diminished. The driving force of the reaction is presumably the intramolecular ring closure by a silicon atom rather than a softer cadmium atom. Due to the weak acceptor properties of cadmium, the binding of the other functional group (such as C- or N-functional groups) with this soft cadmium center is more susceptible to dissociation, which is a possible reaction pathway for the formation of cyclized product **6**. Raston and co-workers have reported a similar result in which the reaction of $CdCl_2$ with Li{N(8-quinolyl)($SiMe_3$)} yielded $CdMe_2$ and the dimeric five-coordinate silicon species [$Me_2Si(\mu\text{-}N\text{-}C_9H_6N)(\mu\text{-}N\text{-}C_9H_6N)SiMe_2$] possessing an Si_2N_2 ring system.[9] Reaction of **2** with mercury(II) halides resulted in the rapid formation of metallic mercury.

Compound **2** is extremely air- and moisture-sensitive. It is soluble in THF and Et_2O, but only sparingly soluble in toluene and saturated hydrocarbons. It darkens and decomposes at temperature above 300 °C. It has been

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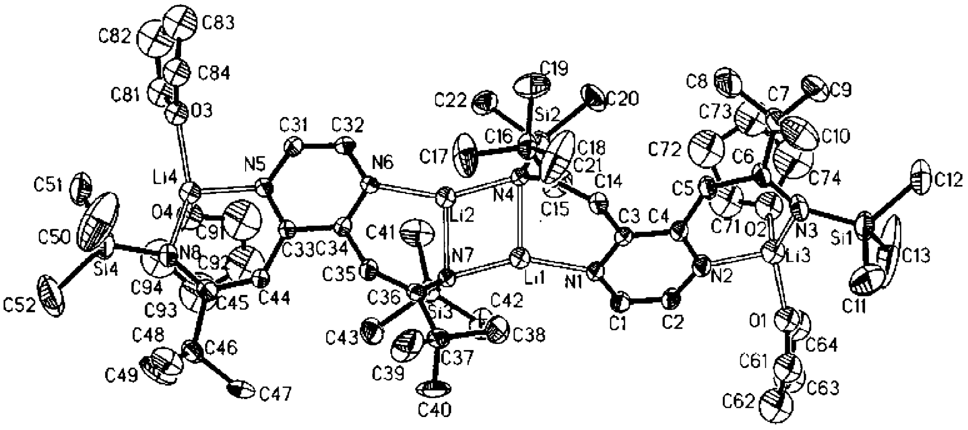

Figure 1. ORTEP drawing of **2** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

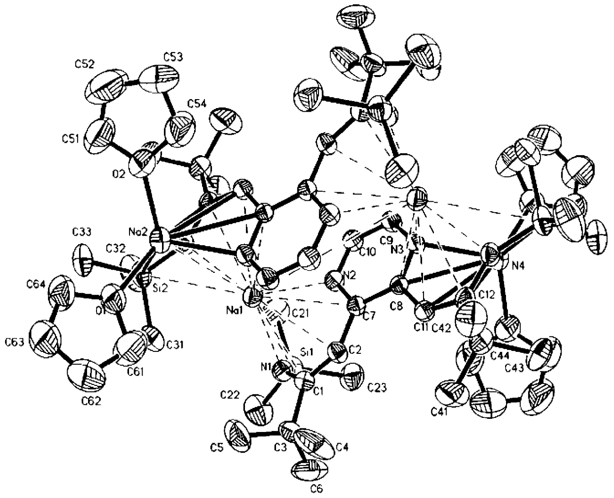

Figure 2. ORTEP drawing of **3** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The ^{1}H NMR spectrum of **2** showed two sharp singlets at δ 0.29 and 1.36 ppm attributed to the protons of $SiMe_3$ and Bu^t groups, respectively. The peak at δ 6.09 ppm was assigned to the methine proton. The pyrazyl protons displayed one singlet in the aromatic region at δ 6.98 ppm. The ^{13}C NMR spectrum of **2** displayed nine peaks that were consistent with the proposed structure. Compounds **3** and **4** are extremely sensitive toward air and moisture. They are soluble in THF and Et_2O, while sparingly soluble in toluene and saturated hydrocarbons. Compounds **3** and **4** darken and decompose at temperature above 180 and 270 °C, respectively. They have been characterized by NMR spectroscopy, elemental analysis (for **3** only), and X-ray crystallography. Due to the extremely air-sensitive nature of the compound, the elemental analysis result of **4** was not satisfactory.

The ^{1}H and ^{13}C NMR spectra of **3** and **4** are similar to those of **2**, showing the corresponding singlets of $SiMe_3$, Bu^t, methine, and pyrazyl protons. In the spectra of **2**−**4**, one set of resonances due to the 1-aza-allyl ligand was observed, indicating that compounds **2**−**4** contain ligands that are bound to the metal centers in symmetrical and equivalent positions.

The molecular structures of **2**−**4** are shown in Figures 1−3, respectively. Selected bond distances and angles are listed in Tables 1−3, respectively.

