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Article

3,5-Dimethyl and 3,5-Di-*tert*-butylpyrazolato Complexes with Alkali Metals: Monomeric, Dimeric, Cluster, and 1D Chain Structures

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The pyrazolato complexes [(Me$_2$pz)(THF)Li] (**1**), [(^{t}Bu$_2$pz)Li]$_4$ (**2**), [(^{t}Bu$_2$pzH)(^{t}Bu$_2$pz)Li]$_2$ (**2a**), [(Me$_2$pz)Na] (**3**), [(^{t}Bu$_2$pz)Na](**4**), [(^{t}Bu$_2$pz)$_6$(OH)Na$_7$] (**4a**), [(^{t}Bu$_2$pz)(18-crown-6)Na] (**4b**), and [(^{t}Bu$_2$pz)K] (**5**) were synthesized by metalation reactions between R$_2$pzH (R = Me, ^{t}Bu) and alkyllithium, elemental sodium, or potassium. All the complexes were characterized by spectroscopic methods and microanalysis, and in addition, the crystal structures of **2**, **2a**, **3**, **4a**, **4b**, and **5** were obtained by single-crystal X-ray diffraction. They show monomeric, dimeric, cluster, and 1D chain structures in the solid state. Ab initio calculations on the structure and stabilities of the monomeric pzM complexes were performed at the MP2 level of theory showing good agreement with the coordination preferences of the pyrazolato ligand to a particular alkali ion.

Introduction

One of the most interesting aspects of the chemistry of pyrazole ligands when they bind a metal center is that they are not restricted to exclusively use one or the two adjacent nitrogen atoms of the five-membered ring.[1] The variety of coordination modes that have been observed in pyrazolyl complexes span from the ligand acting as a bridge (μ-η^1:η^1, μ-η^2:η^2, μ_3-η^1:η^1:η^1, μ_3-η^1:η^2:η^1, etc.)[2] to being terminal (η^1, η^2, and η^5).[3,4] In many syntheses of pyrazolyl complexes, the alkali pyrazolato salts have been used as excellent pyrazolyl transfer reagents. Several crystal structures of complexes based on pyrazolyl ligands containing alkali cations and other metallic centers are known.[5] However, there are limited examples in which the metal center is solely an element of group 1. To date, the complexes [(3,5-bis(fluoren-9-CH$_2$)pz)Li$_2$(THF)$_4$][Li(THF)$_4$],[6] [(3,5-Ph$_2$pz)K(THF)]$_6$,[7]

[K(η^2-3,5-Ph$_2$pz)(η^6-18-crown-6)] and [K(η^2-3,5-Ph$_2$pz)-(H$_2$O)(η^6-18-crown-6)],[8] represent the only known structur-

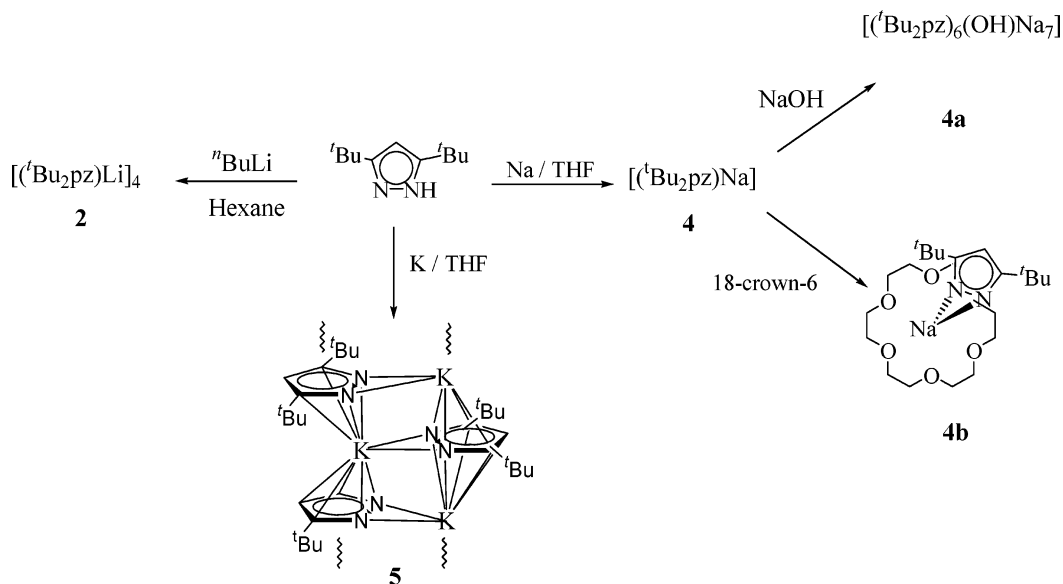* To whom correspondence should be addressed. Fax: +52 777 3297997. E-mail: mamund2@buzon.uaem.mx.
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Scheme 1

ally characterized examples of this type. [(3,5-Bis(fluoren-9-CH$_2$)pz)Li$_2$(THF)$_4$][Li(THF)$_4$] has a monomeric structure, in which the anion has a μ_2-η^1:η^1-pyrazolato ligand coordinating two lithium ions; [(3,5-Ph$_2$pz)K(THF)]$_6$ is a cluster containing bridging η^2-pyrazolato ligands. In the complexes [K(η^2-3,5-Ph$_2$pz)(η^6-18-crown-6)] and [K(η^2-3,5-Ph$_2$pz)-(H$_2$O)(η^6-18-crown-6)], the 18-crown-6 ligand saturates the coordination sites available on the metallic center at the plane formed by the crown; therefore, the pyrazolato ligand is restricted to express a terminal η^2-coordination mode resulting in a monomeric structure for both complexes.

At present, our research group is developing the chemistry of polypyrazolylaluminate ligands;[9] in these complexes, novel bonding modes between the pyrazolato moiety and the alkali metal cations have been observed. During the course of these investigations, we expand the knowledge about the chemistry of alkali pyrazolato compounds, which we use as starting materials. Thus, the synthesis and characterization of several 3,5-dimethylpyrazolate (Me$_2$pz$^-$) and 3,5-di-*tert*-butyl-pyrazolate (^{t}Bu$_2$pz$^-$) complexes of Li$^+$, Na$^+$, and K$^+$ are presented. In these complexes with a dominant ionic bonding, a tendency to form structures which allow the maximization of the interaction between the R$_2$pz$^-$ ligands and the alkali cations forming a cluster or chain structures was observed. Nevertheless, when an additional ligand is at hand (R$_2$pzH or 18-c-6), the structures tend to be less aggregated producing monomers or dimers. To rationalize the bonding in these structures, ab initio calculations have been carried out on monomers of Li$^+$, Na$^+$, and K$^+$ pyrazolato complexes.

