

Poly(pyrazolyl)aluminate Complexes Containing Aluminum–Hydrogen Bonds

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S Supporting Information

ABSTRACT: The treatment of LiAlH_4 with 2, 3, or 4 equiv of the 3,5-disubstituted pyrazoles Ph_2pzH or $i\text{Pr}_2\text{pzH}$ afforded $[\text{Li}(\text{THF})_2][\text{AlH}_2(\text{Ph}_2\text{pz})_2]$ (97%), $[\text{Li}(\text{THF})][\text{AlH}(\text{Ph}_2\text{pz})_3]$ (96%), $[\text{Li}(\text{THF})_4][\text{Al}(\text{Ph}_2\text{pz})_4]$ (95%), and $[\text{Li}(\text{THF})][\text{AlH}(i\text{Pr}_2\text{pz})_3]$ (89%). The treatment of ZnCl_2 with $[\text{Li}(\text{THF})][\text{AlH}(\text{Ph}_2\text{pz})_3]$ afforded $\text{Zn}(\text{AlH}(\text{Ph}_2\text{pz})_3)\text{H}$ (70%). X-ray crystal structures of these complexes demonstrated κ^2 or κ^3 coordination of the aluminum-based ligands to the Li or Zn ions. The treatment of $[\text{Li}(\text{THF})][\text{AlH}(\text{Ph}_2\text{pz})_3]$ with MgBr_2 or CoCl_2 in THF/ Et_2O solutions, by contrast, afforded the pyrazolate transfer products $\text{Mg}_2\text{Br}_2(\text{Ph}_2\text{pz})_2(\text{THF})_3 \cdot 2\text{THF}$ (25%) and $\text{Co}_2\text{Cl}_2(\text{Ph}_2\text{pz})_2(\text{THF})_3 \cdot \text{THF}$ (23%) as colorless and blue crystalline solids, respectively. An analogous treatment of $[\text{Li}(\text{THF})][\text{AlH}(\text{Ph}_2\text{pz})_3]$ with MCl_2 ($\text{M} = \text{Mn, Fe, Ni, Cu}$) afforded metal powders and H_2 , illustrating hydride transfer from Al to M as a competing reaction path.

Poly(pyrazolyl)borate ligands of the formula $\text{B}(\text{pz})_n\text{H}_{4-n}^-$ ($\text{pz} = \text{C}_3\text{H}_3\text{N}_2$; Bp, $n = 2$; Tp, $n = 3$) are very common.¹ In spite of the widespread use of Bp and Tp ligands and C-substituted versions thereof, there has been little development of the heavier group 13 analogues.² An early report described the synthesis of $\text{Na}[\text{AlMe}_2\text{pz}_2]$ and $\text{Na}[\text{Alpz}_4]$, but no characterization was given for $\text{Na}[\text{AlMe}_2\text{pz}_2]$; the only data for $\text{Na}[\text{Alpz}_4]$ was an aluminum microanalysis, and attempts to prepare transition-metal derivatives containing these new aluminum-based ligands were unsuccessful.³ Since this initial report, crystallographically characterized aluminum derivatives have been limited to $\text{Na}[\text{AlMe}_2(\text{Me}_2\text{pz})_2]$ ($\text{Me}_2\text{pz} = 3,5\text{-dimethylpyrazolyl}$),^{4a} $\{[\text{Na}(\text{THF})][\text{AlMe}_2(\text{tBu}_2\text{pz})_2]\}_2$ ($\text{tBu}_2\text{pz} = 3,5\text{-di-tert-butylpyrazolyl}$),^{4b} and $[\text{Na}(\text{THF})][\text{AlMe}(\text{tBu}_2\text{pz})_3]$.^{4b} $\text{Na}[\text{AlMe}_2(\text{Me}_2\text{pz})_2]$ contains a complex ligand coordination mode that does not resemble the common $\kappa^3\text{-N,N,H}$ mode typically observed for Bp complexes;^{4a} the N atoms in $\{[\text{Na}(\text{THF})][\text{AlMe}_2(\text{tBu}_2\text{pz})_2]\}_2$ engage in a $\kappa^3\text{-N,N,N}$ coordination mode that involves a κ^1 interaction between the Na ion and one pyrazolyl group and a κ^2 interaction with the other pyrazolyl group,^{4b} and $[\text{Na}(\text{THF})][\text{AlMe}(\text{tBu}_2\text{pz})_3]$ contains κ^4 bonding between the Na ion and the N atoms that entails κ^1 interactions with two pyrazolyl groups and a κ^2 interaction with the third pyrazolyl group.^{4b} Synthetic routes to gallium analogues are more numerous and include metal complexes containing the $\text{GaMe}_2(\text{pz})_2^-$ and $\text{GaMe}(\text{pz})_3^-$ ligands.^{2,3,5} Notably, the heavier analogues of Bp and Tp ligands reported to date

