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Poly(pyrazolyl)aluminate Complexes Containing Aluminum−Hydrogen Bonds

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Supporting Information

ABSTRACT: The treatment of $LiAlH_4$ with 2, 3, or 4 equiv of the 3,5-disubstituted pyrazoles Ph_2pzH or iPr_2pzH afforded $[Li(THF)_2][AlH_2(Ph_2pz)_2]$ (97%), $[Li(THF)][AlH(Ph_2pz)_3]$ (96%), $[Li(THF)_4][Al(Ph_2pz)_4]$ (95%), and $[Li(THF)][AlH(iPr_2pz)_3]$ (89%). The treatment of $ZnCl_2$ with $[Li(THF)][AlH(Ph_2pz)_3]$ afforded $Zn(AlH(Ph_2Pz)_3)H$ (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 $[Li(THF)][AlH(Ph_2pz)_3]$ with $MgBr_2$ or $CoCl_2$ in THF/Et_2O solutions, by contrast, afforded the pyrazolate transfer products $Mg_2Br_2(Ph_2pz)_2(THF)_3 \cdot 2THF$ (25%) and $Co_2Cl_2(Ph_2pz)_2(THF)_3 \cdot THF$ (23%) as colorless and blue crystalline solids, respectively. An analogous treatment of $[Li(THF)][AlH(Ph_2pz)_3]$ with MCl_2 (M = 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 $B(pz)_nH_{4-n}^-$ (pz = $C_3H_3N_2$; 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 $Na[AlMe_2pz_2]$ and $Na[Alpz_4]$, but no characterization was given for $Na[AlMe_2pz_2]$; the only data for $Na[Alpz_4]$ 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 $Na[AlMe_2(Me_2pz)_2]$ (Me_2pz = 3,5-dimethylpyrazolyl),[4a] $\{[Na(THF)][AlMe_2(tBu_2pz)_2]\}_2$ (tBu_2pz = 3,5-di-*tert*-butylpyrazolyl),[4b] and $[Na(THF)][AlMe(tBu_2pz)_3]$.[4b] $Na[AlMe_2(Me_2pz)_2]$ contains a complex ligand coordination mode that does not resemble the common κ^3-N,N,H mode typically observed for Bp complexes;[4a] the N atoms in $\{[Na(THF)][AlMe_2(tBu_2\text{-}pz)_2]\}_2$ engage in a κ^3-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 $[Na(THF)][AlMe(tBu_2pz)_3]$ 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 $GaMe_2(pz)_2^-$ and $GaMe(pz)_3^-$ 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 $Na[GaH_2(pz)_2]$ was claimed upon the treatment of $GaH_3(NMe_3)$ with Napz and pzH, but it was noted that the treatment of $Na[GaH_2(pz)_2]$ 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 (M = Ca, Sr, Ba) films from $CaTp_2$, $SrTp_2$, and $Ba(Tp^{Et2})_2$ [Tp^{Et2} = hydrotris(3,5-diethylpyrazolyl)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 $AlH_n(R_2pz)_{4-n}^-$ (R_2pz = 3,5-disubstituted pyrazolyl). Herein, we report the synthesis, structure, and properties of lithium complexes containing $AlH_2(Ph_2pz)_2^-$, $AlH(Ph_2pz)_3^-$, $AlH(iPr_2pz)_3^-$, and $Al(Ph_2pz)_4^-$ ligands. The $AlH_2(Ph_2pz)_2^-$ and $AlH(R_2pz)_3^-$ 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 $Zn(AlH(Ph_2pz)_3)H$ has been prepared by a salt metathesis route from $ZnCl_2$ and contains a κ^3-$AlH(Ph_2pz)_3^-$ 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 $[Li(THF)_2][AlH_2(Ph_2pz)_2]$ (**1**, 97%), $[Li(THF)][AlH(Ph_2pz)_3]$ (**2**, 96%), and $[Li(THF)_4][Al(Ph_2pz)_4]$ (**3**, 95%) as colorless crystalline solids (Scheme 1).[8] A similar treatment of $LiAlH_4$ with 3 equiv of iPr_2pzH afforded $[Li(THF)][AlH(iPr_2pz)_3]$ (**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 iPr_2pz 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 $^{13}C\{^1H\}$ NMR spectra at 23 °C

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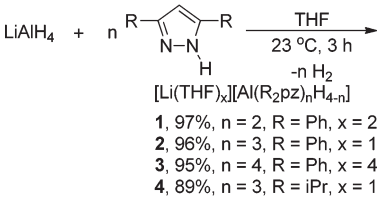
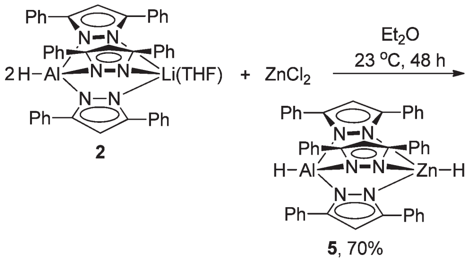
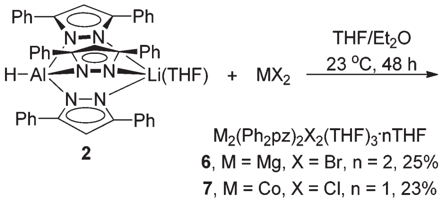
Scheme 1. Synthesis of 1−4