Results and Discussion

The combination of R$_2$pzH (R = Me, ^{t}Bu) and elemental lithium or lithium hydride in refluxing THF resulted in unreacted R$_2$pzH. In a similar procedure used by Rabinovich,[10]

treatment of ^{t}BuLi with Me$_2$pzH in THF led to the formation of compound [(Me$_2$pz)(THF)Li], **1**, as a semisolid product. Multinuclear NMR and microanalysis suggest that, for complex **1**, each lithium atom binds one pyrazolato ligand and one molecule of THF. On the other hand, from the reaction between ^{n}BuLi and ^{t}Bu$_2$pzH in hexane, a white solid [(^{t}Bupz)Li]$_4$, **2**, was obtained (Scheme 1). The solubility of complexes **1** and **2** in common organic solvents as benzene, toluene, and THF allowed the measurement of ^{1}H and ^{7}Li{^{1}H} NMR spectra. There is no significant change in the proton resonance signals on going from the free ligand R$_2$pzH (R = Me, ^{t}Bu) to the lithium complexes. For instance, the chemical shifts in ^{t}BupzH appear at 6.02 and 1.37 ppm, while for **2**, they are at 6.07 and 1.27 ppm. Complex **1**, with one molecule of THF coordinated to the lithium ion, has a ^{7}Li NMR chemical shift of -0.92 ppm, while for complex **2**, which has no coordinated THF, the signal appears at -0.23 ppm. A similar downfield shift with the decrease of the number of THF molecules coordinated to lithium was observed in the aluminates [Mes$_2$Al(NH^{t}Bu)$_2$Li(THF)$_n$] (n = 2, -0.73 ppm; n = 1, 1.464 ppm).[11] The molecular structure of **2** determined by X-ray crystallography is shown in Figure 1, and structural parameters are shown in Tables 1 and 2. Compound **2** is a tetramer in which the lithium atoms are arranged in a distorted tetrahedral fashion each occupying a vertex of the tetrahedron. Every face of the polyhedron is capped by a ^{t}Bu$_2$pz$^-$ ligand, and no intermolecular contacts are observed. One nitrogen from each pyrazolyl ring coordinates one lithium atom with a short Li$-$N distance (1.946(3)$-$1.959(3) Å) and the other coordinates two lithium atoms with longer Li$-$N distances (2.026(3)$-$2.114(3) Å). These Li$-$N bond lengths are comparable to those observed in complexes with Li$-$N bonds, for example [(PhTp$^{t^Bu}$)Li] (1.934(3)$-$1.977(3) Å)[12]

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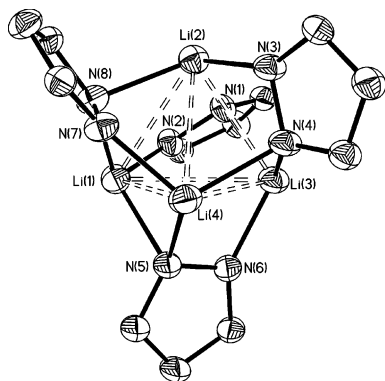
Figure 1. Perspective view of complex [(^{t}Bu$_2$pz)Li]$_4$ (**2**) showing the thermal ellipsoids at the 50% probability level (hydrogen atoms and *tert*-butyl groups have been removed for clarity).

and [HC(Me$_2$pz)$_3$]Li(η^3-BH$_4$) (2.038(5)−2.092(7) Å).[13] Aggregated structures with lithium atoms in a tetrahedral and octahedral arrangement is rather common for organolithium compounds, for example [MeLi]$_4$, [EtLi]$_4$, [(SiMe$_3$)Li]$_4$, [CyLi]$_6$, [^{i}PrLi]$_6$, etc.[14] In these two arrangements, the lithium atoms maximize the use of their valence shell orbitals. However, the Li−Li distances in **2** [2.812(4)−3.095(4) Å] are somewhat longer than those found in lithium-based tetramers (e.g., [(SiMe$_3$)Li]$_4$, 2.749(7)−2.819(4)).[12a] The expansion of the lithium core in **2** can be ascribed to the interaction of each triangular face of the tetrahedron with two nitrogen atoms of the pyrazolyl ligand instead of only one atom (carbon or silicon) in [MeLi]$_4$, [EtLi]$_4$, [Me$_3$Si-SiMe$_2$Li]$_4$, etc.[12]

In an attempt to crystallize **2**, complex [(^{t}Bu$_2$pzH)(^{t}Bu$_2$pz)-Li]$_2$, **2a**, was isolated. Compound **2a** might have resulted either from incomplete deprotonation of the ^{t}Bu$_2$pzH starting material or from partial hydrolysis of **2**. Complex **2a** was characterized by spectral and analytical methods, and the molecular structure was determined by X-ray crystallography. The molecular structure of **2a** shows a dimer with two ^{t}Bu$_2$pzH ligands in a terminal η^1 fashion and two ^{t}Bu$_2$pz$^-$ ligands in a bridging μ_2-η^1:η^2 coordination mode forming a central four-membered Li$_2$N$_2$ ring (Figure 2). Table 1 gives relevant data of the crystal collection, and Table 2 lists selected bond lengths and angles. The bridging and terminal η^1-interactions are characterized by Li−N bond lengths of 2.022(4) and 2.048(4) Å, respectively. These bond lengths are within the range of those found in the dimer [FcB(pz)$_3$Li]$_2$ (Fc = ferrocenyl) which has a central four-membered Li$_2$N$_2$ ring (bridging η^1 Li−N, 2.067(4) Å; terminal η^1 Li−N, 2.007(4) Å).[5a] Complex **2a** also features η^2 interactions of the ligand and the lithium atoms (Li(1)−N(1), 2.009(4) Å; Li(1)−N(2), 2.067(4) Å). The bonding of the η^2-pyrazolato ligand for **2a** is then unsymmetrical, with a difference of 0.058 Å for the Li−N bond lengths. This "slipped" η^2-pyrazolato coordination mode has been frequently observed

in complexes that show η^2 coordination.[3c,3e,7] The coordination geometry about each lithium atom in **2a** can be viewed as distorted trigonal, if the center of the η^2-pyrazolato ligand is considered to be a monodentate donor (N(1)−Li(1)−N(3), 140.8(2)°; N(1)−Li(1)−N(2A), 114.3(2)°; N(2)−Li(1)−N(2A), 101.53(18)°; N(2)−Li(1)−N(3), 131.4(2)°; N(2A)−Li(1)−N(3), 104.89(18)°). To our knowledge, this is the first structurally characterized lithium pyrazolato complex that features a η^2 interaction.

Treatment of either Me$_2$pzH or ^{t}Bu$_2$pzH with elemental sodium (1.1 equiv) in THF at room temperature yielded, upon cessation of hydrogen evolution and workup, [(Me$_2$pz)Na], **3*** (93%),[15] and [(^{t}Bu$_2$pz)Na], **4** (90%), respectively (Scheme 1). Complexes **3*** and **4** were characterized by spectral and analytical methods. The crystallization of **3*** in THF produced crystals of sufficient quality to allow the determination of the crystal structure by X-ray diffraction.[16] Complex [(Me$_2$pz)(THF)Na]$_4$, **3**, exists as a tetramer-like cluster that has a drumlike form, in which all the pyrazolato ligands are coordinated in a bridging μ_3-η^1:η^2:η^1-fashion (Figure 3). Two hexagons are the top and the bottom of the drum; they result from η^1,η^1 coordination of two pyrazolato ligands to two sodium ions. These two hexagons are bound through four η^2 interactions. The sodium ions complete their coordination sphere with one THF ligand. The η^2-pyrazolato ligands are characterized by sodium−nitrogen bond lengths of 2.6203(17) and 2.5886(17) Å (Na(1)−N(1) and Na(1)−N(2), respectively), while the corresponding values for the η^1-coordination modes are 2.3967(18) and 2.3763(16) Å (Na(1)−N(2A), and Na(1)−N(3), respectively). These values are comparable to those observed in the [Yb$_3$(μ-Me$_2$pz)$_6$(η^2-Me$_2$pz)$_3$(μ_3-O)-Na$_2$(THF)$_2$] cluster (2.402(6)−2.976(5) Å), in which the pyrazolato ligands coordinate the sodium ions in a μ_2-η^1:η^1 fashion.[4d] The Na−N bond lengths in the η^1 interactions are smaller than those found for the η^2 interactions, probably as a consequence of the restrictions imposed by the cluster. Contrary to what was observed for **2a**, the bonding of the η^2-pyrazolato ligand is symmetrical (the difference in bond lengths is 0.0137 Å). Of note, tetramer **3** is a small version of the hexamer [(3,5-Ph$_2$pz)K(THF)]$_6$.[7] The smaller size of the cluster **3** can be attributed to the lesser steric requirements of the Me$_2$pz$^-$ ligand than those of the Ph$_2$pz$^-$ ligand.