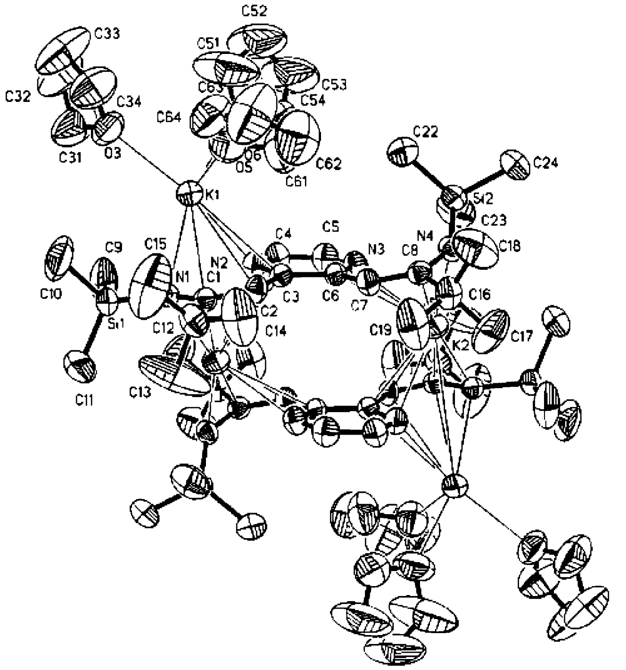

Figure 3. ORTEP drawing of **4** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Compound **2** is a centrosymmetric dimer with C_2 symmetry. It consists of two different lithium environments. One lithium atom is three-coordinate in the central Li_2N_2 trapezoid, and the angles subtended at N (74.5(3)° and 75.2(3)°) are smaller than those at Li (104.9(3) and 105.4(3)°). The second lithium atom is four-coordinate with a terminal *N*,*N′*-chelation by the ligand. The Li(1) atom is coordinated to the ligand in a η^2 fashion with the σ-bonded enamido ligand supplemented by a dative σ-bonded pyrazyl moiety. The bonding within the N(1)C(3)C(14)C(15)N(4) ligand skeleton which is localized with the $Bu^tC{=}C$ double bond is evident from the comparatively short C(14)−C(15) distance of 1.357(4) Å and long N(4)−C(15) distance of 1.395(4) Å. These features are similar to those of $[Li\{N(SiMe_3)C(R)C(H)(C_5H_4N\text{-}2)\}]_2$ (R = Ph, Bu^t).[6] The Li(3) atom is bound to both amido nitrogen and pyrazyl nitrogen atoms. Within the planar N(2)C(4)C(5)C(6)N(3) ring, the two C−C (1.419(5) and 1.391(5) Å) and C−N (1.368(4) and 1.329(5) Å) bond lengths in the backbone show considerable bond delocalization in the NCCCN fragment. Similar delocalization within the NCCCN

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 2

N(1)−Li(1)	1.998(7)	N(6)−Li(2)	1.995(7)
N(4)−Li(1)	2.060(7)	N(7)−Li(2)	2.053(7)
N(7)−Li(1)	1.971(7)	N(4)−Li(2)	1.993(7)
N(2)−Li(3)	1.987(8)	N(3)−Li(3)	2.062(9)
C(3)−C(14)	1.456(5)	C(4)−C(5)	1.419(5)
C(14)−C(15)	1.357(4)	C(5)−C(6)	1.391(5)
C(15)−N(4)	1.395(4)	C(6)−N(3)	1.329(5)
C(1)−C(2)	1.345(5)	C(3)−C(4)	1.442(5)
N(1)−C(3)	1.339(4)	N(1)−C(1)	1.358(4)
N(2)−C(2)	1.335(5)	N(2)−C(4)	1.368(4)
Li(2)−N(4)−Li(1)	74.5(3)	Li(1)−N(7)−Li(2)	75.2(3)
N(7)−Li(1)−N(4)	105.4(3)	N(4)−Li(2)−N(7)	104.9(3)
N(7)−Li(1)−N(1)	154.0(4)	N(4)−Li(2)−N(6)	155.5(4)
N(1)−Li(1)−N(4)	100.2(3)	N(6)−Li(2)−N(7)	99.3(3)
O(2)−Li(3)−N(2)	107.7(4)	O(2)−Li(3)−N(3)	109.3(4)
O(2)−Li(3)−O(1)	99.4(4)	O(1)−Li(3)−N(3)	140.0(4)
N(2)−Li(3)−O(1)	99.0(4)	N(2)−Li(3)−N(3)	98.2(4)
N(4)−C(15)−C(14)	124.7(3)	N(3)−C(6)−C(5)	123.5(4)
C(15)−C(14)−C(3)	128.1(3)	C(6)−C(5)−C(4)	133.9(3)
C(14)−C(3)−N(1)	119.4(3)	C(5)−C(4)−N(2)	121.7(3)
C(4)−C(3)−N(1)	121.0(3)	C(3)−C(4)−N(2)	118.8(3)
C(3)−N(1)−C(1)	117.8(3)	C(4)−N(2)−C(2)	117.1(3)

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 3[a]

Na(1)−N(1)	2.383(2)	Na(1)−N(4′)	2.440(2)
Na(1)−C(1)	2.817(2)	Na(1)−C(12′)	2.924(2)
Na(1)−C(2)	3.063(2)	Na(1)−C(11′)	3.061(2)
Na(1)−C(7)	3.038(2)	Na(1)−C(8′)	2.939(2)
Na(1)−N(2)	2.394(2)	Na(1)−N(3′)	2.529(2)
Na(2)−O(1)	2.298(2)	Na(2)−C(8′)	2.939(2)
Na(2)−N(3′)	2.351(2)	Na(2)−C(11′)	3.018(2)
Na(2)−N(4′)	2.424(2)	Na(2)−C(12′)	2.883(2)
C(7)−C(2)	1.437(3)	C(8)−C(11)	1.443(3)
C(2)−C(1)	1.385(3)	C(11)−C(12)	1.389(3)
C(1)−N(1)	1.320(3)	C(12)−N(4)	1.351(3)
C(7)−C(8)	1.462(3)	C(9)−C(10)	1.340(3)
N(2)−C(7)	1.344(3)	N(2)−C(10)	1.344(3)
N(3)−C(8)	1.346(2)	N(3)−C(9)	1.355(3)
N(1)−Na(1)−N(2)	77.32(7)	N(3′)−Na(1)−N(4′)	75.68(7)
N(3′)−Na(2)−N(4′)	79.33(7)	O(1)−Na(2)−O(2)	104.94(10)
N(1)−C(1)−C(2)	128.0(2)	N(4)−C(12)−C(11)	124.53(19)
C(1)−C(2)−C(7)	129.8(2)	C(12)−C(11)−C(8)	133.69(19)
C(2)−C(7)−N(2)	119.56(19)	C(11)−C(8)−N(3)	120.44(18)
C(8)−C(7)−N(2)	119.19(17)	C(7)−C(8)−N(3)	119.39(17)
C(7)−N(2)−C(10)	118.62(19)	C(8)−N(3)−C(9)	118.21(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

fragment has been found in similar compounds.[10] The Li−N bond distances are in the normal range of 1.895−2.087 Å for the Li−N (amido) bonds.[11−14]

