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Synthesis and Structures of Novel Phenyl-Bridged Bis(1-azaallyl) Alkali-Metal Compounds

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The series of dilithium bis(1-azaallyl) compounds [{*o*-{N(SiMe$_3$)C(R)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (R = Bu^t (**1**), Ph (**3**)), [{*m*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (**5**), and [{*p*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (**6**) have been prepared by addition of the Li−C bond of [{*o*-/*m*-/*p*-(CHSiMe$_3$)$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] to a nitrile RCN (R = Bu^t, Ph) followed by a 1,3-shift of the SiMe$_3$ group. Likewise, the addition of [{*o*-(CHSiMe$_3$)$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] to an isonitrile Bu^{t}NC followed by 1,2-trimethylsilyl migration yielded [{*o*-{N(Bu^t)C(SiMe$_3$)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (**4**). The dilithium compounds **1** and **6** can be further transferred to their potassium analogues [{*o*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$-C$_6$H$_4$}{K$_2$(TMEDA)}]$_n$ (**2**) and [{*p*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{K$_2$(THF)$_3$}]$_2$ (**7**) by reaction with Bu^{t}OK. The structures of compounds **2**−**5** and **7** have been determined by X-ray structural analyses.

Introduction

The reactions of organonitriles with [LiCH(SiMe$_3$)$_2$]$_4$ to afford azaallyl and β-diketiminato lithium complexes have been reported.[1] Recently, we have reported the structures of some lithium derivatives of the monoanionic di-N,N′-chelating pyridyl- and quinolyl-1-azaallyl ligands.[2] Similar to the previously reported scandium-[3] and chromium-mediated[4] nitrile-addition/hydrogen-migration reactions, these reactions rely on a lithium-mediated nitrile-addition/silyl-migration synthetic pathway. These lithium compounds are versatile ligand-transfer agents for preparing transition-metal and main-group-metal complexes.[1a,5] We now draw attention to the reactions of organonitriles and isonitriles with a series of dilithium dialkyl compounds derived from *o*-, *m*-, and *p*-bis((trimethylsilyl)methyl)benzene. The phenyl-bridged bis(1-azaallyl) dilithium compounds formed bear two side chains linked together by the phenyl ring in various steric constraints. We anticipated that the electrons within the 1-azaallyl side chains might be delocalized along the phenyl ring, giving these ligands the properties of an open heteropentadienyl ligand.

The search for alternatives to the cyclopentadienyl ligand is currently an important topic, in particular for early transition metals.[6] Much attention has been focused on nitrogen-containing ligands, such as diamides,[7] porphyrins,[8] tetradentate Schiff base,[9] azamacrocycles,[10] and amidinates.[11] The 1-azaallyl ligand contains of an asymmetric backbone, and it can display various coordination modes: for example, η^1(C) or η^1(N) terminal, η^2 bridging, or η^3 chelating.

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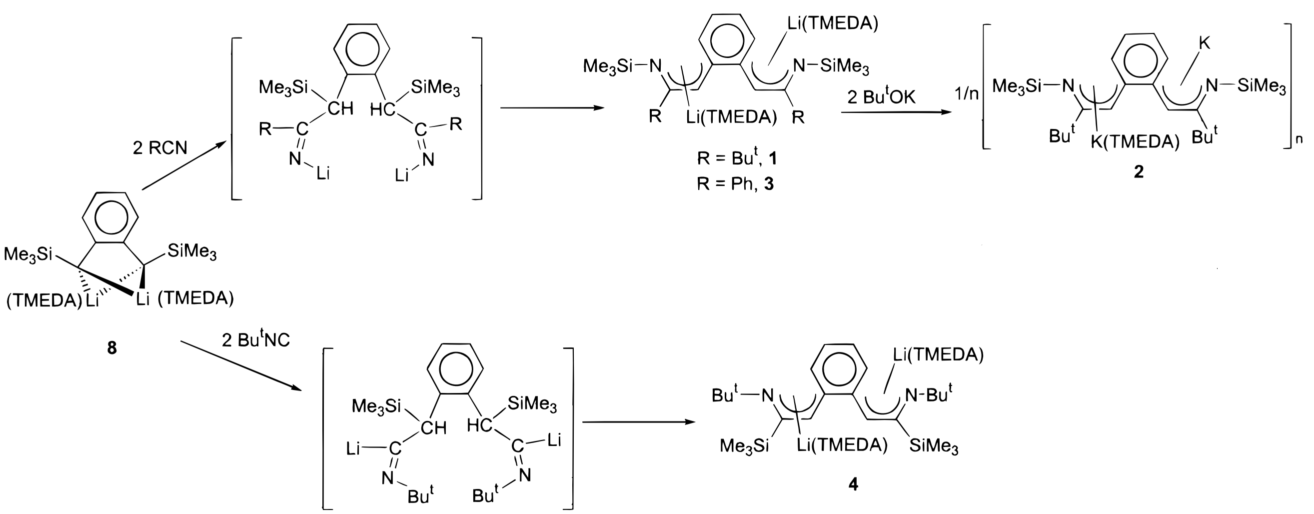
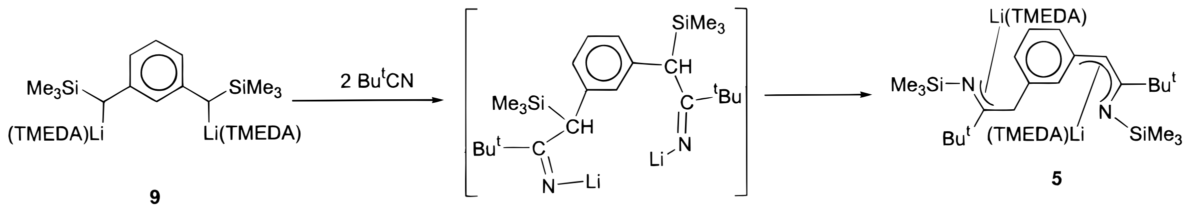
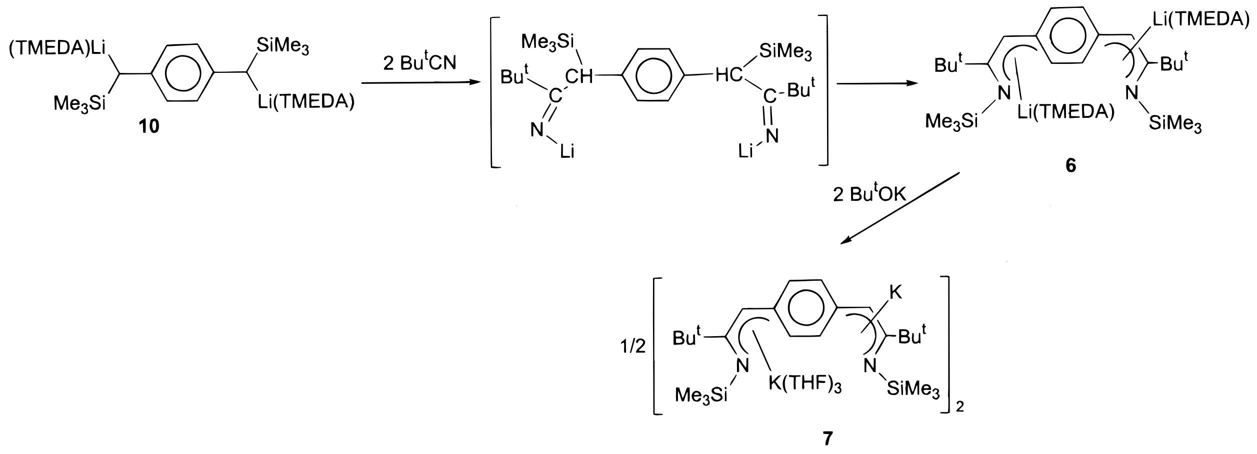
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