Unfortunately, we were unable to solve the X-ray crystal structure of **4** because of severe disorder in the crystal structure. However, in the course of finding suitable crystals of **4** for X-ray crystallography, we obtained the crystal structure of complex [(^{t}Bu$_2$pz)$_6$(OH)Na$_7$], **4a**. The serendipitous formation of this compound may have resulted from traces of sodium hydroxide coming from the layer that usually covers sodium metal. Complex **4a** crystallized as a cluster with six molecules of benzene, no intermolecular interactions are observed in the crystal structure of the solvent

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(15) The crystal structure and synthesis of **3** has been described in a previous communication (ref 9).

(16) The crystal structure obtained by X-ray diffraction for **3** shows that each sodium atom is coordinated to a THF molecule. However, according to the ^{1}H NMR and elemental analysis, when crystals of **3** are dried under vacuum, the THF molecules are decoordinated, producing complex [(Me$_2$pz)Na] **3***.

Table 1. Summary of Crystallographic Data for Complexes **2a**, **3**, **4a**, **4b**, and **5**

	2	**2a**	**3**
formula	$C_{44}H_{76}Li_4N_8 \cdot 0.5C_6H_{14}$	$C_{44}H_{78}Li_2N_8$	$C_{36}H_{60}N_8Na_4O_4$
fw (g/mol)	787.97	733.02	760.88
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.6687(14)	10.310(3)	23.161(3)
b (Å)	10.7314(14)	10.826(3)	11.6112(16)
c (Å)	23.032(3)	11.412(3)	17.233(3)
α (deg)	88.162(2)	83.982(5)	90
β (deg)	77.896(2)	71.500(4)	116.482(2)
γ (deg)	88.166(2)	75.143(5)	90
V (Å³)	2576.1(6)	1167.2(5)	4148.1(10)
Z	2	2	4
D_{calcd} (g/cm³)	1.005	1.043	1.218
$F(000)$	850	404	1632
cryst size (mm³)	$0.26 \times 0.24 \times 0.20$	$0.28 \times 0.25 \times 0.22$	$0.23 \times 0.19 \times 0.17$
temp (K)	100(2)	100(2)	100(2)
2θ range (deg)	1.81−25.50	1.88−24.99	1.96−25.50
reflns collected	26006	7049	10445
independent reflns	9535 [$R_{int} = 0.0335$]	4057 [$R_{int} = 0.0322$]	3851 [$R_{int} = 0.0333$]
observed reflns	7093 [$F > 4.0\sigma(F)$]	3078 [$F > 4.0\sigma(F)$]	2095 [$F > 4.0\sigma(F)$]
params	557	260	239
R	0.0535	0.0694	0.0419
R_w	0.1370	0.1362	0.1057
GOF	1.041	1.102	1.029
largest difference electron density (e/ Å³)	0.290 and −0.200	0.266 and −0.151	0.333 and −0.219

	4a	**4b**	**5**
formula	$C_{66}H_{115}N_{12}Na_7O \cdot 6C_6H_6$	$C_{23}H_{43}N_2NaO_6$	$C_{22}H_{38}K_2N_4$
fw (g/mol)	1722.28	466.68	436.76
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	28.396(6)	9.903(2)	10.540(3)
b (Å)	20.922(4)	19.174(4)	11.043(3)
c (Å)	34.878(7)	14.314(3)	12.168(3)
α (deg)	90	90	105.689(7)
β (deg)	103.42(3)	108.414(4)	104.812(6)
γ (deg)	90	90	100.077(5)
V (Å³)	20155(7)	2578.8(10)	1272.1(6)
Z	8	4	2
D_{calcd} (g/cm³)	1.135	1.202	1.140
$F(000)$	7456	1016	472
cryst size (mm³)	$0.29 \times 0.22 \times 0.27$	$0.30 \times 0.27 \times 0.25$	$0.30 \times 0.28 \times 0.25$
temp (K)	100(2)	100(2)	100(2)
2θ range (deg)	1.43−25.50	1.84−25.50	1.83−25.50
reflns collected	61795	11357	2988
independent reflns	32587 [$R_{int} = 0.0510$]	4619 [$R_{int} = 0.0322$]	2740 [$R_{int} = 0.0956$]
observed reflns	17796 [$F > 4.0\sigma(F)$]	3648 [$F > 4.0\sigma(F)$]	2193 [$F > 4.0\sigma(F)$]
params	2376	375	265
R	0.0694	0.0422	0.0441
R_w	0.1642	0.0969	0.1095
GOF	1.012	1.032	0.979
largest difference electron density (e/Å³)	0.977 and −0.287	0.260 and −0.277	0.387 and −0.249

and the cluster. In the molecular structure of the cluster, six pyrazolato ligands are arranged at the corners of an octahedron with seven sodium ions placed above the midpoint of seven octahedral faces and one hydroxyl group at the center of the cluster (Figure 4). Table 1 gives relevant data of the crystal collection, and Table 2 lists selected bond lengths and angles. The central oxygen should be protonated from charge balance and spectroscopic considerations. The IR spectrum of **4a** shows a small broad band at 3550 cm⁻¹, and the ¹H NMR spectrum shows a strongly deshielded small broad resonance signal at 10.46 ppm, both indicative of the presence of a cluster-bound hydroxide ion. Three pyrazolato ligands are coordinated in a μ_4-η^1:η^1:η^1:η^1 bonding mode, and three are in a μ_3-η^1:η^1:η^1 fashion where pyrazolato ligands in opposite corners are almost parallel and have

different coordination modes. Each sodium ion is thus coordinated to three nitrogen atoms from three different pyrazolato ligands and to the central hydroxyl group. The sodium−nitrogen bond lengths range from 2.278(3) to 2.688(3) Å (2.398(3) Å average). These distances are similar to those observed in **3**. The sodium−oxygen bond lengths (2.487(3) Å average) are similar to those found in [(In)$_2$(μ_2-η^1:η^1-^{t}Bupz)$_4$(μ-O)(Na)$_2$(I)$_2$(THF)] (2.313 Å).[4b] A structure related to **4a** is found for [Na$_{11}$(O^{t}Bu)$_{10}$(OH)] which also shows a hydroxide ion encapsulated in a molecular aggregate.[17]
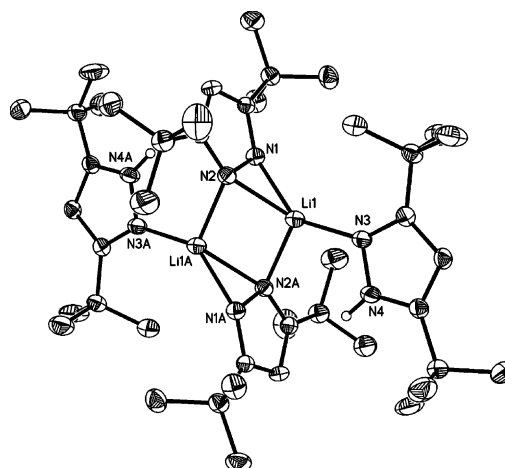
Treatment of **4** with 18-crown-6 (1 equiv) led to the formation of [(^{t}Bu$_2$pz)Na(18-crown-6)], **4b**, in a 96% yield

