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Sodium Polypyrazolylaluminates: Synthesis, Characterization, and Isolation of a Reaction Intermediate of a Trispyrazolylaluminate

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A series of polypyrazolylaluminates $[\mathrm{Na}\{\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})_{4-x}\mathrm{Me}_x\}]$ (x = 3 (**1**); x = 2 (**2**); x = 1 (**3**)) were prepared by treatment of $[\mathrm{Na}({}^t\mathrm{Bu}_2\mathrm{pz})]$ with varying equivalents of AlMe_3. The reaction of $[\mathrm{Na}({}^t\mathrm{Bu}_2\mathrm{pz})]$ with 1 equiv of AlMe_3 afforded the monopyrazolylaluminate $[\{\mathrm{Na}\{\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})\mathrm{Me}_3\}\}_3(\mathrm{THF})_2]_\infty$ (**1**) as a colorless crystalline solid in 85% yield. Addition of 1 and 2 equiv of ${}^t\mathrm{Bu}_2\mathrm{pzH}$ to prepared in situ complex **1** in THF/toluene solutions afforded the bis- and trispyrazolylaluminates $\mathrm{Na}\{\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})_2\mathrm{Me}_2\}(\mathrm{THF})]_2$ (**2**) and $[\mathrm{Na}\{\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})_3\mathrm{Me}\}(\mathrm{THF})]$ (**3**) in 81% and 80% yield, respectively, as colorless crystalline solids. Characterization of **1**−**3** was accomplished by microanalysis and spectroscopic methods as well as single-crystal X-ray crystallography. Crystal structures for **1**−**3** revealed polymeric, dimeric, and monomeric structures, respectively; for **1** and **2**, the aggregation of the complexes is the result of Al−Me$\cdots$Na bridges and the variety of coordination modes displayed by the pyrazolyl moieties. In a different approach to obtain **3**, complex $[\mathrm{Me}_2\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})_2\mathrm{Na}({}^t\mathrm{Bu}_2\mathrm{pzH})]$ (**4**) was isolated from a reaction of $[(\eta^1{:}\eta^1\text{-}{}^t\mathrm{Bu}_2\mathrm{pz})(\mu\text{-}\mathrm{AlMe}_2)]_2$ with 2 equiv of ${}^t\mathrm{BupzH}$ and ${}^t\mathrm{Bu}_2\mathrm{pzNa}$. The molecular structure of **4** shows an Al−Me$\cdots$Na interaction that activates the bridging methyl group to produce unsolvated **3** in solution at room temperature. Complex **4** may be considered a reaction intermediate that affords complex **3** from **2** and constitutes the first example of the isolation of an intermediate in the synthesis of a ligand analogous to the polypyrazolylborates.

Introduction

Although polypyrazolylborate ligands have been one of the most versatile and useful ligands in organometallic chemistry[1] and a variety of analogues with replacement of B have been prepared,[2] there is still a lack of a comprehensive series of polypyrazolylaluminates. A possible explanation for the limited number of polypyrazolylaluminates known stems from the fact that the Al−N bond is weaker in comparison to the B−N bond (B−N = 93 kcal mol^{-1}, Al−N = 71 kcal mol^{-1}),[3] which discourages at first glance their preparation. However, the polypyrazolylgallates $[\mathrm{Me}_2\mathrm{Ga}(\mathrm{pz})_2]^-$ and $[\mathrm{MeGa}(\mathrm{pz})_3]^-$ have been isolated and characterized, as have several of their complexes with transition metals.[4] The use of pyrazolyl-based aluminates as ligands could be very attractive for the preparation of novel mixed main group−transition metal complexes with potential applications in important areas of homogeneous catalysis.[5] Recently, Wright and co-workers showed that the tripodal aluminate $[\{\mathrm{MeAl}(2\text{-py})_3\}\mathrm{Li}\text{-}\mathrm{THF}]$, which is somehow related to the polypyrazolylaluminates, chelates Fe, Mn, Mo, Ca, and Zn.[6] So far, the only structurally characterized polypyrazolylaluminates are the bispyrazolato species $[\mathrm{Na}\{\mathrm{Al}(\mathrm{Me}_2\mathrm{pz})_2\mathrm{Me}_2\}]_\infty$[7] and $[\mathrm{Me}_2\mathrm{Al}(\mu\text{-}\mathrm{pz})_2\mathrm{Mg}(\mu\text{-}\mathrm{pz})_2\mathrm{AlMe}_2\}]$,[8] the former previously reported by us. Inspired by the work of Wright and our first success in the preparation and crystallographic characterization of a polypyrazolylaluminate, we decided to explore a general route for the preparation of pyrazolyl-based aluminates. Herein, we describe a general reaction scheme for the synthesis of the sodium polypyrazolylaluminates $[\mathrm{Na}\{\mathrm{Al}({}^t\mathrm{Bu}_2\mathrm{pz})_{4-x}\mathrm{Me}_x\}]$ (x = 3 (**1**); x = 2 (**2**); x = 1 (**3**)). In the solid state, **1**−**3** exhibit polymeric, dimeric, and monomeric structures, respectively. For complexes **1** and **2**, aggregation is the result of Na$\cdots$CH$_3$−Al bridges and the variety of coordination modes displayed by the pyrazolyl moieties. During the

