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Syntheses of Aluminum and Zinc Alkyl Complexes of a Highly Fluorinated Tris(pyrazolyl)borate Using [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(THF) as the Ligand Transfer Agent

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Dimethylaluminum or ethylzinc complexes of highly fluorinated tris(pyrazolyl)borate ligand [HB(3,5-$(CF_3)_2$Pz)$_3$]$^-$ can be obtained in excellent yield from the reaction between the silver adduct [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(THF) and the metal alkyl reagent Me_3Al or Et_2Zn. The X-ray crystal structure of [HB(3,5-$(CF_3)_2$Pz)$_3$]$AlMe_2$ shows that the tris(pyrazolyl)borate ligand coordinates to the aluminum center in κ^2-fashion. [HB(3,5-$(CF_3)_2$Pz)$_3$]ZnEt features the typical κ^3-bonded ligand.

The chemistry of metal complexes containing fluorinated ligands like [HB(3,5-$(CF_3)_2$Pz)$_3$]$^-$ is of current interest.[1,2] Such highly fluorinated ligands endow exceptional thermal and/or air stability on the complexes. For example, some of the interesting complexes of silver(I) that have been isolated using fluorinated tris(pyrazolyl)borate ligands include [HB(3,5-$(CF_3)_2$Pz)$_3$]AgL where L = CO,[3] $CH_2{=}CH_2$,[4] HC≡CH,[4] ethylene oxide,[5] NNNAd,[6] NNC$(CO_2Me)_2$.[7] Most of these molecules represent the only structurally characterized compounds of the type YAgL (where Y = anionic auxiliary ligand) reported to date. Compounds like [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(THF) show useful catalytic properties as well.[1,8] For example, it catalyzes the C−Cl bond activation reactions under mild conditions.[8] Silver(I) complexes of nonfluorinated ligands like [HB(3,5-$(Me)_2$Pz)$_3$]$^-$ are, in general, thermally and photochemically less stable.[9,10] This is due to the relative ease of reducing silver(I) to metallic silver by the B−H moieties present in these electron-rich ligand systems.

Synthesis of metal adducts containing weakly coordinating ligands (e.g., highly fluorinated ligands) are not straightforward.[11] Metal halides (L′M−Cl) do not easily undergo salt elimination reactions with commonly used alkali metal salts, when large, weakly coordinating anions are involved. Thallium and silver salts are often employed to drive the reaction toward products. Even then, the results are not always predictable. For example, the silver salt [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(toluene) reacts successfully with GaI and InCl to form [HB(3,5-$(CF_3)_2$Pz)$_3$]Ga and [HB(3,5-$(CF_3)_2$Pz)$_3$]In, respectively.[12] It also serves as a good ligand transfer agent for some transition metal ions.[13] However, the reaction between [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(toluene) and M(Cl)[(n-Pr)$_2$ATI] (M = Ge or Sn) does not lead to the expected silver halide precipitate. Instead, 1:1 adducts, [HB(3,5-$(CF_3)_2$Pz)$_3$]AgGe(Cl)[(n-Pr)$_2$ATI] and [HB(3,5-$(CF_3)_2$Pz)$_3$]AgSn(Cl)[(n-Pr)$_2$ATI], featuring unsupported Ag−M bonds were formed in high yield.[14] Arrested halide abstraction has been observed with silver salts of other weakly coordinating anions as well.[11,15–17] Thus, there is a need for developing new methods for introducing large, weakly coordinating ligands to metal ions. In this paper, we describe the use of an alkyl group metathesis process to introduce the [HB(3,5-$(CF_3)_2$Pz)$_3$]$^-$ ligand to an aluminum and a zinc center.

Treatment of [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(THF) with $AlMe_3$ and $ZnEt_2$ led to [HB(3,5-$(CF_3)_2$Pz)$_3$]$AlMe_2$ and [HB(3,5-

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(1) Dias, H. V. R.; Lu, H.-L.; Goh, T. K. H. H.; Polach, S. A.; Browning, R. G.; Lovely, C. J. *Organometallics* **2002**, *21*, 1466−1473 and the references therein.
(2) Thrasher, J. S.; Strauss, S. H. *Inorganic Fluorine Chemistry, Toward the 21st Century*; ACS Symposium Series 555; American Chemical Society: Washington, DC, 1994.
(3) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1995**, *117*, 11381−11382.
(4) Dias, H. V. R.; Wang, Z.; Jin, W. *Inorg. Chem.* **1997**, *36*, 6205−6215.
(5) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724−3727.
(6) Dias, H. V. R.; Polach, S. A.; Goh, S.-K.; Archibong, E. F.; Marynick, D. S. *Inorg. Chem.* **2000**, *39*, 3894−3901.
(7) Dias, H. V. R.; Polach, S. A. *Inorg. Chem.* **2000**, *39*, 4676−4677.
(8) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. *J. Am. Chem. Soc.*, in press.
(9) Effendy; Lobbia, G. G.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2000**, *308*, 65−72.
(10) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999.
(11) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.
(12) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **2000**, *39*, 815−819.
(13) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 3687−3694.
(14) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259−3268 and the references therein.
(15) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133−139.
(16) Patmore, N. J.; Mahon, M. F.; Steed, J. W.; Weller, A. S. *J. Chem. Soc., Dalton Trans.* **2001**, 277−283.
(17) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643−6648.