Compounds **3** and **4** are dimeric in the solid state. The two metal atoms within each compound are in different environments. One metal atom is bridged to two β-diketiminato backbones of different ligands in a sandwich-like manner. The other metal atom is bound to two or three coordinated THF molecules and one β-diketiminato fragment. In compound **3**, the Na(1) atom is coordinated to two NCCCN backbones of different ligands. The average Na(1)−C and Na(1)−N distances are 2.974 and 2.437 Å, respectively. The Na(2) atom is bound to two THF molecules and one NCCCN fragment of the ligand. The average Na(2)−C and Na(2)−N distances are 2.947 and 2.388 Å, respectively. Overall, the average Na−C distance of 2.965 Å, which is slightly longer than that in $[\mathrm{Na}(\eta^5\text{-CHPh}_2)(\mathrm{PMDTA})]$ of 2.843 Å[15] or in $[\mathrm{Na}(\eta^5\text{-C}_5\mathrm{H}_4\mathrm{R})(\mathrm{THF})]_\infty$ (R = (+)-neomenthyl) of 2.771 Å,[16] indicates that the fragment can be rendered as a six-electron donor with some extent of π-interaction. The average Na−N distance of 2.420 Å is comparable with the distance of 2.434 Å in 1,3,5,7-tetraazaheptatrienylsodium[17] and the distance of 2.355 Å in $[\mathrm{Na}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}]$.[18] The trans conformation of Na(2) and Na(2′), existing on opposite sides of the NCCCN moiety, is to minimize the sterical crowding in the ligands.[19,20] Compound **4** consists of two different potassium environments: the K(1) atom is coordinated to three THF molecules and one NCCCN fragment, and the K(2) atom is bound to two NCCCN moieties of different ligands. One more THF molecule was found in the potassium atom when compared with its sodium analogue, due to a larger and more electropositive metal center. The average K−C distance of 3.222 Å is slightly longer than that in $[\mathrm{K}\{\eta^5\text{-C}_5\mathrm{H}_4(\mathrm{SiMe}_3)\}]_\infty$ of 3.027 Å[21] or in $[\mathrm{K}(\eta^5\text{-C}_5\mathrm{H}_4\mathrm{R})(\mathrm{DME})]_\infty$ (R = (+)-neomenthyl) of 3.080 Å,[16] indicating π-interaction between the anionic ligands and potassium metal ions. The average K−N distance (2.788 Å) is similar to that in $[\{\{\mathrm{K}\{2\text{-C}_5\mathrm{H}_4\mathrm{N}(\mathrm{NSiMe}_3)\}(12\text{-crown-4})\}_2\}\cdot 2\mathrm{PhMe}]$ (2.870 Å)[22] and $[\{\mathrm{K}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}\}_2]$ (2.787 Å).[23] The distance of

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 4[a]

K(1)−O(3)	2.768(6)	K(1)−C(1)	3.257(6)
K(1)−N(1)	2.851(5)	K(1)−C(2)	3.356(2)
K(1)−N(2)	2.766(5)	K(1)−C(3)	3.269(6)
K(2)−N(3)	2.716(6)	K(2)−N(2′)	2.808(6)
K(2)−C(6)	3.331(6)	K(2)−C(3′)	3.104(6)
K(2)−C(7)	3.291(6)	K(2)−C(2′)	3.231(6)
K(2)−C(8)	3.018(6)	K(2)−C(1′)	3.145(6)
K(2)−N(4)	2.764(5)	K(2)−N(1′)	2.823(5)
C(6)−C(7)	1.414(7)	C(3)−C(2)	1.445(7)
C(7)−C(8)	1.383(8)	C(2)−C(1)	1.397(7)
C(8)−N(4)	1.333(7)	C(1)−N(1)	1.329(7)
C(3)−C(6)	1.461(7)	C(4)−C(5)	1.332(8)
N(2)−C(3)	1.332(7)	N(2)−C(4)	1.346(7)
N(3)−C(5)	1.344(8)	N(3)−C(6)	1.350(7)
N(1)−K(1)−N(2)	64.80(14)	O(5)−K(1)−O(6)	82.9(3)
N(3)−K(2)−N(4)	67.67(16)	N(1′)−K(2)−N(2′)	64.64(14)
N(1)−C(1)−C(2)	124.0(5)	N(4)−C(8)−C(7)	129.3(6)
C(1)−C(2)−C(3)	132.7(6)	C(8)−C(7)−C(6)	131.3(6)
C(2)−C(3)−N(2)	120.5(5)	C(7)−C(6)−N(3)	118.9(5)
C(6)−C(3)−N(2)	119.9(5)	C(3)−C(6)−N(3)	118.5(5)
C(3)−N(2)−C(4)	119.0(5)	C(5)−N(3)−C(6)	117.9(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z+1$.