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2**, **2a**, **3**, **4a**, **4b**, and **5**

	2		
Li(1)−Li(2)	2.859(4)	Li(3)−Li(1)−Li(4)	56.54(10)
Li(1)−Li(3)	3.095(4)	Li(3)−Li(1)−Li(2)	56.60(9)
Li(3)−Li(4)	2.812(4)	Li(4)−Li(1)−Li(2)	66.06(10)
Li(3)−N(6)	1.946(3)	Li(4)−N(5)−Li(1)	84.99(13)
Li(1)−N(5)	2.114(3)	N(1)−N(2)−Li(1)	108.24(14)
Li(1)−N(8)	2.026(3)	N(6)−N(5)−Li(1)	104.88(13)
	2a		
Li(1)−N(1)	2.009(4)	N(1)−Li(1)−N(2)	39.73(10)
Li(1)−N(2)	2.022(4)	N(1)−Li(1)−N(3)	140.8(2)
Li(1)−N(3)	2.048(4)	N(2)−Li(1)−N(3)	131.4(2)
Li(1)−N(2A)	2.067(4)	N(2A)−Li(1)−N(3)	104.89(18)
N(1)−N(2)	1.386(3)	N(1)−Li(1)−N(2A)	114.3(2)
N(3)−N(4)	1.365(3)	N(2)−Li(1)−N(2A)	101.53(18)
	3		
Na(1)−N(1)	2.6203(17)	N(1)−Na(1)−N(2)	30.88(5)
Na(1)−N(2)	2.5886(17)	N(2A)−Na(1)−N(3)	111.12(6)
Na(1)−N(3)	2.3773(16)	O(1)−Na(1)−N(2A)	110.75(6)
Na(1)−N(2A)	2.3967(18)	O(1)−Na(1)−N(3)	111.27(6)
Na(1)−O(1)	2.3409(14)	O(1)−Na(1)−N(1)	119.35(5)
N(1)−N(2)	1.387(2)	O(1)−Na(1)−N(2)	115.41(5)
		N(3)−Na(1)−N(1)	89.82(5)
		N(2)−Na(1)−N(2A)	88.74(6)
		N(2)−Na(1)−N(3)	117.41(6)
		N(1)−Na(1)−N(2A)	112.78(6)
	4a		
N(2)−Na(2)	2.278(3)	Na(2)−N(2)−Na(1)	76.20(10)
N(1)−Na(7)	2.311(3)	Na(1)−N(2)−Na(1)	101.62(17)
N(2)−Na(1)	2.407(3)	Na(4)−N(27)−Na(3)	73.31(9)
N(28)−Na(6)	2.413(3)	Na(1)−O(1)−Na(6)	174.00(13)
N(27)−Na(4)	2.400(3)	Na(2)−O(1)−Na(1)	72.91(8)
N(28)−Na(5)	2.410(3)	N(2)−Na(1)−N(15)	110.31(10)
N(27)−Na(3)	2.367(3)	O(1)−Na(1)−N(15)	83.41(10)
Na(1)−O(1)	2.357(3)		
Na(3)−O(1)	2.732(3)		
	4b		
Na(1)−N(1)	2.3175(15)	C(1)−N(2)−Na(1)	145.96(11)
Na(1)−N(2)	2.5767(15)	C(3)−N(1)−Na(1)	142.96(11)
Na(1)−O(1)	2.7972(14)		
Na(1)−O(2)	2.5138(14)		
Na(1)−O(3)	2.7081(15)		
Na(1)−O(4)	2.6843(14)		
Na(1)−O(5)	2.4788(14)		
Na(1)−O(6)	2.753(2)		
N(1)−N(2)	1.381(3)		
N(1)−C(3)	1.339(2)		
N(2)−C(1)	1.338(2)		
	5		
K(1)−N(1)	2.885(3)	K(1)−N(1)−N(2)	27.76(8)
K(1)−N(2)	2.803(2)	K(1)−N(3A)−N(4A)	28.05(7)
K(1)−C(3)	3.431(3)	K(1)−N(3)−N(4)	29.20(7)
K(1)−C(1)	3.304(3)	N(1)−K(1)−N(4)	178.07(6)
K(1)−N(3A)	2.820(2)	N(1)−K(1)−N(3)	91.81(7)
K(1)−N(4A)	2.900(3)	N(1)−K(1)−N(3A)	153.59(8)
K(1)−C(12A)	3.188(3)	N(1)−K(1)−N(4A)	178.07(6)
K(1)−C(13A)	3.452(3)	K(1)−N(1)−K(2)	85.77(6)
K(1)−C(14A)	3.288(4)	K(1)−N(2)−K(2)	81.93(6)
K(1)−N(3)	2.787(2)		
K(1)−N(4)	2.713(3)		

Figure 2. Perspective view of complex [(*t*Bu₂pzH)(*t*Bu₂pz)Li]₂ (**2a**) showing the thermal ellipsoids at the 50% probability level (selected hydrogen atoms have been omitted for clarity). Symmetry transformation used to generate equivalent atoms: $1 - x, -y + 1, -z + 2$.
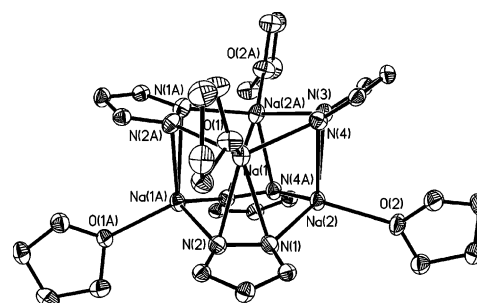
Figure 3. Perspective view of complex [(Me₂pz)(THF)Na]₄ **3** showing the thermal ellipsoids at the 50% probability level, previously reported in ref 9 (hydrogen atoms and methyl groups have been removed for clarity). Symmetry transformation used to generate equivalent atoms: $1 - x, y, -z + 1/2$.
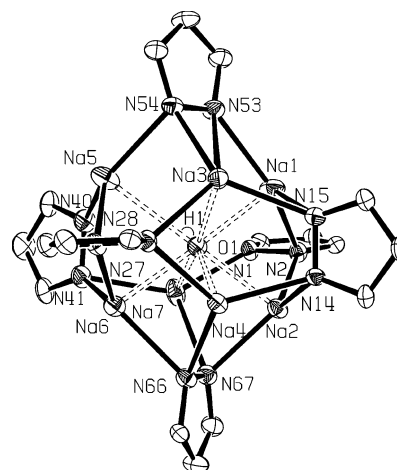
Figure 4. Perspective view of complex [(*t*Bu₂pz)₆(OH)Na₇] (**4a**) showing the thermal ellipsoids at the 50% probability level (hydrogen atoms and *tert*-butyl groups have been removed for clarity).