Treatment of dilithium derivatives of *o*-, *m*-, or *p*-bis((trimethylsilyl)methyl)benzene, [{*o*-/*m*-/*p*-$(CHSiMe_3)_2$-C_6H_4}{$Li_2(TMEDA)_2$}],[12] with 2 equiv of Bu^tCN or PhCN in diethyl ether or hexane afforded the bis(1-azaallyl) dilithium compounds [{*o*-{$N(SiMe_3)C(R)C(H)$}$_2C_6H_4$}-{$Li_2(TMEDA)_2$}] (R = Bu^t (**1**), Ph (**3**)), [{*m*-{$N(SiMe_3)C$-$(Bu^t)C(H)$}$_2C_6H_4$}{$Li_2(TMEDA)_2$}] (**5**), and [{*p*-{$N(SiMe_3)$-$C(Bu^t)C(H)$}$_2C_6H_4$}{$Li_2(TMEDA)_2$}] (**6**) in good yield (Schemes 1−3). The formation of these compounds involves addition of the Li−C to the C≡N bond of the nitrile followed by a 1,3-shift of the $SiMe_3$ group. Subsequently, metathesis reaction between lithium compounds **1** and **6** with Bu^tOK in diethyl ether gave the dipotassium derivatives [{*o*-{$N(SiMe_3)C(Bu^t)C(H)$}$_2$-C_6H_4}{$K_2(TMEDA)$}]$_n$ (**2**) and [{*p*-{$N(SiMe_3)C(Bu^t)C$-(H)}$_2C_6H_4$}{$K_2(THF)_3$}]$_2$ (**7**), respectively (Schemes 1 and 3). The use of metal-exchange reactions between organolithium compounds and alkali-metal alkoxides to prepare compounds of the heavier alkali metals is well-documented.[13]

Similar reaction of 2 equiv of isocyanide Bu^tNC with the dilithium compound [{*o*-$(CHSiMe_3)_2C_6H_4$}{Li_2-$(TMEDA)_2$}] in Et_2O afforded the red crystalline compound [{*o*-{$N(Bu^t)C(SiMe_3)C(H)$}$_2C_6H_4$}{$Li_2(TMEDA)_2$}] (**4**) in 72.9% yield (Scheme 1). The isonitrile reacts with the dilithium compound by insertion into the Li−C bond. In addition, a 1,2-shift of the $SiMe_3$ group from

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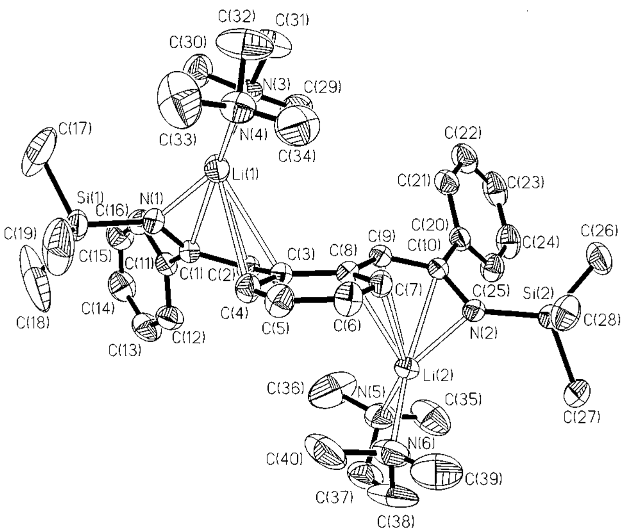

Figure 1. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity.

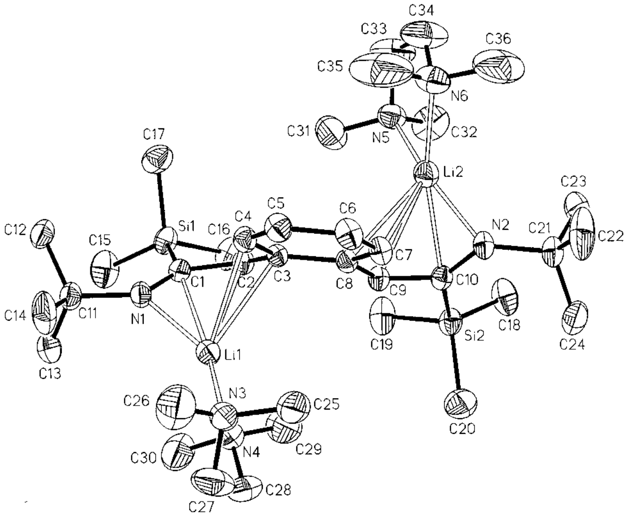

Figure 2. Molecular structure of **4**. Hydrogen atoms have been omitted for clarity.

the α-C to *β*-C atom takes place, instead of a 1,3-shift for the reaction with Bu^tCN or PhCN.