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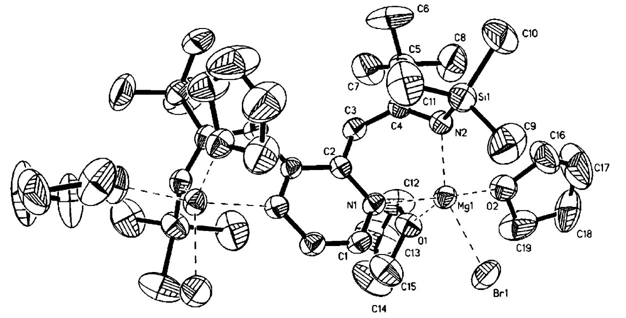

Figure 4. ORTEP drawing of **5** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

the metal atom deviated from the NCCCN plane in **4** (2.29 Å) is longer than the corresponding distances in **3** (1.80 Å). Also, the mean bond angle of N−K−N in **4** (65.70°) is smaller than the corresponding angle in **3** (77.44°), indicating the ionic interactions of the central metal atom with the ligand decrease from Na to K because of differences in their atomic sizes. Similar to compound **3**, the trans conformation of K(1) and K(1′) in **4** presumably reduces the steric interaction within the ligand.

Compounds **5** and **6** are air-sensitive crystalline solids. They are soluble in THF and Et_2O but only sparingly soluble in hexane. They have been characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Compound **7** is an orange crystalline solid with a melting point of 240.2−243.3 °C. It is soluble in THF and Et_2O and only sparingly soluble in hexane and toluene. The NMR and FAB mass spectra of **7** are in full agreement with its X-ray structure and molecular formula. Satisfactory elemental analysis results of **7** could not be obtained, probably due to the extreme air-sensitive nature of the compound.

The ^1H NMR spectrum of **5** displayed three sharp singlets at δ 0.12, 1.30, and 6.10 ppm, assignable to the $SiMe_3$, Bu^t, and methine protons, respectively. The chemical shifts of these three groups of protons are similar to those in **2**; however, the pyrazyl proton of **5** at δ 9.38 ppm was more deshielded than that in **2**. Protons attached to the CN group are more deshielding, and this can also be found in other five-coordinate magnesium compounds $[\{Mg(salen)\}_2]$ (H_2salen = *N*,*N*′-ethylenebis(salicylideneimine)) (δ 10.10 ppm) and $[\{Mg(salphen)\}_2]$ (H_2salen = *o*-phenylenebis(salicylideneimine)) (δ 9.90 ppm).[24] In the ^1H and ^{13}C NMR spectra of **6**, the singlets for the $SiMe_3$, Bu^t, methine, and pyrazyl groups were in the normal range. In all the spectra of **5** and **6**, one set of signals due to the 1-azaallyl side chains was observed, consistent with their solid-state structure in which the chemical environments of the two ligand side chains were symmetrical and equivalent. The ^1H NMR spectrum of **7** displayed two singlets for the $SiMe_2$ and Bu^t groups with the integration ratio of 2:3, which agrees well with the molecular structure of compound **7**. The ^{13}C NMR chemical shifts of **7** are somewhat different from those in compounds **5** and **6**, owing to the presence of localized C=C and C=N double bonds.

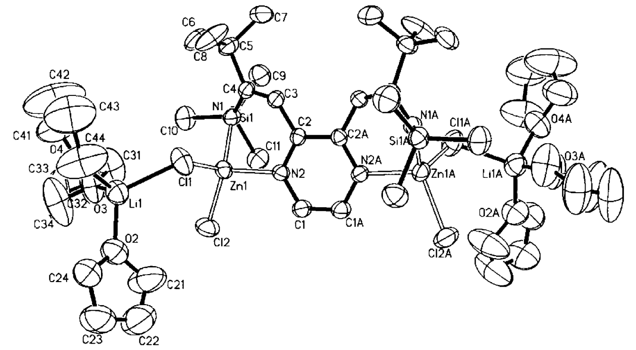

Figure 5. ORTEP drawing of **6** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

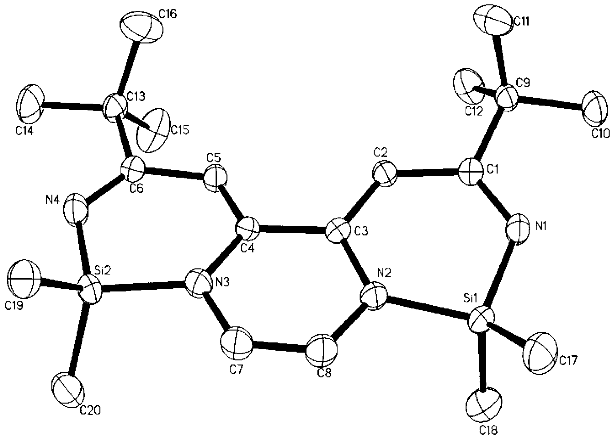

Figure 6. ORTEP drawing of **7** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 5[a]

Mg(1)−N(1)	2.197(4)	Mg(1)−N(2)	2.066(4)
Mg(1)−O(1)	2.100(4)	Mg(1)−O(2)	2.114(4)
Mg(1)−Br(1)	2.5293(18)	C(2)−C(3)	1.438(7)
C(3)−C(4)	1.366(7)	C(4)−N(2)	1.376(6)
C(1)−C(1′)	1.345(10)	C(2)−C(2′)	1.450(9)
N(1)−C(1)	1.342(6)	N(1)−C(2)	1.349(6)
N(1)−Mg(1)−N(2)	85.94(16)	N(1)−Mg(1)−O(2)	171.7(2)
N(1)−Mg(1)−Br(1)	94.78(12)	N(1)−Mg(1)−O(1)	88.05(16)
O(2)−Mg(1)−O(1)	85.48(18)	O(2)−Mg(1)−Br(1)	91.81(15)
O(2)−Mg(1)−N(2)	92.90(17)	Br(1)−Mg(1)−N(2)	135.79(14)
O(1)−Mg(1)−N(2)	121.08(17)	O(1)−Mg(1)−Br(1)	103.11(13)
N(2)−C(4)−C(3)	123.7(4)	C(4)−C(3)−C(2)	125.3(5)
C(3)−C(2)−N(1)	120.8(4)	N(1)−C(2)−C(2′)	119.1(2)
C(2)−N(1)−C(1)	119.1(4)	C(3)−C(2)−C(2′)	120.1(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, z.