2.7972(14) Å and are similar to other structurally characterized complexes containing [Na(18-crown-6)] fragments.[18]

(18) (a) Ellison, M. K.; Nasri, H.; Xia, Y. M.; Marchon, J. C.; Schulz, C. E.; Debrunner, P. G.; Scheidet, W. R. *Inorg. Chem.* **1997**, *36*, 4804. (b) Busetto, L.; Cassani, M. C.; Zanotti, V.; Albano, V. G.; Sabatino, P. *Organometallics* **2001**, *20*, 282. (c) Arliguie, T.; Lescop, C.; Ventelon, L.; Leverd, P. C.; Thuery, P.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2001**, *20*, 3698.
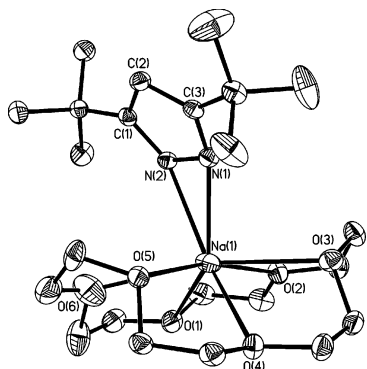
(Scheme 1). Crystals of sufficient quality to allow a X-ray single-crystal structure determination were grown from a concentrated THF solution. A perspective view of the molecular structure is given in Figure 5. Table 1 gives a summary of the data collection, and Table 2 lists selected bond lengths and angles. Complex **4b** exists as a monomer; the sodium atom is coordinated by one η^2-pyrazolato ligand and one 18-crown-6 ligand. The sodium−oxygen bond lengths of the crown ether range between 2.4788(14) and

Figure 5. Perspective view of complex [(^{t}Bu$_2$pz)(18-crown-6)Na] (**4b**) showing the thermal ellipsoids at the 50% probability level (hydrogen atoms have been removed for clarity).

The sodium ion is located 0.56 Å above the best plane of the 18-crown-6 ligand oxygen atoms. In a manner similar to that in cases **2a** and **3**, the bonding of the η^2-pyrazolato ligand to the sodium ion is asymmetric with Na(1)−N(1) = 2.3175(15) and Na(1)−N(2) = 2.5767(15) Å. These bond lengths are marginally shorter than those found for the η^2-pyrazolato ligand in complex **3** probably because of the terminal η^2 coordination in **4b**, while it is a bridge in **3**. The angle formed between the plane of the pyrazolato C$_3$N$_2$ core and the best plane of the 18-crown-6 ligand oxygen atoms is 52.3°. This angle in **4b** is intermediate between the one observed in the related complex [K(η^2-3,5-Ph$_2$pz)(η^6-18-crown-6)] (85.01(10)°) and in complex [K(η^2-3,5-Ph$_2$pz)-(H$_2$O)(η^6-18-crown-6)] (25.40(14)°).[8] Complex **3*** was soluble in THF and DMSO but was insoluble in benzene and toluene. By contrast, because of the presence of the lipophilic *tert*-butyl groups on **4**, **4a**, and **4b**, they are soluble in all common organic solvents. As was observed for complexes **1** and **2**, the ^{1}H NMR spectra of **4**, **4a**, and **4b** show resonance signals for the pyrazolato ligand with a small variation of the chemical shifts. Therefore, additional information about the aggregation number in solution is difficult to deduce from NMR.

Winter et al reported the synthesis of the complex 3,5-di-*tert*-butylpyrazolatopotassium, **5**, through the reaction between ^{t}Bu$_2$pzH and KH.[7] Alternatively, we prepared this complex by reaction of ^{t}Bu$_2$pzH with elemental potassium (1.1 equiv) in THF in a 95% yield (Scheme 1). IR and elemental analysis of **5** were consistent with the proposed composition. X-ray crystallography on **5** revealed a chain structure in which each potassium ion is sandwiched between two pyrazolato ligands (η^4- and η^5-bonded) and also is coordinated to another pyrazolato in a η^2 fashion. To date, there have been few examples reported with a η^5-pyrazolato coordination mode,[4] and to our knowledge, the μ_3-η^2:η^4:η^5 coordination mode observed in **5** is unprecedented. The chain structure has a stairlike form that run through axis *b* (Figure 6b), where the steps are the η^2 interactions, and there are no significant intermolecular contacts between adjacent stairs. Interestingly, in the sandwiched η^4 and η^5 interactions, which involve π-orbital donation to potassium, the ions are located directly above and below the N−N bonds of the pyrazolato ligand, where the planes defined by the atoms N1−N2−K1
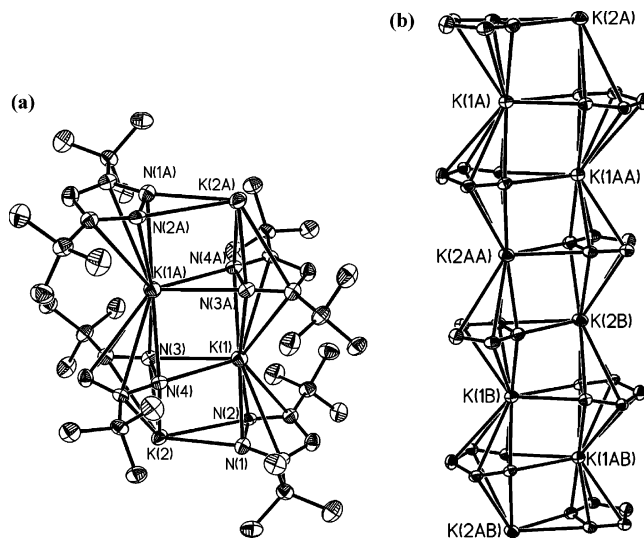

Figure 6. (a) Crystal structure of [(^{t}Bu$_2$pz)K] (**5**) with the thermal ellipsoids at the 50% probability level. (b) Polymeric structure through axis *b* (hydrogen atoms and *tert*-butyl groups have been removed for clarity). Symmetry transformations used to generate equivalent atoms: 1 − *x* + 1, −*y* + 1, −*z* + 1; −x + 1, −*y*, −*z* + 1.