Compounds **1**−**7** are intensely yellow compounds, which are soluble in THF, Et_2O, and toluene and sparingly soluble in hydrocarbon solvents. They were characterized by NMR spectroscopy and elemental analysis. The ^1H NMR spectra of **1**, **2**, and **4**−**7** showed single peaks for the $SiMe_3$ and Bu^t groups, The CH singlet signals were shifted downfield to around *δ* 5.0 ppm. Two multiplets were observed for the ortho compounds **1**−**3**, whereas one singlet, one doublet, and one triplet were observed for the meta analogue **5**. Furthermore, singlet signals were observed for the para analogues **6** and **7** in the aromatic region. In the ^1H NMR spectrum of **4**, the ortho phenyl protons displayed two broad peaks at *δ* 6.49 and 9.67 ppm, respectively. The ^{13}C NMR spectra were consistent with the proposed structures. In all cases, one set of resonances due to the 1-azaallyl ligand was observed, suggesting that the complexes contains ligands bonded to the metal centers in symmetrical equivalent positions.

The molecular structures of **2**−**5** and **7** were determined by single-crystal X-ray crystallography. As shown in Figures 1−3, dilithium bis(1-azaallyl) compounds **3**−**5** are monomeric in the solid state. Selected bond distances and angles are listed in Tables 1−3. The two Li(TMEDA) groups in **3**−**5** are positioned above and below the phenyl plane, respectively. The bond distances from the lithium atoms to the N($SiMe_3$), C(R), C(H),

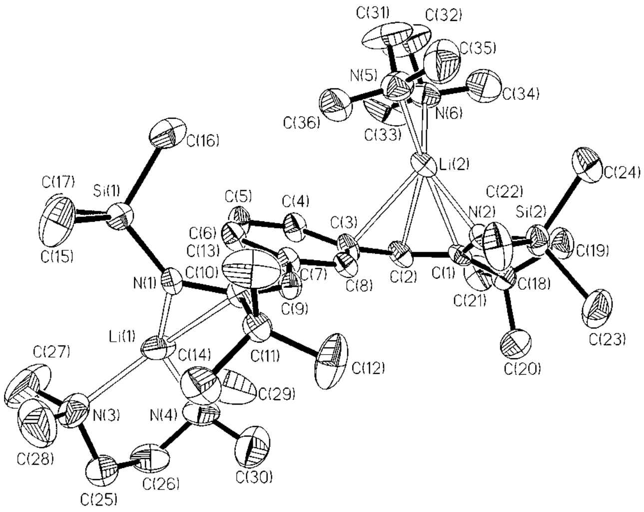

Figure 3. Molecular structure of **5**. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 3

N(1)−Li(1)	1.957(8)	N(3)−Li(1)	2.126(8)
C(1)−Li(1)	2.571(8)	N(4)−Li(1)	2.180(8)
C(2)−Li(1)	2.724(8)	N(1)−C(1)	1.371(5)
C(3)−Li(1)	2.665(8)	C(1)−C(2)	1.381(5)
C(4)−Li(1)	2.793(8)	C(2)−C(3)	1.463(5)
N(2)−Li(2)	1.970(7)	C(3)−C(4)	1.413(5)
C(7)−Li(2)	2.714(8)	C(3)−C(8)	1.438(5)
C(8)−Li(2)	2.568(7)	C(8)−C(9)	1.487(5)
C(9)−Li(2)	2.603(7)	C(9)−C(10)	1.369(5)
C(10)−Li(2)	2.477(7)	N(2)−C(10)	1.365(4)
N(1)−Li(1)−N(3)	118.9(4)	C(3)−C(8)−C(7)	118.7(3)
N(1)−Li(1)−N(4)	142.3(4)	C(10)−C(9)−C(8)	127.5(3)
N(3)−Li(1)−N(4)	84.3(3)	N(2)−C(10)−C(9)	124.1(3)
N(2)−Li(2)−N(5)	118.1(4)	Si(1)−N(1)−Li(1)	129.6(3)
N(2)−Li(2)−N(6)	136.5(4)	Si(1)−N(1)−C(1)	130.7(3)
N(5)−Li(2)−N(6)	85.0(3)	C(1)−N(1)−Li(1)	99.7(3)
N(1)−C(1)−C(2)	123.2(4)	Si(2)−N(2)−Li(2)	130.1(3)
C(1)−C(2)−C(3)	127.7(3)	Si(2)−N(2)−C(10)	135.7(3)
C(4)−C(3)−C(8)	117.5(3)	C(10)−N(2)−Li(2)	94.2(3)

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 4

Li(1)−N(1)	1.950(3)	Li(2)−C(8)	2.519(3)
Li(1)−C(1)	2.404(3)	Li(2)−C(7)	2.522(4)
Li(1)−C(2)	2.407(3)	N(1)−C(1)	1.347(2)
Li(1)−C(3)	2.467(3)	C(1)−C(2)	1.404(2)
Li(1)−C(4)	2.694(3)	C(2)−C(3)	1.461(2)
Li(1)−N(3)	2.154(3)	C(3)−C(8)	1.451(2)
Li(2)−N(2)	1.973(4)	C(8)−C(9)	1.453(2)
Li(2)−C(10)	2.500(4)	C(9)−C(10)	1.404(2)
Li(2)−C(9)	2.552(3)	N(2)−C(10)	1.351(2)
N(1)−Li(1)−N(3)	134.3(2)	C(10)−N(2)−Li(2)	95.8(1)
N(1)−Li(1)−N(4)	122.3(1)	C(21)−N(2)−Li(2)	133.9(1)
N(3)−Li(1)−N(4)	83.9(1)	N(1)−C(1)−C(2)	118.7(1)
N(2)−Li(2)−N(5)	124.6(2)	C(1)−C(2)−C(3)	129.5(2)
N(2)−Li(2)−N(6)	134.7(2)	C(4)−C(3)−C(8)	117.6(1)
N(5)−Li(2)−N(6)	83.0(1)	C(5)−C(4)−C(3)	123.3(2)
C(1)−N(1)−C(11)	125.7(1)	C(6)−C(7)−C(8)	123.5(2)
C(1)−N(1)−Li(1)	91.8(1)	C(7)−C(8)−C(3)	116.6(1)
C(11)−N(1)−Li(1)	135.7(1)	C(10)−C(9)−C(8)	130.2(1)
C(10)−N(2)−C(21)	124.7(1)	N(2)−C(10)−C(9)	118.5(1)