The molecular structures of **5**−**7** are shown in Figures 4−6, respectively. Selected bond distances and angles are listed in Tables 4−6, respectively.

Compound **5** is monomeric with C_2 symmetry in the solid state. The five-coordinate magnesium atom is in a distorted trigonal bipyramidal geometry. The chelating pyrazyl nitrogen atom and THF molecule are in the axial positions, while the equatorial sites are occupied by the chelating amido nitrogen atom, THF molecule, and the bromine atom. The β-diketiminato system thus formed spans equatorial and axial sites, indicating the flexibility of the ligand by twisting the metallacyclic ring. The structural data indicate that the geometry of compound **5** is slightly distorted from a regular trigonal bipyramid. Mg(1) is η^2-bonded to the ligand through the

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Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound 6[a]

Zn(1)−N(1)	1.969(3)	Zn(1)−N(2)	2.038(3)
Zn(1)−Cl(1)	2.3162(15)	Zn(1)−Cl(2)	2.2196(13)
Li(1)−Cl(1)	2.317(9)	Li(1)−O(2)	1.909(11)
Li(1)−O(3)	1.923(11)	C(2)−C(3)	1.432(5)
C(3)−C(4)	1.367(5)	C(4)−N(1)	1.369(5)
C(1)−C(1′)	1.349(7)	C(2)−C(2′)	1.443(7)
N(2)−C(1)	1.361(5)	N(2)−C(2)	1.350(4)
N(1)−Zn(1)−N(2)	93.43(12)	N(1)−Zn(1)−Cl(1)	108.05(10)
N(1)−Zn(1)−Cl(2)	130.08(10)	N(2)−Zn(1)−Cl(1)	104.66(10)
N(2)−Zn(1)−Cl(2)	110.18(10)	Cl(1)−Zn(1)−Cl(2)	107.39(6)
O(2)−Li(1)−Cl(1)	114.4(5)	O(3)−Li(1)−Cl(1)	113.4(5)
O(4)−Li(1)−Cl(1)	106.4(4)	O(2)−Li(1)−O(3)	110.8(5)
O(2)−Li(1)−O(4)	105.1(5)	O(3)−Li(1)−O(4)	105.9(5)
N(1)−C(4)−C(3)	123.2(3)	C(4)−C(3)−C(2)	129.7(4)
C(3)−C(2)−N(2)	119.2(3)	N(2)−C(2)−C(2′)	119.6(2)
C(2)−N(2)−C(1)	118.7(3)	C(3)−C(2)−C(2′)	121.1(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+3/2$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Compound 7

Si(1)−N(1)	1.709(3)	Si(1)−N(2)	1.783(3)
Si(1)−C(17)	1.849(4)	Si(1)−C(18)	1.846(4)
C(3)−C(2)	1.368(4)	C(2)−C(1)	1.446(4)
C(1)−N(1)	1.283(4)	C(3)−C(4)	1.495(3)
N(2)−C(3)	1.387(3)	N(2)−C(8)	1.402(4)
N(1)−Si(1)−N(2)	103.89(12)	N(1)−Si(1)−C(17)	112.12(17)
N(1)−Si(1)−C(18)	112.3(2)	N(2)−Si(1)−C(17)	109.42(18)
N(2)−Si(1)−C(18)	108.25(17)	C(17)−Si(1)−C(18)	110.6(2)
C(1)−N(1)−Si(1)	122.6(2)	C(3)−N(2)−Si(1)	119.9(2)
C(3)−N(2)−C(8)	118.9(2)	C(8)−N(2)−Si(1)	121.0(2)
N(1)−C(1)−C(2)	123.8(3)	C(1)−C(2)−C(3)	125.8(2)

chelating amido and the pyrazyl nitrogen atoms. The C−C bond lengths (1.438(7) and 1.366(7) Å) and C−N bond lengths (1.349(6) and 1.376(6) Å) may indicate some degree of delocalization. The bond distances of the dative Mg(1)−N(1) (2.197(4) Å) and anionic Mg(1)−N(2) (2.066(4) Å) are slightly longer than those in [Mg{N($\overbracket{\text{SiMe}_3)(\text{CH}_2)_3\text{N}}$(Me$_2$)}$_2$] (2.188 and 1.985 Å)[25] and [Mg(N(8-quinolyl)(SiMe$_3$))$_2$] (2.100 and 1.998 Å).[9] The N−Mg−N chelate bite angle is 85.94(16)°, which is moderately smaller than the corresponding angles in other magnesium β-diketiminato compounds.[26−28] Therefore, the bond distances and angles clearly indicate that the five-coordinate magnesium atom is sterically crowded.