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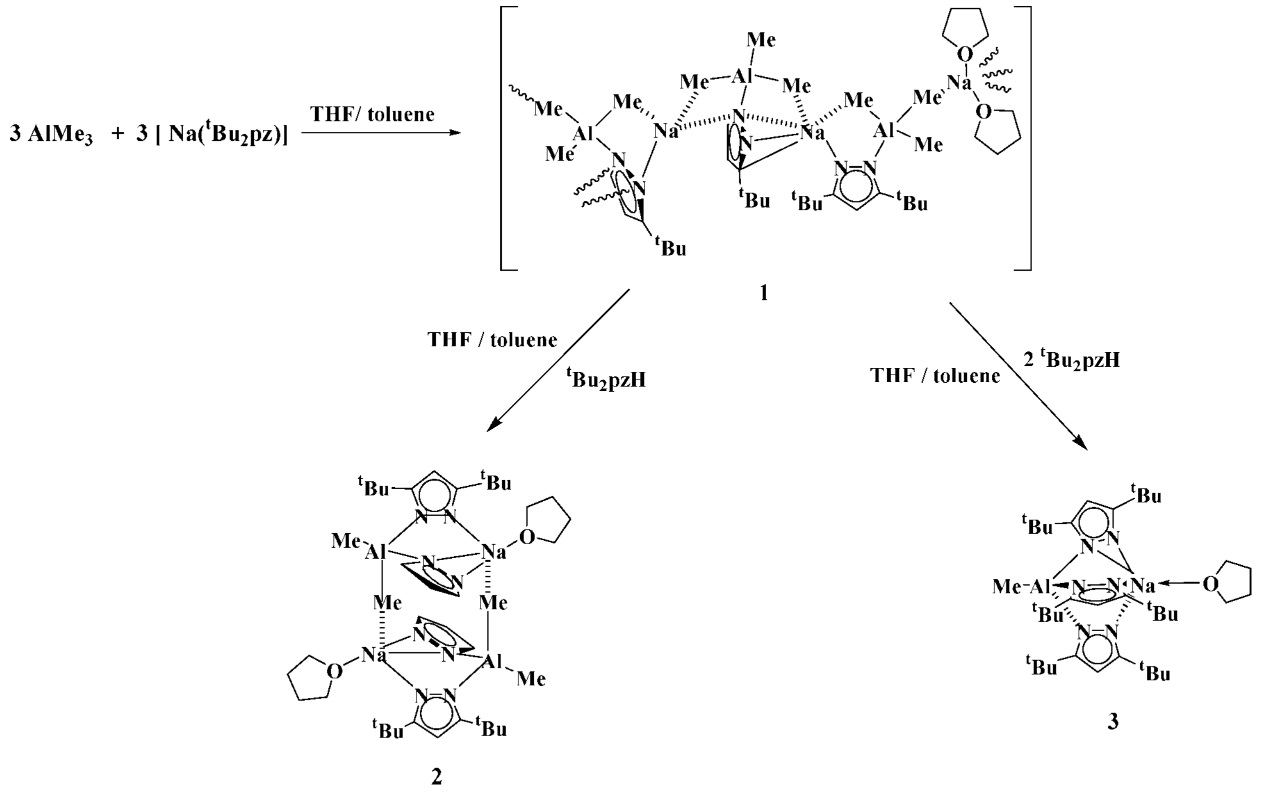
Scheme 1



course of these investigations, we were able to isolate and crystallographically characterize complex $[Me_2Al(^tBu_2pz)_2Na(^tBu_2pzH)]$ (**4**), which is a reaction intermediate that affords complex **3** from **2**. To our knowledge, complex **4** is the first structurally characterized example of a reaction intermediate in the synthesis of a ligand analogous to the polypyrazolylborates.

Results and Discussion

Nucleophilic addition of $[Na(^tBu_2pz)]$[9] to $AlMe_3$ afforded the sodium trimethylpyrazolylaluminate $[\{Na\{Al(^tBu_2pz)Me_3\}\}_3(THF)_2]_\infty$ (**1**) in 85% yield after crystallization from toluene/THF as a colorless crystalline solid (Scheme 1). Complex **1** was fully characterized by elemental analysis, spectroscopic methods, and low-temperature single-crystal X-ray analysis. Details of the data collection and structure refinement of the complex are summarized in Table 1. Selected bond lengths and angles are gathered in Tables 2 and 3. The X-ray crystallographic study of complex **1** reveals a polymeric chain-like structure with 1D dimensionality. There are no intermolecular contacts between adjacent chains (Figure 1). The polymer is made up of the connection of trimeric subunits with a composition of three sodium ions, three trimethylpyrazolylaluminate anions, and two THF molecules. Within the trimer, each sodium ion shows different coordination environments: one binds two methyl groups and two pyrazolyl ligands in η^1-fashion; similarly, the second sodium ion binds also two methyl groups and two pyrazolyl ligands, one in a η^1-fashion and the other in a higher η^3-haptcity. The third sodium ion coordinates two methyl groups, one pyrazolyl ligand in a η^2-fashion, and completes its coordination sphere with two THF molecules. The three aluminum atoms in **1** display a distorted tetrahedral coordination environment; two methyl groups of each aluminum atom participate in Al−Me···Na interactions with Na−C bond lengths between 2.590(4) and 2.873(4) Å. A summary of these interactions is shown in Table 3. These bond lengths are shorter than the sum of the van der Waals radii of the Al and C atoms (4.0 Å)[10] and similar to those observed in complexes with direct Na−carbanion interactions, such as in $[(MeNa)_4]_\infty$ (2.569(4)−2,679(4) Å),[11] $[Na\ (\mu\text{-}Ph)(pmdeta)]_2$ (pmdeta = pentamethyldiethylenetriamine) (2.658(4)−2,682(6) Å),[12] $[(9,10\text{-dihydroanthracenyl})Na(tmeda)]_\infty$ (tmeda = tetramethylethylenediamine) (2.717(2) Å),[13] and $[NaCH(SiMe_3)_2]$ (2.555(10) Å).[14] In addition, the Al−C bond distances that encompass the Al−Me···Na interactions (1.980(4)−2.000(4) Å) are longer than the Al−terminal methyl group distances (1.971(4)−1.976(4) Å). With the exception of the interaction of the fragment Na(1)−C(9)−Al(1), which is approximately 180° (170.1(2)°), the Al−C−Na angles are near 90° (86.68(10)–98.05(16)°). On the other hand, two hydrogen atoms of the methyl groups involving the interactions at 90° and the three hydrogen atoms of the methyl group related to the interaction near 180° are oriented toward the sodium ion with Na−H distances between 2.32(4) and 2.76(4) Å. These distances are shorter than the sum of the van der Waals radii of the Na and H atoms (3.5 Å)[10] and similar to those observed in $[Na_8(O_3C_5H_{11})_6(SiH_3)_2]$,[15] whose X-ray crystal structure showed

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Table 1. Details of Data Collections and Structural Refinements for Complexes 1–4