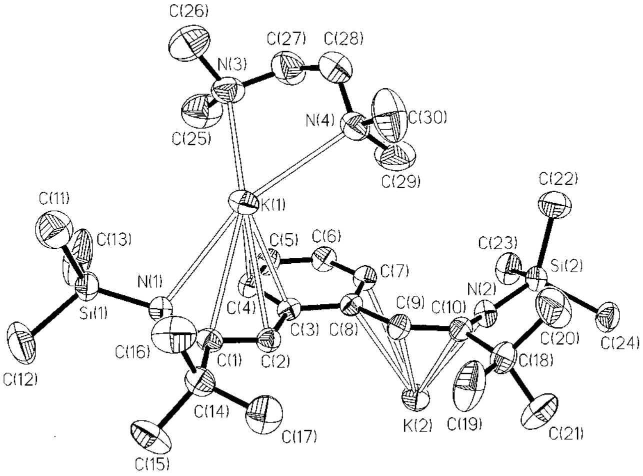

Figure 4. Molecular structure of **2**. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 5

Li(1)−N(1)	1.924(5)	N(1)−C(10)	1.3865(3)
Li(1)−N(3)	2.105(6)	C(9)−C(10)	1.354(3)
Li(1)−C(10)	2.563(6)	C(7)−C(9)	1.457(3)
Li(2)−N(2)	1.993(5)	N(2)−C(1)	1.351(3)
Li(2)−C(1)	2.396(5)	C(1)−C(2)	1.364(4)
Li(2)−C(2)	2.486(5)	C(2)−C(3)	1.460(3)
Li(2)−C(3)	2.544(5)	N(3)−C(27)	1.445(6)
N(1)−Li(1)−N(3)	124.3(3)	C(1)−N(2)−Si(2)	148.95(17)
N(1)−Li(1)−N(4)	146.2(3)	C(1)−N(2)−Li(2)	89.38(19)
N(3)−Li(1)−N(4)	85.8(2)	Si(2)−N(2)−Li(2)	119.64(17)
N(2)−Li(2)−N(6)	130.4(2)	N(2)−C(1)−C(2)	121.5(2)
N(2)−Li(2)−N(5)	132.6(2)	C(1)−C(2)−C(3)	128.5(2)
N(6)−Li(2)−N(5)	83.72(19)	C(8)−C(3)−C(2)	123.8(2)
C(10)−N(1)−Si(1)	132.74(16)	C(6)−C(7)−C(9)	124.6(2)
C(10)−N(1)−Li(1)	100.2(2)	C(10)−C(9)−C(7)	131.8(2)
Si(1)−N(1)−Li(1)	126.1(2)	C(9)−C(10)−N(1)	123.7(2)

C(aromatic), and C(aromatic) atoms of the azaallyl side chain suggest that some extent of π-interaction is present, although the Li−C distances are much longer than the average Li−C distance in the cyclopentadienyl alkali-metal compound $[Li(\eta^5\text{-}C_5H_4SiMe_3)]_4$ (2.304 Å).[14] In contrast, the Li(1) atom in the meta isomeric compound **5** shows significant bonding interaction with the N(1) and C(10) atoms of the azaallyl side chain, while the distances between Li(1) and the C(9), C(7), and C(6) atoms are too long for a bonding interaction. The structures of these bis(1-azaallyl) compounds are similar to that of $[Na(CHPh_2)(pmdeta)]$ (pmdeta = pentamethyldiethylenediamine), where the sodium atom is bonded to the diphenylmethyl ion in an η^5 bonding mode.[15]

By comparison of relevant structural data of compounds **3**−**5,** it had been shown that the bonding within the azaallyl side chain is delocalized, and the aromaticity of the phenyl ring is only slightly affected. The Li−N distances are in the normal range for the Li−N(amido) bonds of 1.89−2.16 Å.

The X-ray structures of the dipotassium compounds derived from their dilithium compounds are shown in Figures 4 and 5, respectively. Selected bond distances and angles for compounds **2** and **7** are presented in Tables 4 and 5, respectively. The structure of **2** is polymeric and that of **7** is dimeric with a C_2 symmetry. In these two potassium compounds, the environments of the two potassium atoms are different. One potassium atom is bonded to the coordinated solvent molecules (i.e., one TMEDA in **2** to three THF's in **7**) and the azaallyl side chain. The second potassium atom bridges to two azaallyl side arms of different ligands in a sandwich-like manner. In compound **2**, the potassium atom which is coordinated to TMEDA has a weak interaction with the carbon atom of the $SiMe_3$ group in the third ligand (K(1)−C(24)#1 = 3.284(3) Å), forming a polymer (Figure 6). In these two potassium compounds, the corresponding bond distances and angles are similar. The average K−C distances are only slightly longer than that in the cyclopentadienyl potassium complexes $[K(\eta^5\text{-}C_5H_4\text{-}$

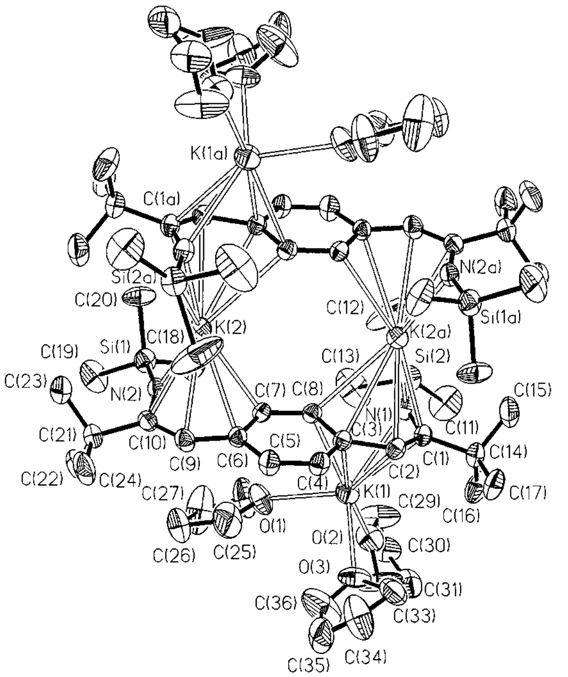

Figure 5. Molecular structure of **7**. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 2[a]