(η^4 interaction) and N3A−N4A−K1 (η^5 interaction) are virtually normal to the ring planes of the pyrazolato ligands (97.4 and 94.6°, respectively). The potassium−nitrogen bond lengths in the η^4 and η^5 interactions are in the range of 2.803(2)−2.967(3) Å, which are smaller than those found for the η^5 interaction of complex [Tp^{CF_3,CH_3}CuK(CO$_3$)-KTp^{CF_3,CH_3}]$_2$, since the potassium ion is located above the center of the pyrazolato ligand (3.277(2)−3.339(3) Å).[5b] However, the potassium−carbon bond lengths (3.177(4)−3.431(3) Å) are similar to those found in the [Tp^{CF_3,CH_3}CuK-(CO$_3$)KTp^{CF_3,CH_3}]$_2$ complex (3.339(3)−3.424(4) Å). The K−C distance of the remaining carbon atom of each η^4 interaction is about 0.35 Å longer; therefore, it is unlikely that it is involved in any significant bonding. On the other hand, in the η^2-coordination mode, the angle formed between the plane of the pyrazolato C$_3$N$_2$ core and the KN$_2$ is 176.5°, which is consistent with donation of the in-plane lone pairs of the nitrogen atoms to the potassium ion. The potassium−nitrogen bond lengths in this interaction (2.713(3)−2.787(2) Å) are comparable to those observed in the [(3,5-Ph$_2$pz)K-(THF)]$_6$ complex (2.763(4)−2.869(4) Å).[8]

Winter et al reported that complexes [(Ph$_2$pz)K(THF)]$_6$ and **5** are soluble in THF; however, while [(Ph$_2$pz)K(THF)]$_6$ is moderately soluble in benzene and toluene, compound **5** is insoluble.[7] They suggested that complex [(Ph$_2$pz)K(THF)]$_6$ is more soluble in nonpolar solvents than **5** because the hexameric structure of the first prevents the ionic bonds from being accessible to the solvent, while for **5**, these bonds may be more exposed. This hypothesis is confirmed with the crystal structure reported herein.

We have performed ab initio calculations on the structure and stabilities of the alkali pyrazolato complexes pzM (M = Li, Na, and K).[19] For the atoms in the pyrazolyl ring, we used a standard aug-cc-VDZ basis set, and for the alkali atoms, a 6-31+G(2d) basis set was used. To predict the most stable structures, we performed full geometry optimizations
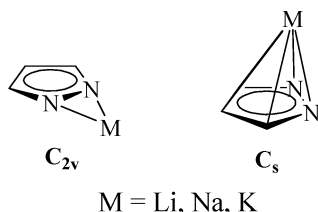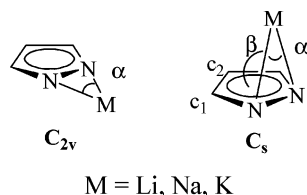
Figure 7. Most stable structures obtained from full geometry optimizations at the MP2 level of theory.

Table 3. Selected Bond Lengths (Å) and Angles (°) Calculated at MP2/VDZ Level of Theory for Isomers C_{2v} and C_s

	Li (C_{2v})	Li (C_s)	Na (C2v)	Na (C_s)	K (C2v)	K (C_s)
N−N	1.39	1.39	1.39	1.39	1.39	1.38
M−N	1.86	2.01	2.23	2.34	2.51	2.62
M−C1		2.21		2.73		2.91
M−C2		2.36		2.99		3.11
α	44.1	40.5	36.3	34.5	32.2	30.6
β		70.8		85.0		82.3

at the MP2 level of theory as well as harmonic frequency analysis. For the three alkali pyrazolato complexes, we found two equilibrium geometries (Figure 7). The first structure has C_{2v} symmetry with the metal and the pyrazolyl ring in the same plane. The second structure has C_s symmetry with the alkali atom located out of the plane of pyrazolato ring, approximately above the N−N bond of the pyrazolato ligand. Table 3 shows the calculated bond lengths for the C_{2v} and C_s geometries. In all cases, the calculated bond lengths inside of the pyrazolyl ring are very close to the experimental values. However, the calculation underestimates the M−N bond lengths by around 0.1 Å, whereas it overestimates the α angles by about 3°. Part of these differences can be ascribed to the steric requirements imposed by the alkyl groups on the pyrazolyl rings and the different types of aggregation displayed in the crystal structures. On the other hand, for the C_s geometry, the calculated M−N and M−C bond lengths fall in the range of those observed in $[\eta^5\text{-CpM}]_\infty$ (M = Li, Na, K);[20] therefore, the metals can be considered to be coordinated by a η^5-bonded pyrazolato ring in this geometry.

(19) All calculations have been performed with the Gaussian 98 program package. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(20) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855.

Table 4. Dissociation Energies for Homo [(pz)·M·] and Heterolytic [M$^+$(pz)$^-$] Breaking and the Relative Stability of the Isomers (ΔE) in kcal/mol Obtained at MP2/VDZ

	C_{2v}	C_s	ΔE ($C_s - C_{2v}$)
(pz)Li·	112.1	102.5	9.5
(pz)$^-$Li$^+$	161.6	152.0	
(pz)Na·	94.8	87.2	7.5
(pz)$^-$Na$^+$	135.6	128.1	
(pz)K·	99.8	95.9	3.8
(pz)$^-$K$^+$	122.1	118.3	

Table 5. Dissociation Energies for Homolytic [(pz)Na·] Breaking and the Relative Stability of the Isomers C_{2v} and C_s (ΔE) in kcal/mol Obtained at Different Levels of Calculation

	MP2/VDZ	CCSD(T)/VDZ	MP2/VTZ	CCSD(T)/VTZ
(pz)Na (C_{2v})	94.8	87.7	98.4	91.8
(pz)Na (C_s)	87.2	80.5	90.3	83.8
ΔE ($C_s - C_{2v}$)	7.5	7.3	8.1	7.9

Table 6. Mulliken Charge on the Alkali Atom (Q) and the Total Dipole Moment (μ in D) for Isomers C_{2v} and C_s

	Q (C_{2v})	μ (C_{2v})	Q (C_s)	μ (C_s)
(pz)Li	0.34	4.8	0.32	5.8
(pz)Na	0.86	7.5	0.92	8.0
(pz)K	0.94	8.9	0.92	9.2

Table 4 shows the dissociation energies for the homo- and heterolytic breakage of the M−N bond and the relative stability of the isomers. As expected, the lithium isomers have stronger binding energies than the sodium and potassium compounds, while the potassium isomers show slightly stronger binding energies than the sodium isomers. It is worth mentioning that the binding energies are stronger than those of the analogous cyclopentadienyl compounds.[21] For all the alkali metals calculated, the C_{2v} complex is more stable than the C_s complex (9.57, 7.53, and 3.83 kcal/mol for Li, Na, and K, respectively) although the difference diminishes appreciably from the lighter to the heavier element. These calculations are in agreement with the trend observed experimentally in the crystal structures: the lithium complexes do not show a coordination close to the C_s symmetry, while for the potassium cases, the ions participate in the two types of geometries (see Figures 3−6). Higher level calculations were performed on the sodium isomers to test the adequacy of the methodology used (Table 5), increasing the basis sets to aug-cc-VTZ and 6-311++G(2df) and repeating the geometry optimization at the MP2 level. Changes in the geometrical parameters of the complexes were negligible. To improve our thermochemical estimates, we performed CCSD(T) calculations at the MP2 equilibrium geometries. In this case, the dissociation energies decreased by less than 10%, and much smaller changes occurred for the relative stability of the isomers. To obtain more information regarding the nature of the chemical bonding, we present in Table 6 the Mulliken charge on the alkali atom and the total dipole moment for both isomers. For sodium and potassium, the bonding is mainly ionic as indicated by the charge being close to unity, while for lithium, the relatively low value of the charge indicates that it is polar covalent.