have only included methyl groups on the group 13 metal, apparently to avoid the high reactivity of the Al–H or Ga–H bond. Supporting this contention, the synthesis of $\text{Na}[\text{GaH}_2(\text{pz})_2]$ was claimed upon the treatment of $\text{GaH}_3(\text{NMe}_3)$ with Napz and pzH, but it was noted that the treatment of $\text{Na}[\text{GaH}_2(\text{pz})_2]$ with nickel or copper salts led to the evolution of H_2 and no complexes could be isolated.³ We have recently reported the atomic layer deposition of MB_2O_4 ($\text{M} = \text{Ca, Sr, Ba}$) films from CaTp_2 , SrTp_2 , and $\text{Ba}(\text{Tp}^{\text{Et}_2})_2$ [$\text{Tp}^{\text{Et}_2} = \text{hydrotris}(3,5\text{-diethylpyrazolyl})\text{borate}$] and water and obtained precise 2:1 B/M ratios in the films.⁶ We have also recently reported potassium complexes containing energetic dihydrobis(tetrazolyl)borate ligands.⁷

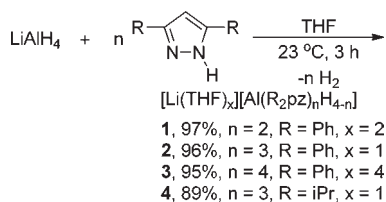
In view of the small number of poly(pyrazolyl)aluminate complexes reported to date,^{2–4} the lack of derivatives containing Al–H bonds, the potential use of complexes containing these ligands as film growth precursors to metal aluminate films with controlled M/Al ratios, and the relationship of poly(pyrazolyl)aluminates to so far unknown potentially highly energetic poly(tetrazolyl)aluminates, we sought to explore the preparation of ligands of the formula $\text{AlH}_n(\text{R}_2\text{pz})_{4-n}^-$ ($\text{R}_2\text{pz} = 3,5\text{-disubstituted pyrazolyl}$). Herein, we report the synthesis, structure, and properties of lithium complexes containing $\text{AlH}_2(\text{Ph}_2\text{pz})_2^-$, $\text{AlH}(\text{Ph}_2\text{pz})_3^-$, $\text{AlH}(i\text{Pr}_2\text{pz})_3^-$, and $\text{Al}(\text{Ph}_2\text{pz})_4^-$ ligands. The $\text{AlH}_2(\text{Ph}_2\text{pz})_2^-$ and $\text{AlH}(\text{R}_2\text{pz})_3^-$ ligands exhibit κ^2 - and κ^3 -coordination modes to the Li ion, in analogy to common bonding motifs of Bp and Tp ligands to metal ions.¹ The complex $\text{Zn}(\text{AlH}(\text{Ph}_2\text{pz})_3)\text{H}$ has been prepared by a salt metathesis route from ZnCl_2 and contains a $\kappa^3\text{-AlH}(\text{Ph}_2\text{pz})_3^-$ ligand bonded to the Zn ion. Attempted salt metathesis reactions with other metal halides leads to pyrazolate or hydride transfer.

The treatment of LiAlH_4 solutions in tetrahydrofuran (THF) with 2, 3, or 4 equiv of Ph_2pzH at ambient temperature led to $[\text{Li}(\text{THF})_2][\text{AlH}_2(\text{Ph}_2\text{pz})_2]$ (**1**, 97%), $[\text{Li}(\text{THF})][\text{AlH}(\text{Ph}_2\text{pz})_3]$ (**2**, 96%), and $[\text{Li}(\text{THF})_4][\text{Al}(\text{Ph}_2\text{pz})_4]$ (**3**, 95%) as colorless crystalline solids (Scheme 1).⁸ A similar treatment of LiAlH_4 with 3 equiv of $i\text{Pr}_2\text{pzH}$ afforded $[\text{Li}(\text{THF})][\text{AlH}(i\text{Pr}_2\text{pz})_3]$ (**4**, 89%) as colorless crystals (Scheme 1).⁸ Complexes **1–4** were characterized by spectral and analytical techniques and by X-ray crystal structure determinations. The IR spectra showed Al–H stretches for **1**, **2**, and **4** at 1826, 1934 and 1869 cm^{-1} , respectively. The ¹H NMR spectra of **1–4** showed resonances consistent with Ph_2pz or $i\text{Pr}_2\text{pz}$ groups and THF ligands. In addition, **1**, **2**, and **4** exhibited broad resonances at δ 5.04, 4.66, and 5.55 for the Al-bound H atoms. Analytically pure crystals of **1** showed a 50:50 mixture of **1** and **2** in the ¹H and ¹³C{¹H} NMR spectra at 23 °C