K(1)−N(3)	2.875(2)	K(2)−N(1)#2	2.9503(17)
K(1)−N(4)	2.890(2)	K(2)−C(1)#2	2.967(2)
K(1)−N(1)	2.9176(18)	K(2)−C(2)#2	3.073(2)
K(1)−C(1)	3.021(2)	K(2)−C(3)#2	3.293(2)
K(1)−C(2)	3.034(2)	K(2)−C(4)#2	3.137(2)
K(1)−C(3)	3.0370(18)	N(1)−C(1)	1.339(3)
K(1)−C(4)	3.183(2)	C(1)−C(2)	1.384(3)
K(1)−C(24)#1	3.283(3)	C(2)−C(3)	1.473(3)
K(2)−N(2)	2.7764(19)	C(3)−C(4)	1.409(3)
K(2)−C(10)	2.980(2)	N(2)−C(10)	1.343(2)
K(2)−C(9)	3.037(2)	C(7)−C(8)	1.426(3)
K(2)−C(8)	3.0856(19)	C(8)−C(9)	1.461(3)
K(2)−C(7)	3.066(2)	C(9)−C(10)	1.380(3)
N(3)−K(1)−N(4)	65.54(7)	C(10)−N(2)−Si(2)	148.49(16)
N(3)−K(1)−N(1)	124.43(6)	C(10)−N(2)−K(2)	85.15(12)
N(4)−K(1)−N(1)	160.82(5)	N(1)−C(1)−C(2)	123.92(18)
N(3)−K(1)−C(24)#1	86.87(7)	C(1)−C(2)−C(3)	130.27(18)
N(2)−K(2)−N(1)#2	139.58(5)	C(4)−C(3)−C(2)	122.54(17)
C(1)−N(1)−Si(1)	154.65(14)	C(7)−C(8)−C(9)	121.50(17)
C(1)−N(1)−K(1)	81.34(11)	C(10)−C(9)−C(8)	130.80(18)
C(1)−N(1)−K(2)#2	77.63(10)	N(2)−C(10)−C(9)	124.52(19)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + {}^1/_2$, $-y + {}^1/_2$, $z + {}^1/_2$; (#2) $-x + 2$, $-y$, $-z + 1$; (#3) $x - {}^1/_2$. $-y + {}^1/_2$. $z - {}^1/_2$.

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(14) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903.

(15) Corbelin, S.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *J. Organomet. Chem.* **1991**, *415*, 293.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound 7[a]

K(1)−O(1)	2.672(3)	K(2)−C(1)#1	3.032(2)
K(1)−N(1)	2.951(2)	K(2)−C(2)#1	3.056(2)
K(1)−C(1)	3.035(2)	K(2)−C(3)#1	3.206(2)
K(1)−C(2)	3.115(2)	K(2)−C(8)#1	3.223(2)
K(1)−C(3)	3.122(2)	N(1)−C(1)	1.338(2)
K(1)−C(8)	3.105(2)	C(1)−C(2)	1.371(3)
K(2)−N(2)	2.791(2)	C(2)−C(3)	1.498(2)
K(2)−C(10)	3.051(2)	C(5)−C(6)	1.415(2)
K(2)−C(9)	3.068(2)	C(7)−C(8)	1.410(2)
K(2)−C(6)	3.131(2)	C(6)−C(9)	1.427(3)
K(2)−C(7)	3.140(2)	C(9)−C(10)	1.370(3)
K(2)−N(1)#1	2.942(2)	N(2)−C(10)	1.333(2)
N(1)−K(1)−O(1)	130.50(8)	N(1)−C(1)−C(2)	123.4(2)
N(1)−K(1)−O(2)	114.26(7)	C(1)−C(2)−C(3)	129.2(2)
N(1)−K(1)−O(3)	125.18(8)	C(4)−C(3)−C(8)	115.7(2)
N(2)−K(2)−N(1)#1	145.66(5)	C(4)−C(3)−C(2)	118.8(2)
K(1)−N(1)−K(2)#1	125.95(5)	C(8)−C(3)−C(2)	125.4(2)
Si(2)−N(1)−C(1)	155.6(1)	C(5)−C(4)−C(3)	123.3(2)
K(1)−N(1)−C(1)	80.62(10)	C(7)−C(6)−C(5)	114.6(2)
K(2)−N(2)−Si(1)	112.59(7)	C(6)−C(7)−C(8)	122.8(2)
K(2)−N(2)−C(10)	88.05(10)	C(10)−C(9)−C(6)	132.6(2)
Si(1)−N(2)−C(10)	154.5(1)	N(2)−C(10)−C(9)	121.4(2)

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

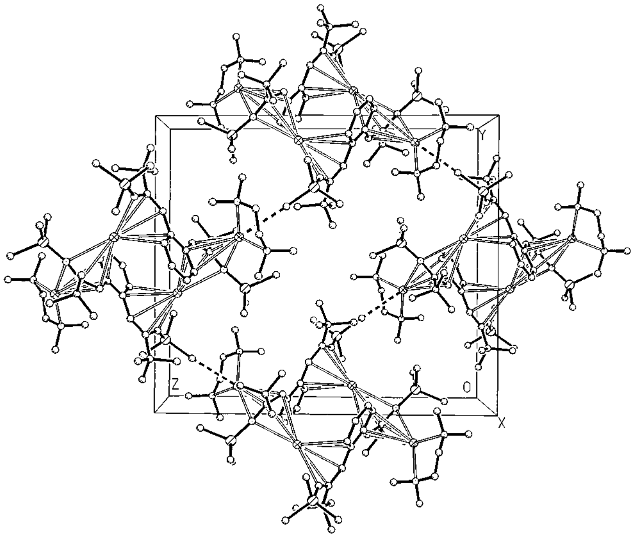
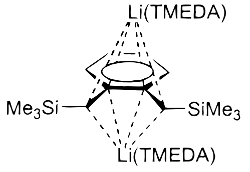


Figure 6. Unit cell content of **2**. Hydrogen atoms have been omitted for clarity.

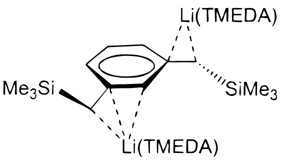
$SiMe_3)]_\infty$ (3.032 Å)[16] and $[K\{\eta^5\text{-(neomenthyl)}C_5H_4\}(DME)]_4$ (3.080 Å),[17] suggesting a strong η^5 interaction between the azaallyl side chain with the potassium atoms.