Compound **6** has C_2 symmetry. The four-coordinate zinc atom adopts a distorted tetrahedral geometry. This is based on the observed N−Zn−N chelate bite angle of 93.43(12)°, which deviates considerably from the ideal tetrahedral angle of 109.5°. The C−C and C−N bond lengths within the NCCCN fragment indicate some extent of delocalization. The anionic Zn(1)−N(1) bond distance of 1.969(3) Å falls into the range 1.940(4)−2.159(3) Å in similar reported systems.[9,29,30] The Zn(1)−N(2) bond distance of 2.038(3) Å represents a relatively short interaction, when compared with the corresponding distances for other dative zinc−nitrogen bonds (2.070(4)−2.113(3) Å).[9,29−31] The distance of Zn(1)−Cl(1) (2.3162(15) Å) is much longer than Zn(1)−Cl(2) (2.2196(13) Å), possibly due to the coordination of Cl(1) to Li(1). The lithium atom is linked to the zinc metal by a bridging chlorine atom, and the other sites in the coordination spheres are filled by three solvated THF molecules. On the basis of the structural data, the four-coordinate Li(1) atom is observed in a slightly distorted tetrahedral environment.

Compound **7** is a silicon-bridged tricyclic species with a slightly distorted tetrahedral geometry around the silicon atom. The average bond distance of Si−N (1.743 Å) is comparable with that found in [Me$_2$Si(μ-N-C$_9$H$_6$N)(μ-N-C$_9$H$_6$N)SiMe$_2$] (1.77 Å).[9] Structural parameters show that C(2)−C(3) and C(4)−C(5) bond distances are fairly short, indicative of C=C double bonds. Both N(1)−C(1) and N(4)−C(6) bond distances of 1.283(4) and 1.292(4) Å, respectively, are consistent with the double bonds. The loss of aromaticity of the pyrazyl ring is clearly evident from the elongation of the C(3)−C(4) bond, shortening of the C(7)−C(8) bond, and lengthening of the four N−C bonds, when compared with the corresponding bond distances of the pyrazyl ring in the X-ray structures of [{CuBr(2,3-dmp)}$_n$][32] and [Cu$_2$(CN)$_2$-(2,3-dmp)][33] (2,3-dmp = 2,3-dimethylpyrazine).

Conclusion

We have prepared the 2,3-pyrazyl-linked bis(1-aza-allyl) dilithium compound and converted it to the disodium and dipotassium analogues by the reaction with Bu^{t}ONa or Bu^{t}OK, respectively. The structures of these compounds show that the charges within the two 1-aza-allyl fragments are more or less delocalized along the pyrazyl ring, showing that the 2,3-pyrazyl-linked bis(1-aza-allyl) ligands carry features of an open heteropentadienyl ligand similar to the cyclopentadienyl or fulvalene ligands. The reactivities of the dilithium compound prepared have been shown by the reactions with magnesium or zinc halide to form the corresponding magnesium and zinc amido compounds.

Experimental Section

General Considerations. All manipulations were performed under dinitrogen using standard Schlenk and vacuum line techniques. Solvents were dried over and distilled from calcium hydride (n-hexane), sodium/benzophenone (diethyl ether and tetrahydrofuran), or sodium/potassium alloy (toluene). Bu^{n}Li, TMEDA, 2,3-dimethylpyrazine, Me$_3$SiCl, Bu^{t}CN, and all metal halides were purchased from Aldrich Chemical and were used without further purification. The ^{1}H and ^{13}C NMR spectra were measured 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 CDCl$_3$ ($\delta = 7.24$ ppm) or C$_6$D$_5$H ($\delta = 7.15$ ppm) and ^{13}C resonances to CDCl$_3$ ($\delta = 77.0$ ppm) or C$_6$D$_6$ ($\delta = 128.0$ ppm). Elemental analyses were carried out by Medac Ltd. (Brunel University, U.K.). EI and FAB mass spectral data were recorded on a 5989-In mass spectrometer

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and a Thermo Finnigan MAT95XL with nitrobenzyl alcohol as matrix, respectively.

$(CH_2SiMe_3)_2C_4H_4N_2$-2,3 (1). To a mixture of 2,3-dimethylpyrazine (3.06 mL, 28.9 mmol) and TMEDA (8.80 mL, 58.3 mmol) in diethyl ether (150 mL) at −78 °C was added dropwise a solution of Bu^nLi (36.0 mL, 57.6 mmol, 1.6 M solution in hexane). After warming the mixture to room temperature, it was stirred for 5 h. Me_3SiCl (15.0 mL, 118.2 mmol, 100% excess) was then added to the reaction mixture at 0 °C and stirred at room temperature for a further 16 h. To the resulting yellow slurry was added a dilute NaOH solution, and the organic layer was separated. The aqueous layer was extracted with two 100 mL portions of diethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$. Filtration and removal of volatiles under vacuum afforded a yellow oil. Purification by distillation at reduced pressure gave the colorless oil of **1** (5.61 g, 76.7%). Bp = 74−76 °C/0.03 mmHg. Anal. Calcd (%) for $C_{12}H_{24}N_2Si_2$: C 57.08, H 9.58, N 11.09. Found: C 56.89, H 9.35, N 11.10. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 0.32 (s, 18H, Si*Me₃*), 2.31 (s, 4H, C*H₂*), 8.11 (s, 2H, $C_4H_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (ppm) −0.33 (Si*Me₃*), 27.33 (*C*H), 140.08, 155.36 ($C_4H_2N_2$). MS (EI, 70 ev): *m/z* 252 (100, $[M]^+$).