	1	2	3	4
formula	$C_{50}H_{100}Al_3N_6Na_3O_2$	$C_{56}H_{104}Al_2N_8Na_2O \cdot C_7H_8$	$C_{38}H_{68}AlN_6NaO$	$C_{35}H_{64}AlN_6Na \cdot C_7H_8$
fw (g/mol)	966.70	1004.78	674.52	618.49
cryst syst	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P\bar{1}$	*Pbca*	$P\bar{1}$
a (Å)	19.751(3)	10.2984(10)	11.3646(10)	9.8013(13)
b (Å)	10.5371(16)	13.0764(13)	20.8314(18)	10.5746(14)
c (Å)	29.873(6)	15.4157(16)	34.466(3)	21.951(3)
α (deg)	90.0	102.456(2)	90	95.412(2)
β (deg)	104.926(3)	107.236(2)	90	99.459(2)
γ (deg)	90.0	109.556(2)	90	110.421(2)
V (Å^3)	6007.5(17)	1750.3(3)	8159.4(12)	2074.6(5)
Z	4	2	8	2
D_{calc} (g/cm^3)	1.067	1.070	1.099	1.034
F(000)	2112	618	2960	698
cryst size (mm^3)	0.24 × 0.19 × 0.14	0.35 × 0.35 × 0.32	0.24 × 0.17 × 0.13	0.23 × 0.21 × 0.21
temp (K)	100(2)	150(2) K	100(2)	100(2) K
2θ range (deg)	1.41 to 25.00	1.48 to 25.00	1.96 to 25.00	1.91 to 25.00
no. of collected reflns	14 087	17 057	38 993	20 218
no. of indep reflns	9960 [R(int) = 0.0462]	6157 [R(int) = 0.0305]	7181 [R(int) = 0.0540]	7299 [R(int) = 0.0234]
no. of obsd reflns	6679 [$F > 4.0\ \sigma(F)$]	5485 [$F > 4.0\ \sigma(F)$]	5740 [$F > 4.0\ \sigma(F)$]	6563 [$F > 4.0\ \sigma(F)$]
no. of params	703	388	424	548
R	0.0671	0.0776	0.0463	0.0481
R_w	0.1663	0.1751	0.1148	0.1274
GOF	0.990	1.212	0.946	1.075
largest diff electron density (e/Å^3)	0.689 and −0.365	0.472 and −0.502	0.505 and −0.304	0.380 and −0.193

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1–4

1	Al(1)−C(9)	1.979(4)	C(10)−Al(1)−C(11)	105.27(19)
	Al(1)−C(10)	1.971(4)	C(10)−Al(1)−C(9)	112.47(18)
	Al(1)−C(11)	1.983(4)	C(10)−Al(1)−N(1)	116.07(17)
	Al(1)−N(1)	1.968(3))	C(9)−Al(1)−N(1)	104.51(14)
	N(2)−Na(2)	2.335(3)	C(9)−Al(1)−C(11)	108.26(19)
	C(9)−Na(1)	2.764(4)	C(11)−Al(1)−N(1)	110.15(15)
	C(11)−Na(2)	2.589(4)	Al(1)−C(11)−Na(2)	98.10(17)
	O(1)−Na(1)	2.332(3)	Al(1)−N(1)−N(2)	109.9(2)
	O(2)−Na(1)	2.304(3)	Al(1)−C(9)−Na(1)	170.1(2)
	Na(2)−N(4)	2.531(3)	Al(2)−C(24)−Na(3)	97.31(16)
	Na(3)−C(24)	2.608(5)	Al(3)−C(37)−Na(3)	88.31(16)
	Na(3)−N(37)	2.652(5)	C(24)−Na(3)−C(37)	104.09(15)
2	Al(1)−C(23)	1.974(3)	C(23)−Al(1)−C(24)	112.52(15)
	Al(1)−C(24)	1.971(3)	C(23)−Al(1)−N(3)	102.07(13)
	Al(1)−N(1)	1.935(2)	C(23)−Al(1)−N(1)	108.84(13)
	Al(1)−N(3)	1.924(2)	Al(1)−C(23)−Na(1A)	172.55(18)
	C(23)−Na(1A)	2.782(3))	C(24)−Al(1)−N(1)	106.83(12)
	Na(1)−N(1)	2.562(3)	C(24)−Al(1)−N(3)	121.82(12)
	Na(1)−N(2)	2.516(3)	N(1)−Al(1)−N(3)	104.03(10)
	Na(1)−N(4)	2.456(3)	N(2)−Na(1)−N(4)	104.83(8)
	Na(1)−O(1)	2.324(2)		
3	Al(1)−C(1)	1.972(2)	C(1)−Al(1)−N(5)	116.24(8)
	Al(1)−N(2)	1.9314(16)	C(1)−Al(1)−N(3)	117.46(8)
	Al(1)−N(3)	1.9202(16)	C(1)−Al(1)−N(2)	109.33(8)
	Al(1)−N(5)	1.9200(16)	N(3)−Al(1)−N(5)	102.94(7)
	N(6)−Na(1)	2.4319(17)	N(5)−Al(1)−N(2)	105.98(7)
	N(4)−Na(1)	2.4480(17)	N(2)−Al(1)−N(3)	103.61(7)
	N(2)−Na(1)	2.5614(17)	C(2)−N(1)−Na(1)	109.96(12)
	O(1)−Na(1)	2.3129(15)	Al(1)−N(2)−Na(1)	89.64(6)
	Na(1)−C(19)	3.073(3)		
4	Al(1)−C(34)	1.9743(18)	N(3)−Al(1)−N(5)	103.39(6)
	Al(1)−C(35)	1.9734(19)	N(3)−Al(1)−C(35)	108.21(7)
	Al(1)−N(5)	1.9422(14)	N(5)−Al(1)−C(35)	105.07(8)
	Al(1)−N(3)	1.9395(14)	Al(1)−N(3)−Na(1)	82.54(5)
	Na(1)−N(2)	2.3692(16)	Al(1)−C(35)−Na(1)	76.33(6)
	Na(1)−N(3)	2.8844(15)	C(34)−Al(1)−C(35)	111.44(9)
	Na(1)−C(35)	3.101(2)	C(34)−Al(1)−N(3)	110.29(7)
	Na(1)−N(6)	2.3693(15)		
	Na(1)−N(4)	2.3466(15)		

an inverted SiH_3−Na interaction that was favored electrostatically (Na−H = 2.52–2.67 Å), and in [$NaCH(SiMe_3)_2$], which also displays a polymeric structure with Na−H interactions (Na−H 2.43–2.65 Å) that were claimed to be agostic.[14] Klinkhammer and others[16] postulated the existence of electrostatic agostic interactions in organyls of the alkali metals with a strong electrostatic component. Similarly for **1**, the Al−CH_3···Na interactions could be described as consisting of an electrostatic interaction between the dipoles Al−$CH_3^{\delta-}$···$Na^{\delta+}$ and a donor–acceptor interaction between the C−H bonding density and the metal cation.[16c] These agostic interactions in **1** complete the coordination spheres of the sodium