The structures of dilithium phenyl-bridged bis(1-azaallyl) complexes **1** and **3**−**5** are somewhat different from those of the lithium derivatives of monoanionic di-N,N′-chelating pyridyl- and quinolyl-1-azaallyl ligands.[2] In those structures, the lithium atoms are bonded to the $NSiMe_3$ group and the pyridyl or quinolinyl nitrogen atoms in an η^1 mode, forming the LiNCCCN metallacycles, and a significant contribution of a π-interaction is not evident.

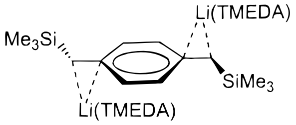
The structural changes of adding the Li−C bond of dilithium compounds of *o*-, *m*-, or *p*-bis((trimethylsilyl)methyl)benzene, $[\{o\text{-}/m\text{-}/p\text{-}(CHSiMe_3)_2C_6H_4\}\{Li_2(TMEDA)_2\}]$,[12] to a nitrile are shown in the structures of these phenyl-bridged dilithium bis(1-azaallyl) complexes **1** and **3**−**5**. The ortho compound $[\{o\text{-}(CHSiMe_3)_2C_6H_4\}\{Li_2(TMEDA)_2\}]$ (**8**) is a "contact-ion-pair" structure possessing two η^4-Li centers above and below the *o*-xylenediyl plane at 2.37 Å to the C_α atoms and 2.36 Å to the $C_{aromatic}$ atoms. In the meta isomeric compound (**9**), the Li atoms are bonded to the anion in η^3 and η^2 modes. The para isomeric compound (**10**) shows evidence of a dominant *p*-quinodimethyl contribution with each lithium, on opposite sides of the benzene ring, interacting with both C_α and its adjacent ring-carbon atoms ($Li-C_\alpha = 2.10(1)$ Å and $Li-C_{aromatic} = 2.38(1)$ Å) unsymmetrically.



(**8**)



(**9**)



(**10**)

The addition of each $Li-C_\alpha$ bond to a nitrile has led to the formation of an azaallyl chain after migration of the $SiMe_3$ groups. The "bent" azaallyl arms show structural effects resulting from their steric requirements. Because of the steric crowding of the ortho substituents in ortho compounds **1** and **3**, the azaallyl arms are positioned away from each other on each side of the phenyl bridge. In the meta-substituted compound **5**, the azaallyl arms are positioned along the benzene ring toward a single direction. The azaallyl arms in the para-substituted compound **10** are positioned in a "cis" arrangement.

These phenyl-bridged bis(1-azaallyl) alkali-metal compounds have been used as transfer reagents for the synthesis of some bimetallic lanthanide bis(1-azaallyl) complexes. The report on this aspect will be followed in due course.

Conclusion

We have shown that the novel phenyl-bridged bis(1-azaallyl) ligands are readily prepared by the reaction of phenyl-linked bis((trimethylsilyl)methyl) dilithium compound with organonitriles or isonitriles followed by 1,3- or 1,2-trimethylsilyl migration. They can be converted to the dipotassium analogues by the reaction with Bu^tOK. Through the nitrogen atoms within the azaallyl chain, they can behave as good σ- and π-donors. By varying the alkyl groups on the organonitrile or isonitrile, the substituents on the ligand backbone can be easily changed, thus providing a facile route to fine-tune the ligands' steric and electronic properties. These bis(azaallyl) ligands are expected to have potential use

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(16) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583.

(17) Leung, W.-P.; Song, F.-Q.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 4307.

Table 6. Summary of Crystallographic Data for Compounds 2–5 and 7

	2	**3**	**4**	**5**	**7**
formula	$C_{30}H_{58}K_2N_4Si_2$	$C_{40}H_{66}Li_2N_6Si_2$	$C_{36}H_{74}Li_2N_6Si_2$	$C_{36}H_{74}Li_2N_6Si_2$	$C_{72}H_{132}N_4O_6Si_4K_4$
fw	609.18	701.05	661.07	661.07	1418.58
temp (K)	293(2)	293(2)	294(2)	293(2)	293(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P\bar{1}$	Cc	$P2_1/n$
cryst size (mm)	0.40 × 0.40 × 0.40	0.50 × 0.30 × 0.10	0.48 × 0.38 × 0.36	0.24 × 0.16 × 0.13	0.40 × 0.32 × 0.22
a (Å)	11.146(2)	10.716(2)	10.5380(9)	28.365(3)	13.467(3)
b (Å)	17.632(4)	15.817(2)	13.280(2)	9.709(1)	20.821(4)
c (Å)	20.160(4)	13.9940(10)	16.545(3)	16.383(1)	16.404(3)
α (deg)	90	90	100.630(4)	90	90
β (deg)	93.96(3)	103.730(10)	100.18(1)	92.87(1)	95.52(3)
γ (deg)	90	90	97.977(9)	90	90
V (Å^3)	3952.5(14)	2304.1(5)	2204.4(5)	4506.1(7)	4578(2)
Z	4	2	2	4	2
d(calcd) (Mg/m^3)	1.024	1.010	0.996	0.974	1.029
abs coeff (mm^{-1})	0.322	0.108	0.109	0.107	0.289
F(000)	1328	764	732	1464	1544
θ range (deg)	2.03–25.00	1.50–25.57	1.81–25.71	2.22–25.01	2.48–24.94
limiting indices	$0 \le h \le 11$	$-12 \le h \le 12$	$-11 \le h \le 11$	$0 \le h \le 33$	$-15 \le h \le 14$
	$-20 \le k \le 20$	$-17 \le k \le 17$	$0 \le k \le 15$	$0 \le k \le 11$	$0 \le k \le 22$
	$-23 \le l \le 23$	$-16 \le l \le 0$	$-20 \le l \le 19$	$-19 \le l \le 19$	$0 \le l \le 18$
no. of rflns collected	9015	6830	5826	4062	2726
no. of indep rflns (R_{int})	5300 (0.0569)	6715 (0.0298)	5826 (0.0000)	4062 (0.0000)	2726 (0.0000)
no. of data/restraints/params	5300/0/343	6715/1/452	5826/0/416	4062/2/417	2726/0/503
GOF/F^2	1.125	1.061	1.100	0.995	1.140
R indices ($I > 2\sigma(I)$)					
R1	0.0758	0.0622	0.0734	0.0573	0.0595
wR2	0.2186	0.1615	0.2004	0.1422	0.1516
R indices (all data)					
R1	0.0933	0.0729	0.0905	0.1855	0.0658
wR2	0.2346	0.1708	0.2155	0.1798	0.1550
extinction coeff	0.0092(9)	0.015(3)	0.0224(13)	0.00058(12)	0.0002(2)
largest diff peak/hole (e Å^{-3})	0.493/−0.254	0.206/−0.127	0.242/−0.199	0.146/−0.141	0.259/−0.133

as substitute ligands for cyclopentadienyl ligands and to play an important role in homogeneous catalysis.