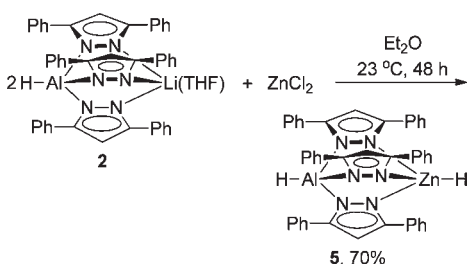
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Scheme 1. Synthesis of 1–4



Scheme 2. Synthesis of 5 from 2

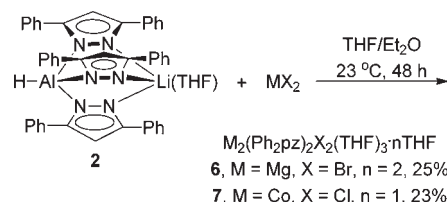


in benzene- d_6 , and variable-temperature ^1H NMR spectra taken at -80 and $+80$ $^\circ\text{C}$ in toluene- d_8 also showed $\sim 50:50$ mixtures of **1** and **2**. Complex **1** may exist in equilibrium with **2** and another pyrazolyl species in solution. A pyrazolyl 4-CH resonance for a possible third species was observed at δ 6.86 in the ^1H NMR spectrum in benzene- d_6 , at 23 $^\circ\text{C}$, but the other resonances for this species were of too low intensity to provide further insight. We have recently reported that $\text{CaBp}_2(\text{THF})_2$ decomposes to CaTp_2 and $\text{CaTp}(\text{BH}_4)$ upon thermolysis at 190 $^\circ\text{C}$.⁹ The weaker bond energies in **1**, relative to $\text{CaBp}_2(\text{THF})_2$, apparently allow a similar process to occur at 23 $^\circ\text{C}$. Additionally, the NMR spectra of **1**, **2**, and **4** recorded at 23 $^\circ\text{C}$ in benzene- d_6 showed only one type of pyrazolyl carbon substituent, demonstrating that there is rapid exchange between the 3- and 5-substituent sites on the NMR time scale. A similar pyrazolate site exchange process was observed in $[\text{Na}(\text{THF})][\text{AlMe}(\text{tBu}_2\text{pz})_3]$.^{4b} ^1H NMR spectra of **2** and **4** in toluene- d_8 at -80 $^\circ\text{C}$ showed two types of pyrazolyl carbon group resonances, confirming that the exchange processes are slow at these temperatures.

The reactivity of **2** toward metal(II) halides was investigated to establish the relationship of hydrotris(pyrazolyl)aluminate ligands to analogous Tp systems. The treatment of ZnCl_2 with **2** in diethyl ether afforded $\text{Zn}(\text{AlH}(\text{Ph}_2\text{Pz})_3)\text{H}$ (**5**, 70%) as colorless crystals upon workup (Scheme 2).⁸ Complex **5** was identified from spectral and analytical data and by X-ray crystallography. The IR spectrum of **5** showed an Al–H stretch at 1963 cm^{-1} and a Zn–H stretch at 1842 cm^{-1} . The ^1H NMR spectrum of **5** contained a sharp Zn–H resonance at δ 4.72 and a very broad Al–H signal at δ 4.40. While the solubility of **5** was too low in benzene- d_6 and other unreactive solvents to permit collection of a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the ^1H NMR spectrum in benzene- d_6 suggested two different types of phenyl groups.