Table 3. Bond Lengths (Å) and Angles (deg) That Characterize the Al−CH$_3$Na Interactions in Complexes 1, 2, and 4

Al−C	Na−C	Na−H	Na−C−Al
1			
Al(1)−C(9) 1.979(4)	Na(1)−C(9) 2.764(4)	Na(1)−H(9A) 2.43(4) Na(1)−H(9B) 2.69(4) Na(1)−H(9C) 2.64(5)	Nal(1)−C(9)−Al(1) 169.94(19)
Al(1)−C(11) 1.983(4)	Na(2)−C(11) 2.591(4)	Na(2)−H(11A) 2.36(4) Na(2)−H(11B) 2.41(4)	Nal(2)−C(11)−Al(1) 98.05(16)
Al(2)−C(23) 1.997(4)	Na(2)−C(23) 2.740(4)	Na(2)−H(23A) 2.53(3) Na(2)−H(23B) 2.48(4)	Na(2)−C(23)−Al(2) 89.01(17)
Al(2)−C(24) 1.992(4)	Na(3)−C(24) 2.605(4)	Na(3)−H(24B) 2.40(3) Na(3)−H(24C) 2.32(4)	Na(3)−C(24)−Al(2) 97.38(15)
Al(3)−C(37) 2.000(4)	Na(3)−C(37) 2.651(5)	Na(3)−H(37B) 2.37(4) Na(3)−H(37C) 2.49(4)	Na(3)−C(37)−Al(3) 88.31(15)
Al(3)−C(38) 1982(4)	Na(1)−C(38) 2.873(4)	Na(1)−H(38A) 2.76(4) Na(1)−H(38B) 2.59(4)	Na(1)−C(37)−Al(3) 86.43(15)
2			
Al(1)−C(23) 1.974(3)	Na(1)−C(23) 2.782(3)	Na(1)−H(23A) 2.54 (4) Na(1)−H(23B) 2.45(4) Na(1)−H(23C) 2.68(4)	Na(1)−C(23)−Al(1) 172.55(18)
4			
Al(1)−C(35) 1.973(2)	Na(1)−C(35) 3.103(2)	Na(1)−H(35B) 2.55(2)	Na(1)−C(35)−Al(1) 76.33(6)

ions and favor the chain growth, a remarkable aspect of the structure of the complex considering it is synthesized in the solvent system THF/toluene.[17]

A sodium bispyrazolylaluminate, [Na{Al(^{t}Bu$_2$pz)$_2$Me$_2$}(THF)]$_2$ (**2**), was isolated as a colorless crystalline solid via alkane elimination from in situ generated complex **1** in toluene/THF solution and slow addition of a solution of ^{t}Bu$_2$pzH in toluene (Scheme 1). The identity of complex **2** was confirmed by elemental analysis, spectroscopic methods, and single crystal X-ray analysis. Complex **2** crystallized in the triclinic $P\bar{1}$ space group with two bispyrazolylaluminate molecules in the unit cell and one molecule of toluene. The molecular structure of **2** reveals that the chain-like structure of complex **1** was cleaved by the pyrazolyl ligand, ^{t}Bu$_2$pzH, affording a dimer (Figure 2). A distorted tetrahedral coordination geometry about each aluminum atom is achieved by coordination of two pyrazolyl ligands in a η^1-mode and two methyl groups. The pyrazolyl ligands attached to aluminum also are coordinated to two sodium ions, one in a η^1-fashion and the other with higher η^2-hapticity. The two [Me$_2$Al(^{t}Bu$_2$pz)(NaTHF)] subunits that create the dimer are exclusively bound through two Al−Me···Na interactions with an angle almost linear (172.55(18)°). The sodium ion in this complex achieves a distorted tetrahedral coordination geometry with the coordination of a THF molecule. The bispyrazolylaluminate [Na{Al(Me$_2$pz)$_2$Me$_2$}]$_\infty$, previously reported by us,[7] was also prepared in the presence of THF and shows a 1D infinite chain similar to that of **1**, but in this case there is complete absence of THF in the solid state and in solution. The differences in aggregation observed in **2** and [Na{Al(Me$_2$pz)$_2$Me$_2$}]$_\infty$ may be related to the larger steric requirements of the *tert*-butyl groups on the pyrazolyl rings in **2**, which in turn makes a polymeric structure unfavorable.

Addition of 2 equiv of ^{t}Bu$_2$pzH to in situ generated complex **1** afforded the trispyrazolylaluminate [Na{Al(^{t}Bu$_2$pz)$_3$Me}(THF)] (**3**); see Scheme 1. Complex **3** was characterized by analytical and spectroscopic methods including X-ray diffraction. The molecular structure of **3** reveals a monomeric complex consisting of a [Al(^{t}Bu$_2$pz)$_3$Me]$^-$ anion that is coordinated to a [Na(THF)]$^+$ cation, using four nitrogen atoms of the pyrazolyl rings (Figure 3). The methyl group bound to the aluminum atom is oriented in the opposite direction of the sodium ion, preventing the formation of a tricentric Al−Me···Na interaction. The sodium ion completes its coordination sphere with a molecule of THF. In addition, one carbon atom of a *tert*-butyl group of the most proximal pyrazolyl ring shows a short Na···C contact of 3.073(3) Å (C(19) in Figure 3), and only one hydrogen atom of this methyl group is oriented toward the sodium ion (Na(1)−H(19A) 2.52(3) Å). This Na−C bond length is comparable to those observed in complexes with interactions between the sodium ion and alkyl groups attached to aromatic rings, i.e., [Na(THF)$_2$]$_2$[AlMe$_2$(C$_{14}$H$_{10}$)$_2$] (3.03–3.24 Å).[18]

Complexes **1**−**3** are air- and moisture-sensitive in the solid state and in solution. However, they are stable in solution for long periods of time under an argon atmosphere, as evidenced by samples prepared for multinuclear NMR spectroscopy.