$[Li_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2$-2,3$\}(THF)_2]_2$ (2). To a solution of **1** (2.65 g, 10.49 mmol) in THF (50 mL) at −78 °C was added dropwise Bu^nLi (13.8 mL, 22.00 mmol, 1.6 M solution in hexane). After stirring at room temperature for 5 h, Bu^tCN (2.4 mL, 21.70 mmol) was added gradually to the reaction mixture at 0 °C. It was allowed to stir at room temperature for 12 h and became a clear deep red solution. Concentration and cooling of the solution yielded **2** as dark red crystals (5.45 g, 90.4%). Anal. Calcd (%) for $C_{60}H_{112}Li_4N_8O_4Si_4$: C 62.68, H 9.82, N 9.74. Found: C 62.37, H 9.90, N 10.01. ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.29 (s, 18H, Si*Me₃*), 1.36 (s, 18H, C*Me₃*), 1.39−1.44 (m, 8H, THF), 3.48−3.52 (m, 8H, THF), 6.09 (s, 2H, C*H*), 6.98 (s, 2H, $C_4H_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 5.88 (Si*Me₃*), 25.69 (*C*Me₃), 31.58 (C*Me₃*), 41.69 (THF), 67.73 (THF), 94.00 (*C*H), 129.71 (CBu^t), 154.52, 176.33 ($C_4H_2N_2$).

$[Na_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2$-2,3$\}(THF)_2]_2$ (3). To a deep red suspension of **2** (1.37 g, 1.19 mmol) in hexane (30 mL) was added gradually Bu^tONa (0.46 g, 4.79 mmol) at 0 °C. The reaction mixture was continuously stirred at room temperature for 12 h and became a bright red suspension. After filtration and removal of the solvent under vacuum, the residue was recrystallized from THF/toluene and afforded **3** as dark red crystals (0.91 g, 62.9%). Anal. Calcd (%) for $C_{60}H_{112}N_8Na_4O_4Si_4$: C 59.37, H 9.30, N 9.23. Found: C 59.12, H 8.99, N 9.42. ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.31 (s, 18H, Si*Me₃*), 1.38 (s, 18H, C*Me₃*), 3.46−3.50 (m, 8H, THF), 5.96 (s, 2H, C*H*), 7.13 (s, 2H, $C_4H_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 3.50 (Si*Me₃*), 25.68 (*C*Me₃), 31.13 (C*Me₃*), 41.11 (THF), 67.70 (THF), 93.08 (*C*H), 131.74 (CBu^t), 158.21, 177.54 ($C_4H_2N_2$).

$[K_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2$-2,3$\}(THF)_3]_2$ (4). To a deep red suspension of **2** (1.92 g, 1.67 mmol) in hexane (30 mL) was added slowly Bu^tOK (0.79 g, 7.04 mmol) at 0 °C. The reaction mixture was then stirred at ambient temperature for 12 h and became a bright orange suspension. After filtration, the solvent was removed under vacuum and the residue was recrystallized from THF, forming **4** as dark red crystals (1.42 g, 53.9%). ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.31 (s, 18H, Si*Me₃*), 1.39−1.44 (m, 12H, THF),1.50 (s, 18H, C*Me₃*), 3.47−3.52 (m, 12H, THF), 5.92 (s, 2H, C*H*), 7.37 (s, 2H, $C_4H_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 3.78 (Si*Me₃*), 25.68 (*C*Me₃), 31.18 (C*Me₃*), 41.36 (THF), 67.70 (THF), 88.93 (*C*H), 131.01 (CBu^t), 155.84, 174.90 ($C_4H_2N_2$).

$[Mg_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2$-2,3$\}Br_2(THF)_4]$ (5). To a solution of $MgBr_2(Et_2O)$ (1.45 g, 5.60 mmol) in Et_2O (20 mL) was added a red solution of **2** (1.59 g, 1.39 mmol) in

Table 7. X-ray Crystallographic Data for Compounds 2−7

	2	**3**	**4**	**5**	**6**	**7**
formula	$C_{60}H_{112}Li_4N_8O_4Si_4$	$C_{60}H_{112}N_8Na_4O_4Si_4$	$C_{76}H_{144}K_4N_8O_8Si_4$	$C_{38}H_{72}Br_2Mg_2N_4O_4Si_2$	$C_{46}H_{88}Cl_4Li_2N_4O_6Si_2Zn_2$	$C_{20}H_{34}N_4Si_2$
fw	1149.70	1213.90	1566.75	913.62	1135.80	386.69
color/shape	dark red block	dark red block	dark red block	red block	reddish orange block	orange block
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$P2_1/n$	$P\bar{1}$	$P2_12_12$	$C2/c$	$P2_1$
cryst size (mm^3)	0.91 × 0.86 × 0.78	1.15 × 0.86 × 0.54	0.82 × 0.61 × 0.24	0.6 × 0.5 × 0.4	0.98 × 0.83 × 0.11	0.48 × 0.35 × 0.23
a (Å)	28.5345(14)	15.3212(8)	12.9978(10)	14.829(3)	26.0478(16)	9.2926(7)
b (Å)	9.9753(5)	15.8023(8)	14.3404(11)	15.135(3)	10.5134(6)	11.6805(9)
c (Å)	26.3743(13)	16.3189(9)	14.8662(12)	11.084(2)	22.4770 (13)	11.0279(8)
α (deg)	90	90	89.845(2)	90	90	90
β (deg)	90	108.1340(10)	70.976(2)	90	90.261(2)	108.399(2)
γ (deg)	90	90	68.740(2)	90	90	90
V (Å^3), Z	7507.2(6), 4	3754.7(3), 2	2420.3(3), 1	2487.7(9), 2	6155.3(6), 4	1135.80(15), 2
density (Mg/m^3)	1.017	1.074	1.075	1.220	1.226	1.131
abs coeff (mm^{-1})	0.122	0.147	0.282	1.740	1.034	0.167
F(000)	2512	1320	852	964	2408	420
θ range for data collection (deg)	1.43 to 23.99	1.59 to 28.01	1.54 to 25.00	1.92 to 25.67	1.56 to 28.01	1.95 to 28.01
no. of reflns collected	35 643	24 953	13 277	7013	20 462	7765
no. of indep reflns (R_{int})	10 587(0.0597)	9023(0.0303)	8507(0.0486)	4168(0.0458)	7406(0.0730)	5211(0.0298)
goodness-of-fit on F^2	0.940	0.977	0.918	1.027	0.799	0.952
R1, wR2 [$I > 2\sigma(I)$]	0.0732, 0.1983	0.0600, 0.1891	0.0826, 0.2173	0.0621, 0.1507	0.0528, 0.1255	0.0458, 0.1017
R1, wR2 (all data)	0.1227, 0.2294	0.1022, 0.2176	0.2087, 0.2945	0.0765, 0.1599	0.1580, 0.1504	0.0643, 0.1096
largest diff peak and hole (e Å^{-3})	0.320 and −0.333	0.364 and −0.274	0.285 and −0.226	0.203 and −0.633	0.391 and −0.255	0.243 and −0.243