Scheme 2. Synthesis of 5 from 2



Scheme 3. Synthesis of 6 and 7 from 2



in benzene-d_6, and variable-temperature ^{1}H NMR spectra taken at −80 and +80 °C in toluene-d_8 also showed ~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 ^{1}H NMR spectrum in benzene-d_6, at 23 °C, but the other resonances for this species were of too low intensity to provide further insight. We have recently reported that $CaBp_2(THF)_2$ decomposes to $CaTp_2$ and $CaTp(BH_4)$ upon thermolysis at 190 °C.[9] The weaker bond energies in **1**, relative to $CaBp_2(THF)_2$, apparently allow a similar process to occur at 23 °C. Additionally, the NMR spectra of **1**, **2**, and **4** recorded at 23 °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 $[Na(THF)][AlMe(tBu_2pz)_3]$.[4b] ^{1}H NMR spectra of **2** and **4** in toluene-d_8 at −80 °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 $Zn(AlH(Ph_2Pz)_3)H$ (**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 ^{1}H 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 $^{13}C\{^1H\}$ NMR spectrum, the ^{1}H 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$_2$O solutions afforded $Mg_2Br_2(Ph_2pz)_2(THF)_3 \cdot 2THF$ (**6**, 25%) and $Co_2Cl_2(Ph_2pz)_2(THF)_3 \cdot THF$ (**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 pyrazolate transfer to the metal centers occurred. The ^{1}H NMR of **6** contained resonances from the Ph$_2$pz and THF ligands, but no resonances from the Al−H or Mg−H bond were observed. The treatment of **2** with other MCl_2 (M = Mn, Fe, Ni, Cu) at ambient temperature in THF led to gas evolution over 0.5 h and the formation of insoluble silver-black (M = Mn, Fe, Ni) or copper-colored (M = Cu) powders, which are presumably the metals.

Perspective views of **2**, **5**, and **6** are shown in Figure 1. Complexes **2** and **5** contain κ^3-*N*,*N*,*N*-$AlH(Ph_2pz)_3$ ligands, with Li−N distances of 2.061(2), 2.072(2), and 2.137(3) Å and Zn−N distances of 2.042(4), 2.061(4), and 2.112(4) Å, respectively. The Al−N distances in **2** and **5** fall between 1.88 and 1.91 Å. The N−Al−N and N−Li−N angles in **2** lie between 100.49(5) and 110.58(5)° [avg = 105(5)°] and between 95.03(10) and 101.68(10)° [avg = 99(3)°] 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)°, avg = 106(4)°; N−Zn−N, 90.07(13)−97.85(14)°, avg = 94(4)°] are similar to those of **2**. Complex **6** exists as a dimer that is held together by bridging Ph$_2$pz 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) Å, the Mg−Br bond lengths are 2.478(1) and 2.482(1) Å, and the Mg−O distances are 2.268(2) and 2.285(2) Å and 2.050(2) and 2.052(2) Å 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 $AlH(R_2pz)_{4-n}^-$ 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 $AlH(Ph_2pz)_3^-$ 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 $ZnHTp^{tBu}$ [Tp^{tBu} = hydrotris(3-*tert*-butylpyrazolyl)borate][10a] and $ZnHTp^{p\text{-}Tol,Me}$ [$Tp^{p\text{-}Tol,Me}$ = hydrotris[3-(4-tolyl)-5-methylpyrazolyl]borate][10b] were prepared upon the treatment of ZnH_2 with $TlTp^{tBu}$ and $ZnFTp^{p\text{-}Tol,Me}$, 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

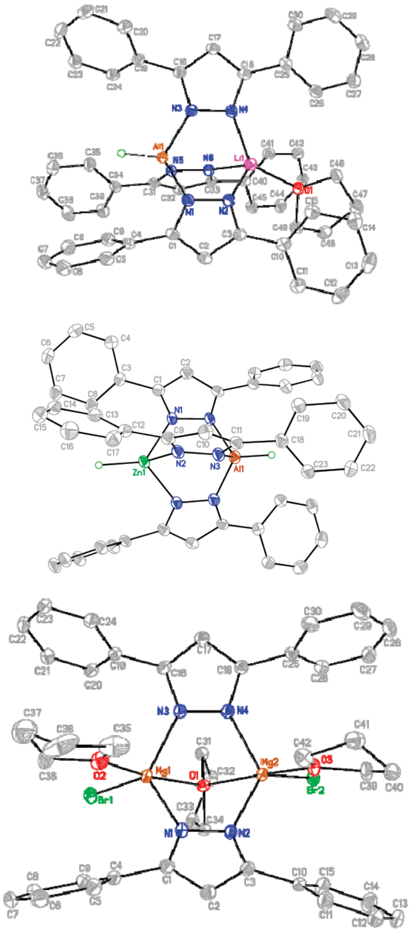


Figure 1. Perspective views of **2**, **5**, and **6** with selected bond lengths (Å) and angles (deg): (top) **2**, Al−N1 1.884(1), Al−N3 1.899(1), Al−N5 1.893(1), Li−N2 2.072(2), Li−N4 2.061(2), Li−N6 2.137(3), Li−O1 1.967(2), Al−H 1.46(1); N1−Al−N3 110.58(5), N1−Al−N5 100.49(5), N3−Al−N5 104.53(5), 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 H_2 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 $GaH_2(pz)_2^-$ ligands.[3] Pathways that lead to hydride and pyrazolate transfer with **2** presumably also afford the neutral species $Al(Ph_2pz)_3$ and $[AlH(Ph_2pz)_2]_n$, but examples of these complexes have not been crystallized in pure form so far. However, $Al(tBu_2pz)_3$[12] and Al hydride pyrazolates[13] 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 $LiAlH_4$ 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

Ⓢ 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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