The room-temperature ^{1}H NMR spectrum of **1** in toluene-d_8 shows three singlets at 6.19, 1.36, and −0.43 ppm corresponding to methyne, *tert*-butyl, and Al−Me groups, respectively, and two multiplets ascribed to THF at 3.24 and 1.27 ppm (two THF molecules per [Na{Al(^{t}Bu$_2$pz)Me$_3$}]$_3$ unit). ^{1}H VT-NMR spectroscopy over the range 203–323 K showed the division of the singlet assigned to *tert*-butyl groups into two broad signals with ratio 1:1 (1.60 and 1.15 ppm, $T_c = 243$ K); the rest of the signals remained constant through the temperature range. Additional information for **1** was obtained from its ^{27}Al NMR spectrum. Since the ^{27}Al nucleus possesses a large quadrupole moment, the line width of the resonance signal is a sensitive function of the local symmetry of the complex and therefore of the arrangement of ligands about the nucleus. Consequently, the combination of line width and chemical shift determination can provide information about the chemical and physical environment about an aluminum atom.[19] If parts of the interactions observed in the solid state for **1** are persistent in solution, a large anisotropy would be expected for the aluminum nuclei environment. The ^{27}Al NMR spectra in benzene and in toluene show a very broad signal ($w_{1/2} = 5831$ and 5825 Hz, respectively). This observation could suggest that,

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(17) It has been shown by IR and multinuclear NMR spectroscopy that up to four molecules of THF solvate the sodium ion in the system THF/cyclohexane using as a source of sodium Na[AlBu$_4$]. (a) Schaschel, E.; Day, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 503. (b) Hoehn, E. G.; Olander, J. A.; Day, M. C. *J. Phys. Chem.* **1969**, *73*, 3880. (c) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989.

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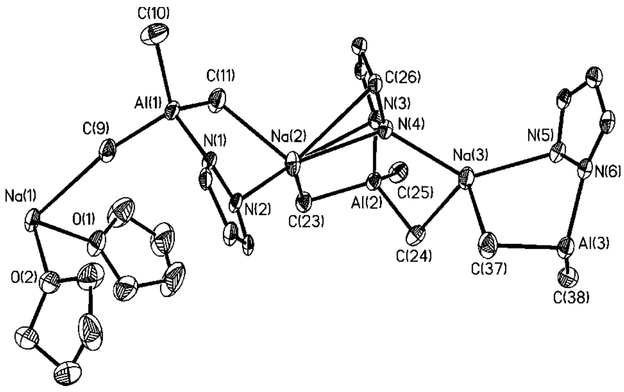

Figure 1. Perspective view of the trimeric subunit of the polymeric structure of $[\{Na\{Al(^tBu_2pz)Me_3\}\}_3(THF)_2]_\infty$ (**1**) showing thermal ellipsoids at the 50% probability level. Hydrogen atoms and *tert*-butyl groups have been omitted for clarity.

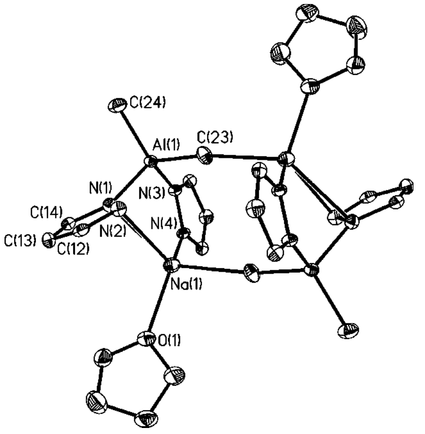

Figure 2. Perspective view of $[Na\{Al(^tBu_2pz)_2Me_2\}(THF)]_2$ (**2**) showing thermal ellipsoids at the 50% probability level (hydrogen atoms and *tert*-butyl groups have been removed for clarity). Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$; #2 $-x+2$, $-y+2$, $-z+1$.

in noncoordinating solvents like toluene or benzene, part of the interactions observed in the solid state persist in solution. However in coordinating solvents it may be anticipated that these interactions are lost, and narrow lines in the ^{27}Al NMR spectrum result. Consistent with this hypothesis, the addition of 9 or 12 equiv of THF per equivalent of **1** resulted in a decrease of the ^{27}Al NMR signal amplitude in benzene and toluene ($w_{1/2} = 2808$ and 2766 Hz, respectively). The solvent system toluene/THF in 1:1 ratio significantly reduced the amplitude of this signal ($w_{1/2} = 155$ Hz), and consistently neat THF gave an even narrower signal ($w_{1/2} = 42$ Hz). Interestingly, when 1 equiv of 18-crown-6 was added to a benzene solution of **1**, the narrowest signal was observed ($w_{1/2} = 14$ Hz).

These experiments suggest that for compound **1** Lewis bases induce dissociation of the interactions observed in the solid state into oligomeric and monomeric solvated species, like those of **i**−**iv** shown in Figure 4. The observation that no further decoalescence of the proton signals occurred in the VT-NMR study could be the result of high fluxionality of the terminal and bridging alkyl ligands as well as changes in their hapticity. A similar situation was observed for several heterobimetallic aluminum-lanthanide compounds such as $\{Yb[AlR_4]_2\}$ (R = Me, Et, ^{t}Bu) and $Nb(AlMe_4)_3$, with terminal and bridging methyl groups, where experimental findings of VT-NMR studies showed only one proton signal for both types of methyl groups.[20]

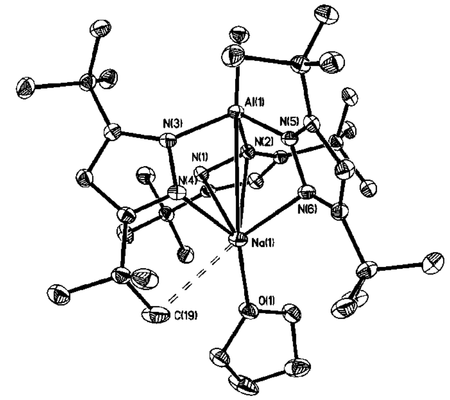

Figure 3. Perspective view of $[Na\{Al(^tBu_2pz)_3Me\}(THF)]$ (**3**) showing thermal ellipsoids at the 50% probability level.