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Conclusion

Lithium pyrazolato complexes (**1**, **2**, and **2a**) are easily accessed by metalation of R$_2$pzH (R = Me, ^{t}Bu) with alkyllithium reagents. Complexes of the heavier alkali metals, sodium (**3**, **4**, **4a**, and **4b**) and potassium (**5**) were synthesized through the reaction between R$_2$pzH and the respective metal; this method is an easy and efficient route which, in comparison to previous reports, avoids the use of hydrides. A common feature of the X-ray structures of the alkali pyrazolato complexes is that the structures adopted are adjusted to maximize the interactions between the pyrazolato ligand and the alkali cations as shown in clusters **2**, **3**, and **4a** and the 1D chain in **5**. However, when an additional ligand binds the metal center, monomers (**4b**) or dimers (**2a**) are obtained. Complex **2a** constitutes the first example of a η^2-pyrazolato ligand coordinated to lithium. Also it is observed in the crystal structures of these complexes that the bigger the metal ion is the greater the hapticity displayed by the pyrazolato ligand. This observation is in agreement with the results obtained from molecular orbital calculations which revealed that, for the lithium pyrazolato complex, the C_{2v} geometry is clearly favored, while for sodium and especially for potassium, the C_{2v} and C_s complexes become closer in stability. In addition, the calculations show that the binding energies in the alkali pyrazolato complexes are stronger than those of the analogous cyclopentadienyl compounds, and as may be expected, the ionic character increases in the order Li < Na < K.

Experimental Section

General Procedures. All experiments were carried out under Ar using standard Schlenk techniques in conjunction with an inert atmosphere glovebox. THF and hexane were distilled from Na/benzophenone and stored under N$_2$ prior to use. ^{t}Bu$_2$pzH was prepared as described in the literature.[22] Solutions 1.6 M ^{t}BuLi and ^{n}BuLi in hexane were used. All other chemicals were purchased from Aldrich and used as received. ^{1}H, ^{13}C, and ^{7}Li NMR spectra were obtained on a Varian Gemini-200 MHz spectrometer (200 MHz for ^{1}H, 50.30 MHz for ^{13}C, and 77.7 MHz for ^{7}Li) at ambient probe temperature (293 K). ^{1}H and ^{13}C NMR chemical shifts were determined by reference to the residual solvent peaks. ^{7}Li NMR chemical shifts are reported versus LiCl in D$_2$O. Elemental analyses were obtained on a Bruker Analyzer. IR data were recorded as KBr pellets on a FT-IR Bruker spectrometer and are reported in cm^{-1}.

Single Crystal X-ray Crystallography. X-ray data for **2a**, **3**, **4a**, **4b**, and **5** were collected using the program SMART[23] on a Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were carried out with the use of the program SAINT; the program SADABS was employed to make incident beam and decay corrections in the SAINT-Plus version 6.23c suite.[24] Then, the structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL version 6.10 suite.[25]

Hydrogen atoms attached to C atoms were generated in calculated positions and constrained with the use of a riding model, while those bonded to heteroatoms (N or O) were located on difference Fourier maps at advanced stages and their positional parameters were refined. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Even at low temperature, some groups of atoms display some degree of disorder. In the most affected (compounds **4a** and **4b**), the disorder was modeled splitting the group into two orientations (*tert*-butyl groups) or into two conformations (O6, C20−C23 atoms in the crown ether moiety of compound **4b**). The refinements were achieved using combination of the SIMU, DELU, and SAME restraints in SHELXTL.

(3,5-Dimethylpyrazolato)(tetrahydrofuran)lithium [Li(Me$_2$pz)-(THF)] (1). A stirred mixture of Me$_2$pzH (0.5 g, 5.2 mmol) in THF (25 mL) was treated with 3.25 mL of a 1.6 M solution of ^{t}BuLi in hexane (5.2 mmol) at 0° C. After that, the reaction mixture was warmed to room temperature and stirred two more hours. The volatiles were removed under vacuum leaving a colorless semisolid residue (0.86 g, 95%). ^{1}H NMR (benzene-d_6, 25 °C): δ 6.04 (s, 1H, CH), 3.25 (m, 4H, O−CH_2), 2.41 (s, 6H, CH_3), 1.28 (m, 4H, O−CH$_2$−CH_2). ^{13}C NMR (benzene-d_6, 25 °C): δ 150.09 (s, C-CH$_3$), 103.37 (s, CH), 68.35 (s, O-CH$_2$), 26.17 (s, O−CH$_2$-CH$_2$), 14.82 (s, CH$_3$). ^{7}Li NMR (benzene-d_6, 25 °C): δ −0.92. IR (KBr, cm^{-1}): 2974 (s), 2902 (m), 2877 (s), 2721 (w), 1698 (w), 1516 (s), 1413 (s), 1371 (w), 1318 (m), 1257 (w), 1210 (w), 1051 (s), 1022 (s), 972 (m), 901 (m), 762 (s), 668 (w). Anal. Calcd for C$_9$H$_{15}$N$_2$LiO: C, 62.21; H, 8.72; N, 16.13; Li, 3.74; O, 9.21. Found: C, 62.07; H, 8.42; N, 16.41.

(3,5-Di-*tert*-butyl-pyrazolato)lithium, Hexane Hemisolvate [(^{t}Bu$_2$pz)Li]$_4$ (2). A stirred solution of ^{t}Bu$_2$pzH (0.5 g, 2.8 mmol) in hexane (25 mL) was treated with 1.73 mL of a 1.6 M solution of ^{n}BuLi in hexane (5.2 mmol) at room temperature. After the reaction mixture was stirred for 2 h, the solution was concentrated to approximately 10 mL and placed in a −20 °C freezer for 12 h to yield **2** as colorless crystals, which were isolated by cannula filtration and dried under dynamic vacuum (0.45 g, 88%). mp: 200 °C (dec). ^{1}H NMR (benzene-d_6, 25 °C): δ 6.07 (s, 1H, CH), 1.27 (s, 18H, CH_3). ^{13}C NMR (benzene-d_6, 25 °C): δ 165.31 (s, C-^{t}Bu$_2$pz), 97.88 (s, CH), 32.85 (s, C-CH$_3$), 32.00 (s, CH$_3$). ^{7}Li NMR (benzene-d_6, 25 °C): δ −0.23. IR (KBr, cm^{-1}): 2962 (s), 2903 (m), 2863 (m), 1565 (w), 1507 (m), 1463 (m), 1436 (w), 1411 (w), 1360 (m), 1310 (w), 1250 (m), 1207 (w), 1065 (w), 1028 (m), 1004 (m), 927 (w), 784 (w), 729 (w), 632 (w), 491 (s), 433 (w). Anal. Calcd for C$_{11}$H$_{19}$N$_2$Li: C, 71.10; H, 10.33; N, 15.08; Li, 3.49. Found: C, 70.58; H, 10.47; N, 15.39.