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Et_2O (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. After filtration and removal of the solvent under vacuum from the reaction mixture, the residue was extracted with THF (15 mL). Concentration and cooling of the filtered solution yielded **5** as red aggregated crystals (1.56 g, 61.4%); mp = 132.8−134.9 °C. Anal. Calcd (%) for $C_{34}H_{64}Br_2Mg_2N_4O_3Si_2$ (**5**−THF): C 48.53, H 7.67, N 6.66. Found: C 48.64, H 8.06, N 6.23. ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.12 (s, 18H, $Si\mathit{Me}_3$), 1.30 (s, 18H, $C\mathit{Me}_3$), 1.40−1.44 (m, 4H, THF), 3.47−3.52 (m, 4H, THF), 6.10 (s, 2H, C*H*), 9.38 (s, 2H, $C_4\mathit{H}_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 4.22 ($Si\mathit{Me}_3$), 25.69 ($\mathit{C}Me_3$), 31.54 ($C\mathit{Me}_3$), 41.27 (THF), 67.71 (THF), 100.48 (*C*H), 153.51, 179.50 ($\mathit{C}_4H_2N_2$).

$[Zn_2\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}Cl_2(\mu\text{-}Cl)_2Li_2(THF)_6]$ (6). A red solution of **2** (1.72 g, 1.50 mmol) in Et_2O (30 mL) was added slowly to a precooled (0 °C) solution of $ZnCl_2$ (0.82 g, 6.02 mmol) in Et_2O (20 mL). The reaction mixture was stirred at room temperature for 12 h to become an orange suspension. After filtration, the solvent was removed under vacuum and the residue was recrystallized from THF afforded **6** as reddish orange crystals (3.06 g, 89.8%); mp = 97.1−99.6 °C. Anal. Calcd (%) for $C_{30}H_{56}Cl_4Li_2N_4O_2Si_2Zn_2$ (**6**−4THF): C 42.52, H 6.66, N 6.61. Found: C 42.78, H 6.84, N 6.60. ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.43 (s, 18H, $Si\mathit{Me}_3$), 1.24 (s, 18H, $C\mathit{Me}_3$), 1.40−1.44 (m, 4H, THF), 3.48−3.52 (m, 4H, THF), 5.92(s, 2H, C*H*), 7.76 (s, 2H, $C_4\mathit{H}_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 5.88 ($Si\mathit{Me}_3$), 25.69 ($\mathit{C}Me_3$), 31.61 ($C\mathit{Me}_3$), 42.07 (THF), 67.71 (THF), 94.15 (*C*H), 128.84 ($\mathit{C}Bu^t$), 152.14, 180.72 ($\mathit{C}_4H_2N_2$).

$[\{Me_2Si\{NC(Bu^t)C(H)\}\}_2C_4H_2N_2\text{-}2,3]$ (7). To a solution of $CdCl_2$ (1.50 g, 8.18 mmol) in Et_2O (20 mL) was added a red solution of **2** (1.92 g, 1.67 mmol) in Et_2O (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 day to become an orange suspension. After filtration and removal of the solvent under vacuum, the residue was recrystallized from THF. Concentration of the solution gave **7** as orange crystals (1.12 g, 86.7%); mp = 240.2−243.3 °C. ^1H NMR (300 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.29 (s, 12H, $Si\mathit{Me}_2$), 1.26 (s, 18H, $C\mathit{Me}_3$), 5.73 (s, 2H, C*H*), 6.16 (s, 2H, $C_4\mathit{H}_2N_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6:C_5D_5N = 2:1, 25 °C): δ (ppm) 0.00 ($Si\mathit{Me}_2$), 28.45 ($C\mathit{Me}_3$), 90.31 (*C*H), 110.89 ($\mathit{C}Bu^t$), 142.22, 186.34 ($\mathit{C}_4H_2N_2$). MS (FAB): *m/z* 387 (85, $[M + 1]^+$), 405 (100, $[M + 19]^+$).

X-ray Crystallography. Selected single crystals were mounted and sealed in Lindemann glass capillaries under nitrogen.

X-ray intensities were measured on a MSC/Rigaku RAXIS IIc imaging-plate diffractometer for compound **5**. A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflection was applied by using the ABSCOR program.[34]

Diffraction experiments of compounds **2**−**4** and **6**−**7** were carried out on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube, ω scan mode with increments of 0.3°. Preliminary unit cell parameters were obtained from 45 frames, while final unit cell parameters were obtained from global refinements of reflections by integrating all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants. SAINT-PLUS was used for integration of intensity of reflections and scaling. SADABS was used for absorption correction.[35]

All crystal structures were determined by a direct method that yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically (C−H bond distance was fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. They 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, SHELXTL-93, or SHELXTL-97 program package.[36] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[37] Crystallographic data collection and structure refinement of all compounds are summarized in Table 7.

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Supporting Information Available: Tables of crystallographic data, data collection details, bond distances and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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