The ^{1}H NMR spectra of **2** and **3** show three singlets assigned to the methine, *tert*-butyl, and Me-Al groups, respectively (6.10, 1.33, and 0.11 ppm for compound **2** and 6.10, 1.32, and 0.58 ppm for compound **3**). Although for these compounds in their crystalline structures each sodium atom is coordinated by a THF molecule, no signals for THF were observed in the NMR spectra. A plausible explanation arises from the fact that complexes **2** and **3** during their isolation were exposed to a dynamic vacuum for long periods of time, favoring the loss of THF. On the other hand, a comparison of the ^{1}H NMR chemical shifts of the methyl groups attached to the aluminum atom in benzene-d_6 of compounds **1**−**3** (−0.34, 0.11 and 0.58 ppm, respectively) reveals a decrease of the carbanionic character of the alkyl group as the number of nitrogen atoms binding the aluminum atom is increased. This is also in agreement with the experimental observation that the reaction to obtain **2** is faster (almost instantaneous) than the reaction to obtain **3**, which requires at least 12 h to complete.[21] The origin of the observed trend in chemical shifts could be ascribed to the higher electron-withdrawing character of the nitrogen atom than the methyl group, which reduces the electron density on the aluminum center and hence stabilizes the Al−C bond.[22]

For comparison, a different approach to obtain **3** was explored. Reaction between the neutral bimetallic aluminum complex $[(\eta^1:\eta^1\text{-}^tBu_2pz)(\mu\text{-}AlMe_2)]_2$[23] with 2 equiv of ^{t}BupzH and ^{t}Bu$_2$pzNa afforded, instead of **3**, complex $[Me_2Al(^tBu_2pz)_2Na(^tBu_2pzH)]$, **4** (eq 1). Complex **4** was isolated as a crystalline solid from the reaction medium after storage in the freezer at −20 °C for 24 h and characterized by IR, microanalysis, and single-crystal X-ray crystallography. The molecular structure (Figure 5) reveals a monomer with the aluminum atom bound to two methyl groups and two pyrazolato ligands in a η^1-fashion. The two ligands are coordinated to the sodium atom in a η^1- and η^3-fashion, respectively. Additionally, the sodium ion bonds to a neutral pyrazolyl ligand and completes its coordination sphere with an Al−Me···Na interaction (Na(1)−C(35) 3.103(2) Å; Na(1)−H(35B) 2.55(2) Å) and a Me···Na interaction of the most proximal methyl of a *tert*-

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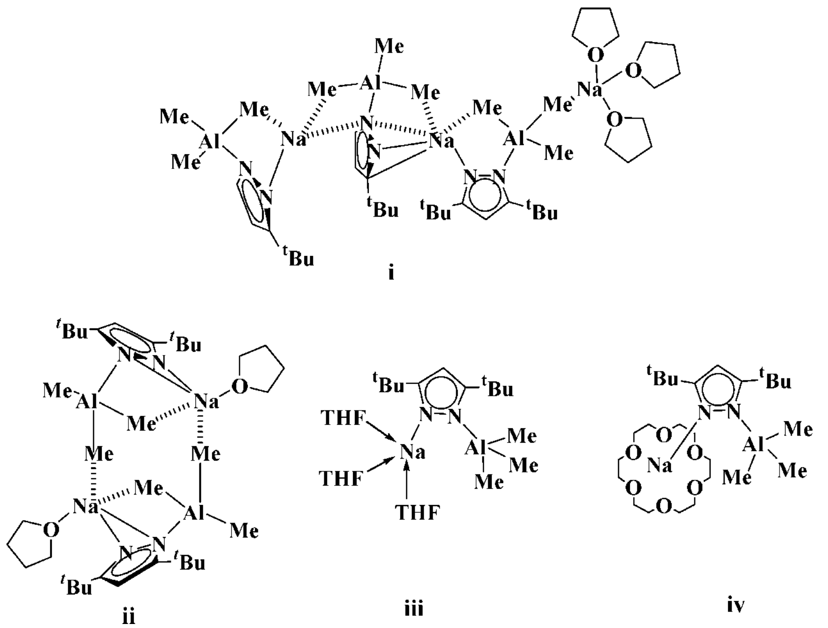
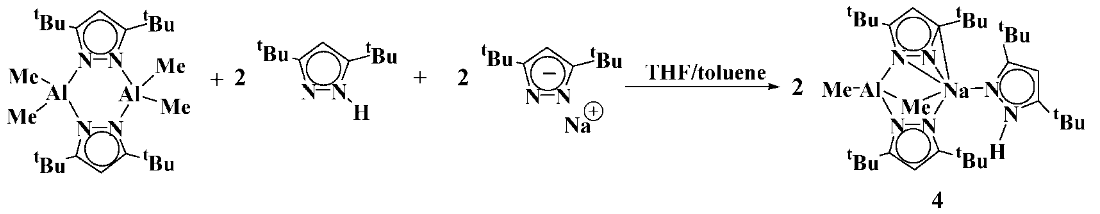


Figure 4. Structures proposed for **1** in solution in the presence of coordinating ligands.



(1)

butyl group (Na(1)−C(33) 3.074(2) Å; Na(1)−H(33B) 2.58(2) Å), although the Na−C distance in the fragment Al−Me···Na is longer than those observed in complexes **1** and **2**. Attempts to characterize **4** by multinuclear NMR spectroscopy in solution of benzene-d_6 at ambient temperature showed formation of unsolvated **3**. Repeated synthesis of **4** under the same conditions was carried out. This resulted in crystals that showed the molecular structure of **4** depicted in Figure 5, but whose multinuclear NMR spectroscopy in solution at ambient temperature was consistent with unsolvated **3**. These results indicate that methane elimination in **4** is favored by the activation of the methyl group bridging the aluminum and sodium atoms, affording unsolvated **3** in solution. Therefore, complex **4** may be considered a reaction intermediate that affords **3** on addition of ^{t}BupzH to **2** (Scheme 2).

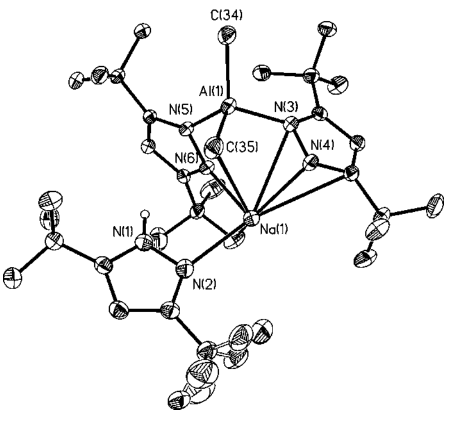


Figure 5. Perspective view of the monomeric structure of [$Me_2Al(^tBu_2pz)_2Na(^tBu_2pzH)$] (**4**) showing thermal ellipsoids at the 50% probability level. Hydrogen atoms (except H1) and toluene have been omitted for clarity.