In contrast to the formation of **5**, the treatment of **2** with MgBr_2 or CoCl_2 in THF/ Et_2O solutions afforded $\text{Mg}_2\text{Br}_2(\text{Ph}_2\text{pz})_2(\text{THF})_3 \cdot 2\text{THF}$ (**6**, 25%) and $\text{Co}_2\text{Cl}_2(\text{Ph}_2\text{pz})_2(\text{THF})_3 \cdot \text{THF}$ (**7**, 23%) as colorless and blue crystalline solids, respectively (Scheme 3).⁸ Complexes **6** and **7** were identified from spectral and analytical data and by X-ray crystallography. The IR spectra of **6** and **7** lacked Al–H stretches, suggesting that

Scheme 3. Synthesis of 6 and 7 from 2



pyrazolate transfer to the metal centers occurred. The ^1H NMR of **6** contained resonances from the Ph_2pz and THF ligands, but no resonances from the Al–H or Mg–H bond were observed. The treatment of **2** with other MCl_2 ($\text{M} = \text{Mn}$, Fe , Ni , Cu) at ambient temperature in THF led to gas evolution over 0.5 h and the formation of insoluble silver-black ($\text{M} = \text{Mn}$, Fe , Ni) or copper-colored ($\text{M} = \text{Cu}$) powders, which are presumably the metals.

Perspective views of **2**, **5**, and **6** are shown in Figure 1. Complexes **2** and **5** contain $\kappa^3\text{-N,N,N-AlH}(\text{Ph}_2\text{pz})_3$ ligands, with Li–N distances of 2.061(2), 2.072(2), and 2.137(3) \AA and Zn–N distances of 2.042(4), 2.061(4), and 2.112(4) \AA , respectively. The Al–N distances in **2** and **5** fall between 1.88 and 1.91 \AA . The N–Al–N and N–Li–N angles in **2** lie between $100.49(5)$ and $110.58(5)^\circ$ [$\text{avg} = 105(5)^\circ$] and between $95.03(10)$ and $101.68(10)^\circ$ [$\text{avg} = 99(3)^\circ$] and are slightly smaller than the 109.5° value expected for tetrahedral geometry, probably because of the tight chelate. The related values of **5** [N–Al–N, $101.7(3)$ – $109.9(4)^\circ$, $\text{avg} = 106(4)^\circ$; N–Zn–N, $90.07(13)$ – $97.85(14)^\circ$, $\text{avg} = 94(4)^\circ$] are similar to those of **2**. Complex **6** exists as a dimer that is held together by bridging Ph_2pz and THF ligands. Each Mg ion is also bonded to one Br and one THF ligand, and the molecule crystallizes with two THF solvates in the lattice. The Mg–N distances range from 2.098(2) to 2.108(2) \AA , the Mg–Br bond lengths are 2.478(1) and 2.482(1) \AA , and the Mg–O distances are 2.268(2) and 2.285(2) \AA and 2.050(2) and 2.052(2) \AA for the bridging and terminal THF ligands, respectively. The X-ray crystal structures of **1**, **3**, **4**, and **7** are not described in detail herein but are contained in the Supporting Information.

The aluminum analogues **1**–**4** of the well-known Bp, Tp, and Bpz_4^- ligands are easily prepared upon the treatment of LiAlH_4 with the appropriate stoichiometry of a pyrazole. The coordination modes of the $\text{AlH}(\text{R}_2\text{pz})_{4-n}^-$ ligands in **1**–**4** are analogous to the common bonding motifs of the Bp and Tp ligands.¹ Complex **5** is obtained upon the treatment of **2** with ZnCl_2 , which demonstrates that the $\text{AlH}(\text{Ph}_2\text{pz})_3^-$ ligand can be transferred from Li to Zn by a standard salt metathesis reaction. However, this reaction is more complex because the second chloride ion is also replaced by a hydride to afford **5**. Hence, hydride transfer from aluminum to metal with **1**, **2**, and **4** in salt metathesis reactions is a potential complication that is generally absent with the Bp and Tp ligands.¹ The zinc hydrides $\text{ZnHTp}^{\text{tBu}}$ [$\text{Tp}^{\text{tBu}} = \text{hydrotris}(3\text{-tert-butylpyrazolyl})\text{borate}$]^{10a} and $\text{ZnHTp}^{\text{p-Tol,Me}}$ [$\text{Tp}^{\text{p-Tol,Me}} = \text{hydrotris}[3\text{-(4-tolyl)-5-methylpyrazolyl}]\text{borate}$]^{10b} were prepared upon the treatment of ZnH_2 with TTP^{tBu} and $\text{ZnFTp}^{\text{p-Tol,Me}}$, respectively, and, like **5**, have distorted tetrahedral geometries about the Zn ion. The treatment of **2** with MgCl_2 and CoCl_2 afforded the pyrazolate complexes **6** and **7**. This reaction path may be driven by the formation of crystalline **6** and **7** and is consistent with previous reports of pyrazolate transfer from boron to metals upon the treatment of KBp and KTp with metal halides.¹¹ Many metal(II) chlorides