(3,5-Di-*tert*-butylpyrazole)(3,5-di-*tert*-butylpyrazolato)lithium [(^{t}Bu$_2$pzH)(^{t}Bu$_2$pz)Li] (2a). A stirred solution of ^{t}Bu$_2$pzH (0.5 g, 2.8 mmol) in hexane (25 mL) was treated with 0.87 mL of a 1.6 M solution of ^{n}BuLi in hexane (1.4 mmol), and a white solid was precipitated; the reaction mixture was stirred for 1 h. This solid was isolated by cannula filtration and dried under dynamic vacuum (0.38 g, 75%). IR (KBr, cm^{-1}): 3237 (s), 2963 (s), 2869 (w), 1570 (w), 1467 (m), 1365 (w), 1287 (w), 1256 (w), 1199 (w), 1093 (w), 1002 (m), 873 (w), 805 (s), 730 (w), 672 (w), 513 (m), 450 (m). Anal. Calcd for C$_{22}$H$_{39}$N$_4$Li: C, 72.16; H, 10.76; N, 15.31; Li, 1.77. Found: C, 72.58; H, 10.65; N, 15.27.

(3,5-Dimethylpyrazolato)sodium [(Me$_2$pz)Na] (3*). A 100 mL Schlenk flask was charged with Me$_2$pzH (0.5 g, 5.2 mmol), elemental sodium (0.13 g, 5.7 mmol), and tetrahydrofuran (25 mL). The reaction mixture was stirred at room temperature for 12 h,

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after which hydrogen evolution was complete. The solution was concentrated to approximately 10 mL and placed in a −20 °C freezer for 12 h to give **3*** as colorless crystals (0.57 g, 93%). mp: >300 °C. ^{1}H NMR (DMSO-d_6, 25 °C): δ 5.39 (s, 1H, C*H*), 2.08 (s, 6H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 25° C): δ 144.26 (s, *C*-CH$_3$), 99.67 (s, *C*H), 14.37 (s, *C*H$_3$). IR (KBr, cm^{-1}): 2918 (s), 2798 (m), 2719 (w), 2455 (w), 2102 (w), 1690 (w), 1511 (s), 1441 (m), 1409 (s), 1315 (m), 1261 (w), 1035 (m), 1011 (m), 965 (w), 770 (s), 732 (w), 664 (w), 590 (w), 535 (w). Anal. Calcd for C$_5$H$_7$N$_2$Na: C, 50.83; H, 5.98; N, 23.72; Na, 19.46. Found: C, 50.14; H, 6.11; N, 23.42.

[(^{t}Bu$_2$pz)$_6$(OH)Na$_7$] Bencene Solvate (4a). In a procedure similar to the synthesis of **3**, ^{t}Bu$_2$pzH (0.5 g, 2.77 mmol) and elemental sodium (0.07 g, 3.05 mmol) were reacted in THF (25 mL). Yield: 0.50 g, 90%. mp: 119−123° C. ^{1}H NMR (benzene-d_6, 25 °C): δ 6.11 (s, 1H, C*H*), 1.29 (s, 18H, C*H*$_3$). ^{13}C NMR (benzene-d_6, 25° C): δ 163.96 (s, *C*-(C(CH$_3$)$_3$)), 96.97 (s, *C*H), 32.79 (s, *C*-CH$_3$), 32.37 (s, *C*H$_3$). IR (KBr, cm^{-1}): 2962 (s), 2867 (m), 1697 (w), 1568 (w), 1498 (m), 1463 (m), 1400 (w), 1360 (m), 1306 (w), 1052 (m), 1207 (w), 1052 (m), 1017 (m), 894 (w), 803 (m), 727 (w), 669 (w), 628 (w), 517 (w), 455 (w). Anal. Calcd for C$_{11}$H$_{19}$N$_2$Na: C, 65.30; H, 9.48; N, 13.85; Na, 11.37. Found: C, 65.13; H, 9.57; N, 13.98.

[(^{t}Bu$_2$pz)$_6$(OH)Na$_7$] (4a). Complex **4a** was obtained from the accidental introduction of NaOH in the reaction mixture for the synthesis of **4**. mp: >300 °C. ^{1}H NMR (benzene-d_6, 25 °C): δ 10.46 (s, 0.16H, O*H*), 6.11 (s, 1H, C*H*), 1.17 (s, 18H, C*H*$_3$). ^{13}C NMR (benzene-d_6, 25° C): δ 165.76 (s, *C*-^{t}Bu), 97.38 (s, *C*H), 32.27 (s, *C*H$_3$), 31.69 (s, *C*-CH$_3$). IR (KBr, cm^{-1}): 3550 (w), 2960 (s), 2868 (s), 1567 (w), 1505 (s), 1464 (s), 1399 (w), 1361 (s), 1306 (m), 1252 (s), 1207 (m), 1012 (s), 787 (s), 729 (m), 683 (m), 630 (w), 517 (w), 457 (m). Anal. Calcd for C$_{66}$H$_{115}$N$_{12}$Na$_7$O: C, 63.21; H, 9.26; N, 13.41; Na, 12.84; O, 1.28. Found: C, 62.97; H, 9.23; N, 13.38.

(3,5-Di-*tert*-butylpyrazolato)(18-crown-6)sodium [(^{t}Bu$_2$pz)(18-crown-6)Na] (4b). A 100 mL Schlenk flask was charged with **4** (0.25 g, 1.24 mmol), 18-crown-6 (0.33 g, 1.24 mmol), and tetrahydrofuran (25 mL). The reaction mixture was stirred at room temperature for one h; then it was concentrated to approximately 8 mL and placed in a −20 °C freezer for 12 h to give **4b** as colorless crystals (0.55 g, 96%). mp: 122 °C. ^{1}H NMR (benzene-d_6, 25 °C): δ 6.20 (s, 1H, C*H*), 3.39 (s, 24H, O−C*H*$_2$), 1.61 (s, 18H, C*H*$_3$). ^{13}C NMR (benzene-d_6, 25° C): δ 159.16 (s, ^{t}Bu), 94.93 (s, *C*H), 70.71 (s, O-*C*H$_2$) 33.06 (s, *C*-CH$_3$), 32.94 (s, *C*H$_3$). IR (KBr, cm^{-1}): 2961 (m), 2905 (m), 1463 (w), 1355 (w), 1260 (m), 1106 (s), 959 (w), 802 (m), 748 (w), 714 (w), 460 (w). Anal. Calcd for C$_{23}$H$_{43}$N$_2$NaO$_6$: C, 59.19; H, 9.31; N, 6.00; Na, 4.93; O, 20.57. Found: C, 58.95; H, 9.25; N, 6.17.

(3,5-Di-*tert*-butylpyrazolato)potassium [(^{t}Bu$_2$pz)K] (5). In a procedure similar to that used for the synthesis of **3**, ^{t}Bu$_2$pzH (0.5 g, 2.77 mmol) and elemental potassium (0.12 g, 3.05 mmol) were reacted in THF (25 mL). Yield: 0.58 g, 95%. mp: >300 °C. IR (KBr, cm^{-1}): 2962 (s), 2865 (m), 1568 (w), 1493 (m), 1462 (m), 1392 (w), 1359 (m), 1285 (w), 1249 (m), 1207 (w), 1128 (w), 999 (m), 805 (m), 775 (w), 732 (w), 629 (w), 517 (w), 452 (w). Anal. Calcd for C$_{11}$H$_{19}$N$_2$K: C, 60.48; H, 8.79; N, 12.83; K, 17.90. Found: C, 60.25; H, 8.70; N, 12.94.

Supporting Information Available: Crystallographic data are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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