Experimental Section

General Procedures. All manipulations were carried out in either a nitrogen-filled drybox or under nitrogen using standard Schlenk techniques. Solvents were dried over and distilled from sodium/benzophenone (diethyl ether and tetrahydrofuran), calcium hydride (hexane), or sodium/potassium alloy (pentane). Trimethylacetonitrile, *tert*-butyl isocyanide, *n*-butyllithium, and potassium *tert*-butoxide were purchased from Aldrich and used without further purification. Benzonitrile and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were purchased from Aldrich and distilled from KOH prior to use. *o*-, *m*-, and *p*-Bis((trimethylsilyl)methyl)benzene were prepared by an in situ Grignard reaction as described in the literature.[18] ^{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) or $CDCl_3$ (δ 7.26 ppm) and ^{13}C resonances to C_6D_6 (δ 128.0 ppm) or $CDCl_3$ (δ 77.0 ppm). Mass spectral data were recorded on a 5989-In mass spectrometer. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, U.K.

Preparation of [{*o*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (1). To a mixture of 4.44 g (17.76 mmol) of *o*-$(CH_2SiMe_3)_2C_6H_4$ and 5.4 mL (35.84 mmol) of TMEDA in 20 mL of Et_2O was added 22.4 mL (35.84 mmol, 1.6 M in hexane) of Bu^{n}Li dropwise at 0 °C. The resulted orange solution was stirred at 24 °C for 8 h, and 4.0 mL (36.18 mmol) of Bu^{t}CN was injected via syringe at 0 °C. After the mixture was stirred at 24 °C for 12 h, a yellow solution was formed. Removal of solvent under vacuum gave a yellow solid, which was washed twice with 10 mL of pentane. Yield: 10.2 g (87.0%) of **1**. ^{1}H NMR (300 MHz, C_6D_6/C_5D_5N (2:1)): δ 0.56 (s, 18 H, $SiMe_3$), 1.40 (s, 18 H, CMe_3), 2.05 (s, 24 H, NMe_2), 2.27 (s, 8 H, CH_2N), 5.77 (s, 2 H, CH), 6.71 (dd, 2 H, C_6H_4), 9.14 (dd, 2 H, C_6H_4). ^{13}C NMR (75.5 MHz, C_6D_6): δ 1.06 ($SiMe_3$), 29.58 (^{t}Bu), 28.31 (−C), 46.38 (TMEDA), 58.76 (TMEDA), 106.27 (CH), 119.88, 125.88, 128.71. 128.39, 131.57, 150.79 (C_6H_4).

Preparation of [{*o*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{K$_2$(TMEDA)}]$_n$ (2). To a yellow solution of **1** (5.84 g, 8.85 mmol) in Et_2O (20 mL), 1.99 g (17.77 mmol) Bu^{t}OK was added gradually at 0 °C. The mixture was then stirred at 24 °C for an additional 16 h, during which time a yellow solid precipitated. After removal of solvent, the solid residue was washed with 10 mL of pentane and dried under vacuum to yield **2** (4.63 g, 86.0%) as a yellow solid. ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.56 (s, 18 H, $SiMe_3$), 1.52 (s, 18 H, CMe_3), 2.05 (s, 12 H, NMe_2), 2.26 (s, 4 H, CH_2N), 5.70 (s, 2 H, CH), 6.89 (dd, 2 H, C_6H_4), 9.42 (dd, 2 H, C_6H_4).^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 6.25 ($SiMe_3$), 31.15 (^{t}Bu), 40.92 (−C), 45.81 (TMEDA), 58.07 (TMEDA), 88.13 (CH), 119.88, 124.67, 138.50, 166.25 (C_6H_4).

Preparation of [{*o*-{N(SiMe$_3$)C(Ph)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (3). To a freshly prepared solution of [{*o*-$(CHSiMe_3)_2C_6H_4$}{Li_2(TMEDA)$_2$}] (10.13 mmol) in 20 mL of Et_2O was added 2.1 mL (20.59 mmol) of PhCN slowly at 0 °C. The mixture was warmed to 24 °C and stirred for 15 h. A red slurry was obtained. The solvent was removed under vacuum, and the orange residue was washed twice with 10 mL of pentane. Recrystallization of the orange solid from Et_2O yielded 5.90 g (83.2%) of **3** as a crystalline solid which was suitable for X-ray diffraction. ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.18 (s, 18 H, $SiMe_3$), 2.03 (s, 24 H, NMe_2), 2.24 (s, 8 H, CH_2N), 5.27 (s, 2 H, CH), 6.72 (dd, 2 H, C_6H_4), 7.09–7.13 (m, 6 H, C_6H_5), 7.50–7.53 (m, 4 H, C_6H_5), 9.25 (dd, 2 H, C_6H_4). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 4.90 ($SiMe_3$), 46.28 (TMEDA), 58.52 (TMEDA), 98.13 (CPh), 121.99 (CH), 126.68, 127.07, 127.79, 129.07, 139.66, 152.04, 161.67 (C_6H_4). MS (EI, 70 eV): m/z 456 (8.4, $[M - 2\ Li - 2\ TMEDA + 2]^+$). Anal.

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(18) Bock, H.; Alt, H. *J. Am. Chem. Soc.* **1970**, *92*, 1569.

Calcd for $C_{40}H_{66}N_6Si_2Li_2$: C, 68.53; H, 9.49; N, 11.98. Found: C, 68.40; H, 8.18; N, 12.18.