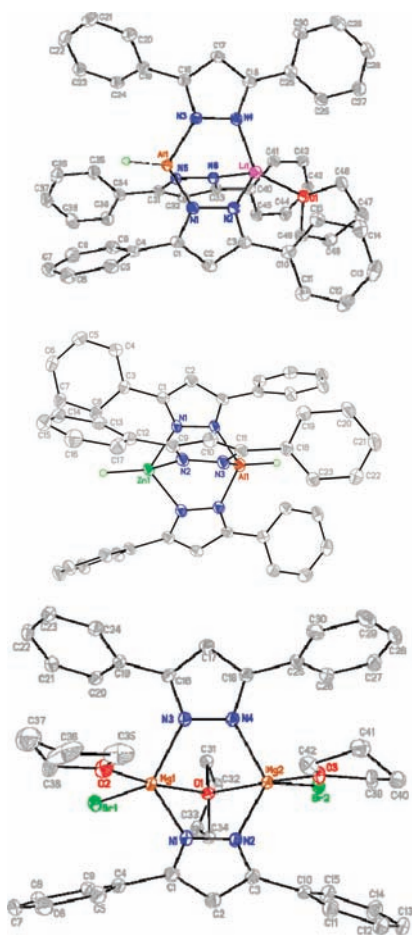


Figure 1. Perspective views of **2**, **5**, and **6** with selected bond lengths (Å) and angles (deg): (top) **2**, Al–N1 1.884(1), Al–N3 1.899(1), Al–N5 1.893(1), Li–N2 2.072(2), Li–N4 2.061(2), Li–N6 2.137(3), Li–O1 1.967(2), Al–H 1.46(1); N1–Al–N3 110.58(5), N1–Al–N5 100.49(5), N3–Al–N5 104.53(5), N2–Li–N4 98.8(1), N2–Li–N6 101.7(1), N4–Li–N6 95.0(1); (middle) **5**, Al–N1' 1.897(8), Al–N2' 1.892(9), Al–N3 1.907(9), Zn–N1 2.112(4), Zn–N2 2.042(4), Zn–N3' 2.061(4); N1'–Al–N2' 101.7(3), N1'–Al–N3 106.6(4), N2'–Al–N3 109.0(4), N1–Zn–N2 90.1(1), N1–Zn–N3' 93.9(1), N2–Zn–N3' 97.8(1); (bottom) **6**, Mg1–Br1 2.478(1), Mg2–Br2 2.482(1), Mg1–N1 2.098(2), Mg1–N3 2.108(2), Mg2–N2 2.104(2), Mg2–N4 2.105(2), Mg1–O1 2.268(2), Mg1–O2 2.050(2), Mg2–O1 2.285(2), Mg2–O3 2.052(2).

exhibited vigorous gas evolution upon the treatment with **2** and concomitant formation of metallic precipitates. This behavior is consistent with hydrogen transfer from aluminum to metal, followed by H₂ reductive elimination and the formation of metal powders, and is similar to Storr's observations upon the attempted synthesis of nickel and copper complexes containing GaH₂(pz)₂[−] ligands.³ Pathways that lead to hydride and pyrazolate transfer with **2** presumably also afford the neutral species Al(Ph₂p_z)₃ and [AlH(Ph₂p_z)₂]_m but examples of these complexes have not been crystallized in pure form so far. However, Al(tBu₂p_z)₃¹² and Al hydride pyrazolates¹³ have been reported. The present work also implies that analogues of **1–4** containing 1,2,4-triazolyl and tetrazolyl groups should be easily prepared by protonolysis routes between LiAlH₄ and the hydrogen-substituted heterocycles because some of the corresponding B ligands are known.^{1,7,14} Al-based ligands containing 1,2,4-triazolyl and

tetrazolyl groups would have high nitrogen contents, should be highly endothermic, and would thus be relevant to ongoing efforts to construct energetic metal salts for a variety of applications.¹⁵

ASSOCIATED CONTENT

S Supporting Information. Synthetic procedures and analytical and spectroscopic data for **1–7** and X-ray crystallographic data for **1–7** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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