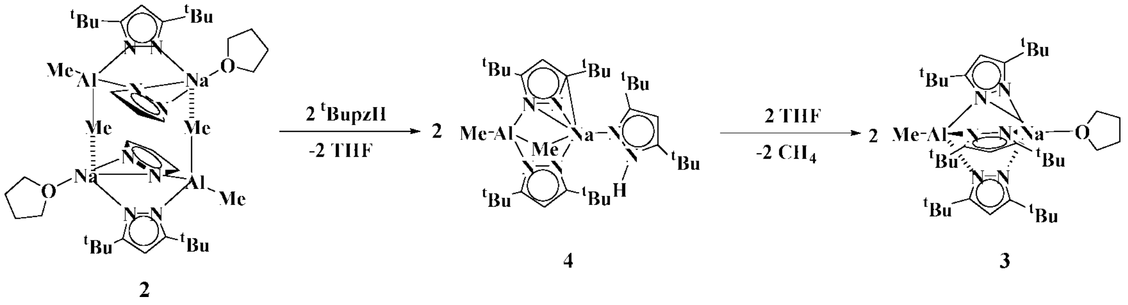
Conclusions

Mono-, bis-, and trispyrazolylaluminates **1**−**3** were prepared in a general reaction scheme from the initial nucleophilic addition of [$Na(^tBu_2pz)$] to $AlMe_3$ and successive sequential addition of 1 and 2 equiv of $^tBu_2pzH$ in THF/toluene solution. An important feature of complexes **1** and **2** is the presence of $Al-CH_3\cdots Na$ interactions, although they were isolated in the presence of the donor solvent THF, which possesses a high affinity for the Na^+ ion. These $Al-CH_3\cdots Na$ interactions also may be an important driving force that allows the formation of **2** and **3** through CH_3 activation. Complex **4** may be considered a reaction intermediate that affords complex **3** from **2** via coordination of $^tBu_2pzH$ to the sodium ion, elimination of THF, subsequent alkane elimination promoted also by CH_3 activation of a bridging methyl group like those observed for **1** and **2**, and last further coordination to aluminum by the pyrazolyl ring attached to sodium (Scheme 2). To the best of our knowledge complex **4** constitutes the first example of the isolation of a reaction intermediate in the synthesis of a ligand analogous to the polypyrazolylborates. Future work will focus on the preparation of other aluminates with different pyrazolyl rings and alkali cations and the exploration of the new ligands for the preparation of novel mixed main group−transition metal complexes.

Experimental Section

General Procedures. All experiments were carried out under Ar using standard Schlenk techniques in conjunction with an inert atmosphere glovebox. THF, toluene, and hexanes were distilled

Scheme 2



from Na/benzophenone and stored under N_2 prior to use. 3,5-Di-*tert*-butylpyrazole,[24] [Na(^{t}Bu$_2$pz)],[9] and $[(\eta^1{:}\eta^1\text{-}{}^t\text{Bu}_2\text{pz})(\mu\text{-Al})\text{Me}_2]_2$[23] were prepared by literature procedures. All other chemicals were purchased from Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury-400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) at ambient probe temperature (292 K). ^{27}Al NMR spectra were obtained on a Varian Gemini-200 MHz spectrometer (52 MHz for ^{27}Al). ^{1}H and ^{13}C NMR chemical shifts were determined by reference to the residual solvent peaks. ^{27}Al NMR chemical shifts are reported versus $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. 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. Crystals of **1**−**4** were mounted directly from solution under argon using an inert oil, which protects them from atmospheric oxygen and moisture. X-ray intensity data were collected using the program SMART[25] on a Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were carried out using the program SAINT; the program SADABS was employed to make incident beam, decay, and absorption corrections in the SAINT-Plus v. 6.0 suite.[26] 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 v. 6.1 suite.[27] Crystals of **2** show one molecule of toluene in a σ crystallographic plane or C_2 proper axis that was refined with restraints to obtained satisfactory anisotropic displacement parameters for the C atoms. In the case of **4**, toluene solvate is located in an inversion center giving two split positions of the ring. Refinement including restraints to obtain satisfactory anisotropic displacement parameters for the C atoms gave an occupancy factor level of 0.463. Additionally, statistical disorder was found for one *tert*-butyl group of the ^{t}Bu$_2$pzH ligand attached to sodium in **4**. Refinement of the two split positions gave an occupancy factor level of 0.691. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model with the exception of the hydrogen atoms that define the $\text{Al}-\text{CH}_3\cdots\text{Na}$ interactions, which were located and refined with isotropic displacment parameters. The final models involved anisotropic displacement parameters for all nonhydrogen atoms. Further details of the structure analyses are given in Table 1.

Sodium (3,5-di-*tert*-butylpyrazolyl)trimethylaluminate, [{Na{Al(^{t}Bu$_2$pz)Me$_3$}}$_3$(THF)$_2$]$_\infty$ (1). Trimethylaluminum (0.09 g, 1.29 mmol) in toluene was added to a solution of [Na(^{t}Bu$_2$pz)] (0.26 g, 1.29 mmol) in THF. The reaction mixture was stirred for 30 min. The solution then was concentrated to 8 mL and placed in a −20 °C freezer for 12 h to afford **1** as colorless crystals (0.35 g, 85%). Isolation of **1** was accomplished by cannula filtration for X-ray crystallography and then dried under dynamic vacuum for further characterization. Mp: 199–203. ^{1}H NMR (benzene-*d*$_6$): δ 6.10 (s, 1H, C*H*), 3.19 (t, 2.66 H, O-C*H*$_2$), 1.38 (s, 18H, C-C*H*$_3$),1.22 (m, 2.6H, O-CH$_2$-C*H*$_2$), −0.33 (s, 9H, Al-C*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): δ 163.49 (s, *C*-^{t}Bu), 99.84 (s, *C*H), 68.91 (s, O-*C*H$_2$), 32.40 (*C*-CH$_3$), 32.21 (s, C-*C*H$_3$), 25.76 (s, O-CH$_2$-*C*H$_2$), −3.48 (Al-*C*H$_3$). ^{27}Al NMR (benzene-*d*$_6$): δ 149.34 ($w_{1/2}$, 5831 Hz). IR (KBr, cm^{-1}): 2964 (s), 1861 (w), 1568 (w), 1512 (w), 1466 (w), 1403 (w), 1364 (w), 1298 (w), 1258 (s), 1196 (m), 1046 (s), 802 (s), 692 (s), 526 (w), 461 (w). Anal. Calcd for $C_{50}H_{100}N_6Al_3Na_3O_2$: C, 62.07; H, 10.44; N, 8.69. Found: C, 61.55; H, 10.30; N, 8.73.