Preparation of [{*o*-{N(Bu^t)C(SiMe$_3$)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (4). To a freshly prepared yellow slurry of [{*o*-(CHSiMe$_3$)$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (6.38 mmol) in 10 mL of hexane was added 1.5 mL (13.26 mmol) of Bu^{t}NC at 0 °C. After the mixture was stirred at 24 °C for 12 h, a red slurry was obtained. Removal of solvent and recrystallization of the residue from Et$_2$O afforded **4** (3.07 g, 72.9%) as orange crystals, which were washed with pentane (5 mL) and dried under vacuum. ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.52 (s, 18 H, SiMe$_3$), 1.57 (s, 18 H, CMe$_3$), 2.03 (s, 24 H, NMe$_2$), 2.12 (s, 8 H, CH$_2$N), 5.11 (s, 2 H, CH), 6.49 (br, 2 H, C$_6$H$_4$), 9.67 (br, 2 H, C$_6$H$_4$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 4.95 (SiMe$_3$), 34.80 (^{t}Bu), 46.03 (TMEDA), 53.34 ($-$C), 57.73 (TMEDA), 94.73 (CSiMe$_3$), 119.22 (CH), 133.41, 137.45, 162.73 (C$_6$H$_4$). MS (EI, 70 eV): *m/z* 416 (21.9, $[M - 2\ Li - 2\ TMEDA + 2]^+$). Anal. Calcd for $C_{37}H_{74}N_6Si_2Li_2$: C, 65.41; H, 11.28; N, 12.71. Found: C, 65.03; H, 10.99; N, 12.62.

Preparation of [{*m*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (5). To a solution of *m*-(CH$_2$SiMe$_3$)$_2$C$_6$H$_4$ (3.42 g, 13.68 mmol) and TMEDA (4.12 mL, 27.38 mmol) in 30 mL of hexane was added Bu^{n}Li (17.1 mL, 27.36 mmol, 1.6 M in hexane) at 0 °C. The resulting solution was stirred at 24 °C for 12 h, and Bu^{t}CN (3.0 mL, 27.36 mmol) was added dropwise at 0 °C. The mixture was stirred for a further 6 h at 24 °C, and a clear solution was formed. Concentration of the solution gave pale yellow crystals of **5** (7.95 g, 88%). ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.53 (s, 18 H, SiMe$_3$), 1.31 (s, 18 H, CMe$_3$), 2.01 (s, 24 H, NMe$_2$), 2.17 (s, 8 H, CH$_2$N), 5.71 (s, 2 H, CH), 7.02 (t, $J = 7.8$ Hz, 1 H, C$_6$H$_4$), 7.98 (d, $J = 7.5$ Hz, 2 H, C$_6$H$_4$), 8.73 (s, 1 H, C$_6$H$_4$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 5.94 (SiMe$_3$), 31.02 (^{t}Bu), 40.20 ($-$C), 45.81 (TMEDA), 57.93 (TMEDA), 97.54 (C^{t}Bu), 119.11 (CH), 123.61, 128.49, 143.16, 168.29 (C$_6$H$_4$).

Preparation of [{*p*-{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$}{Li$_2$(TMEDA)$_2$}] (6). To a mixture of *p*-(CH$_2$SiMe$_3$)$_2$C$_6$H$_4$ (2.50 g, 10.0 mmol) and TMEDA (3.1 mL, 20.6 mmol) in 25 mL of hexane was added Bu^{n}Li (12.5 mL, 20.0 mmol, 1.6 M in hexane) at 0 °C. After the mixture was stirred for 5 h at 24 °C, to the red solution thus formed was added slowly 2.3 mL (20.8 mmol) of Bu^{t}CN at 0 °C. The resulting solution was stirred at 24 °C for a further 12 h. Volatiles were removed under vacuum, and recrystallization from hexane yielded yellow crystals of **6** (5.44 g, 82.4%), which were collected, washed with ice-cold pentane, and dried under vacuum. ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.50 (s, 18 H, SiMe$_3$), 1.37 (s, 18 H, CMe$_3$), 2.03 (s, 24 H, NMe$_2$), 2.22 (s, 8 H, CH$_2$N), 5.70 (s, 2 H, CH), 8.10 (s, 4 H, C$_6$H$_4$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 5.81 (SiMe$_3$), 31.12 (^{t}Bu), 45.84 (TMEDA), 58.01 (TMEDA), 70.02 ($-$C), 97.43 (C^{t}Bu), 118.89 (CH), 126.30, 136.88 (C$_6$H$_4$). Anal. Calcd for $C_{36}H_{74}N_6Si_2Li_2$: C, 65.41; H, 11.28; N, 12.71. Found: C, 64.86; H, 10.29; N, 12.57.

Preparation of [{{N(SiMe$_3$)C(Bu^t)C(H)}$_2$C$_6$H$_4$-1,4}{K$_2$(THF)$_3$}]$_2$ (7). To a yellow solution of **6** (10.00 mmol) in Et$_2$O (10 mL) was added 2.32 g (20.71 mmol) of Bu^{t}OK slowly at 0 °C to give a yellow slurry. After the mixture was stirred at 24 °C for 16 h, the solvent was removed and the residue was recrystallized from THF/hexane; 6.23 g (88.0%) of **10** was obtained as a yellow solid. ^{1}H NMR (300 MHz, C_6D_6/C_5D_4N (2:1)): δ 0.52 (s, 18 H, SiMe$_3$), 1.40 (m, 12 H, THF), 1.46 (s, 18 H, CMe$_3$), 3.52 (m, 12 H, THF), 5.43 (s, 2 H, CH), 8.14 (br, 4 H, C$_6$H$_4$). ^{13}C NMR (75.5 MHz, C_6D_6/C_5D_4N (2:1)): δ 6.26 (SiMe$_3$), 31.29 (^{t}Bu), 40.29 (C ^{t}Bu), 91.78 (CH), 124.52, 137.23, 165.47 (C$_6$H$_4$). Anal. Calcd for $C_{48}H_{84}N_4Si_4K_4$ (**7**·6THF): C, 58.47; H, 8.59; N, 5.68. Found: C, 57.15; H, 8.09; N, 5.79.

X-ray Structural Determinations and Refinements for 2−5 and 7. Selected single crystals were sealed in Lindemann glass capillaries under dinitrogen. X-ray intensities were measured on an MSC/Rigaku RAXIS IIc imaging-plate diffractometer for compounds **2**−**4**, using Mo Kα radiation ($\lambda = 0.710\ 73$ 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**−**4**.[19] X-ray intensities were measured on a MSC/Rigaku AFC7R four-circle diffractometer for compound **5**, and on Siemens P4/PC diffractometer for compound **7**, using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles.[19]

The crystal structures of compounds **2**−**5** and **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 program package,[20] SHELXTL-93[21] or SHELXTL-97 program package.[22] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[23] Crystallographic data collection and structure refinement of all compounds are summarized in Table 6.

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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.

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