Sodium Bis(3,5-di-*tert*-butylpyrazolyl)dimethylaluminate, [Na{Al(^{t}Bu$_2$pz)$_2$Me$_2$}(THF)]$_2$ (2). To a solution of [Na(^{t}Bu$_2$pz)] (0.25 g, 1.24 mmol) in THF (10 mL) was slowly added trimethylaluminum (0.09 g, 1.24 mmol) in toluene (20 mL) at room temperature. The reaction mixture was stirred for 30 min. Then ^{t}Bu$_2$pzH (0.22 g, 1.24 mmol) in toluene (10 mL) was added dropwise, and the reaction mixture was stirred for 3 h. The solution was concentrated to 8 mL and placed in a −20 °C freezer for 24 h to afford **2** as colorless crystals (0.51 g, 81%). Isolation of **2** was accomplished by cannula filtration for X-ray crystallography and then dried under dynamic vacuum for further characterization. Mp: 135–137 °C. ^{1}H NMR (benzene-*d*$_6$): δ 6.10 (s, 2H, C*H*), 3.20 (t, 4H, O-C*H*$_2$), 1.33 (s, 36H, C-C*H*$_3$),1.16 (m, 4H, O-CH$_2$-C*H*$_2$), 0.11 (s, 6H, Al-C*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): δ 162.86 (s, *C*-^{t}Bu), 99.37 (s, *C*H), 68.76 (s, O-*C*H$_2$), 32.65 (*C*-CH$_3$), 32.00 (s, C-*C*H$_3$), 25.75 (s, O-CH$_2$-*C*H$_2$), −1.23 (br, Al-*C*H$_3$). ^{27}Al NMR (benzene-*d*$_6$): δ 136.12 ($w_{1/2}$, 2723 Hz). IR (KBr, cm^{-1}): 2963 (s), 2872 (m), 1568 (w), 1527 (w), 1463 (m), 1409 (w), 1362 (m), 1319 (w), 1252 (m), 1202 (m), 1152 (w), 1068 (m), 999 (w), 800 (m), 675 (m), 580 (w), 513 (w), 469 (w). Anal. Calcd for $C_{28}H_{52}N_4AlNaO$: C, 65.83; H, 10.28; N, 10.97. Found: 65.25; H, 10.11; N, 12.88.

Sodium Methyl Tris(3,5-di-*tert*-butylpyrazolyl)aluminate, [Na{Al(^{t}Bu$_2$pz)$_3$Me}(THF)] (3). This compound was prepared and purified in a similar manner to that describeded for complex **2**, using [Na(^{t}Bu$_2$pz)] (0.25 g, 1.24 mmol) in THF (10 mL), trimethylaluminum (0.09 g, 1.24 mmol) in toluene (10 mL), and 3,5-di-*tert*-butylpyrazole (0.446 g, 2.48 mmol) in toluene (10 mL). Yield: 0.60 g (80%). Mp: 184–188 °C. ^{1}H NMR (benzene-*d*$_6$): δ 6.10 (s, 3H, C*H*), 1.32 (s, 54H, C-C*H*$_3$), 0.58 (s, 3H, Al-C*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): δ 163.40 (s, *C*-^{t}Bu), 99.78 (s, *C*H), 32.57 (*C*-CH$_3$), 31.82 (s, C- *C*H$_3$), 1.76 (br, Al- *C*H$_3$). ^{27}Al NMR (benzene-*d*$_6$): δ 115.47 ($w_{1/2}$, 2354 Hz). IR (KBr, cm^{-1}): 2962 (s), 2865 (m), 1568 (w), 1524 (m), 1464 (m), 1361 (m), 1313 (m), 1251 (m), 1199 (m), 1080 (s), 1047 (w), 1003 (w), 791 (m), 724 (w), 679 (s), 639 (w), 536 (w), 477 (m). Anal. Calcd for $C_{34}H_{60}N_6AlNa$: C, 67.72; H, 10.05; N, 13.94. Found: 67.33; H, 10.21; N, 13.87.

Sodium Bis(3,5-di-*tert*-butylpyrazolyl)dimethylaluminate (3,5-di-*tert*-butylpyrazole), [Me$_2$Al(^{t}Bu$_2$pz)$_2$Na(^{t}Bu$_2$pzH)] (4). A Schlenk flask was charged with $[(\eta^1,\eta^1\text{-3,5-}{}^t\text{Bu}_2\text{pz})(\mu\text{-AlMe}_2)]_2$ (0.3 g, 0.63

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mmol), ^{t}Bu$_2$pzH (0.23 g, 1.26 mmol), [Na(3,5- ^{t}Bu$_2$pz)] (0.26 g, 1.26 mmol), and THF (20 mL). The reaction mixture was stirred for 4 h at ambient temperature, concentrated to 8 mL, and placed in a −20 °C freezer for 24 h to afford **4** as a crystalline colorless solid, which was isolated by cannula filtration for X-ray crystallography. The crystalline solid was exposed to dynamic vacuum for several hours to performe further characterization; multinuclear NMR spectroscopy in benzene-d_6 solution at ambient temperature showed that **4** had been transformed to **3**. IR (KBr, cm^{-1}): 3237 (m), 2963 (s), 2708 (w), 1567 (m), 1519 (m), 1464 (m), 1363 (m), 1313 (w), 1253. (m), 1206 (m), 1157 (w), 1066 (m), 1001 (w), 894 (w), 796 (m), 675 (s), 579 (m), 468 (m). Anal. Calcd for $C_{35}H_{64}N_6AlNa$: C, 67.90; H, 10.44; N, 13.58. Found: C, 67.58; H, 10.34; N, 13.43.

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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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