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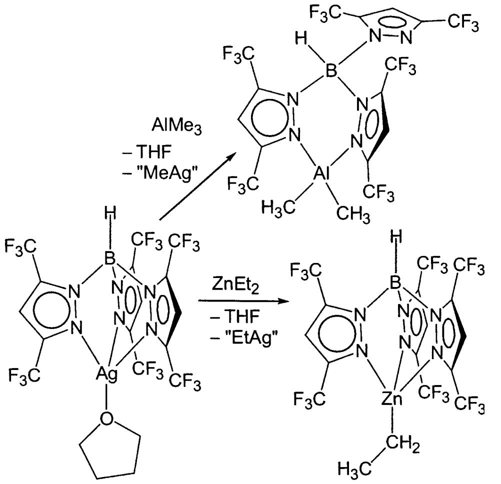
Scheme 1. Synthesis of Aluminum and Zinc Alkyl Compounds Using $[HB(3,5-(CF_3)_2Pz)_3]Ag(THF)$



$(CF_3)_2Pz)_3]ZnEt$, respectively (Scheme 1).[18,19] Products were isolated in quantitative yield. This represents an interesting new route to prepare aluminum and zinc alkyl compounds bearing weakly coordinating ligands. These reactions are accompanied by the deposition of a black precipitate. This is presumably due to the decomposition of expected metathesis products MeAg and EtAg. Alkyl silver(I) compounds like MeAg and EtAg are highly unstable (above −50 °C) both photochemically and thermally, and they decompose easily to metallic silver.[20] The treatment of the indium(I) adduct $[HB(3,5-(CF_3)_2Pz)_3]In$ with $ZnEt_2$ also leads to $[HB(3,5-(CF_3)_2Pz)_3]ZnEt$. $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$ and $[HB(3,5-(CF_3)_2Pz)_3]ZnEt$ are colorless solids. These compounds dissolve in most common organic solvents (e.g., toluene, hexane, ether, CH_2Cl_2) and may be handled in air without notable decomposition.

Solution ^1H and ^{13}C NMR data of $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$ in C_6D_6 at room temperature indicate the presence of three equivalent pyrazolyl groups and two equivalent methyl groups (similar to that observed for the nonfluorinated analogue $[HB(3,5-(Me)_2Pz)_3]AlMe_2$).[21] The ^{19}F NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$ displays two signals corresponding to the trifluoromethyl groups at the pyrazole ring 3- and 5-positions. Fluorines of the CF_3 groups at the pyrazolyl 5-position show coupling to the proton of the B−H moiety ($^5J = 3.4$ Hz).

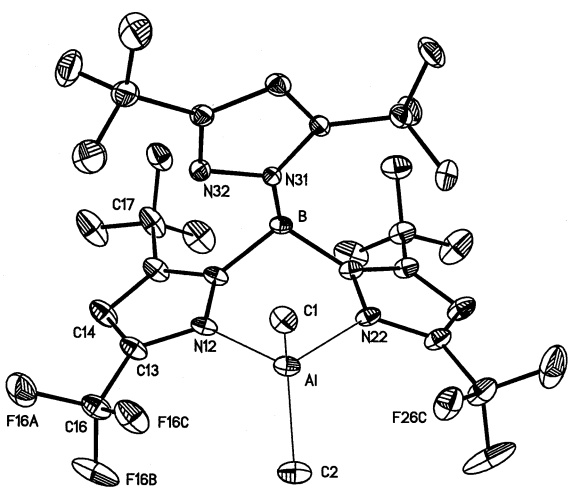


Figure 1. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$ (hydrogen atoms have been removed for clarity). Selected bond lengths (Å) and angles (deg): Al−C(1) 1.933(4), Al−C(2) 1.952(4), Al−N(12) 2.004(3), Al−N(22) 2.014(3), N(11)−N(12) 1.370(4), N(11)−B 1.549(5), N(21)−N(22) 1.366(4), N(21)−B 1.546(5), N(31)−N(32) 1.359(4), N(31)−B 1.564(5); C(1)−Al−C(2) 128.5(2), C(1)−Al−N(12) 111.03(15), C(2)−Al−N(12) 104.3(2), C(1)−Al−N(22) 108.57(15), C(2)−Al−N(22) 104.6(2), N(12)−Al−N(22) 94.45(12), N(21)−B−N(11) 108.6(3), N(21)−B−N(31) 111.1(3), N(11)−B−N(31) 105.6(3).

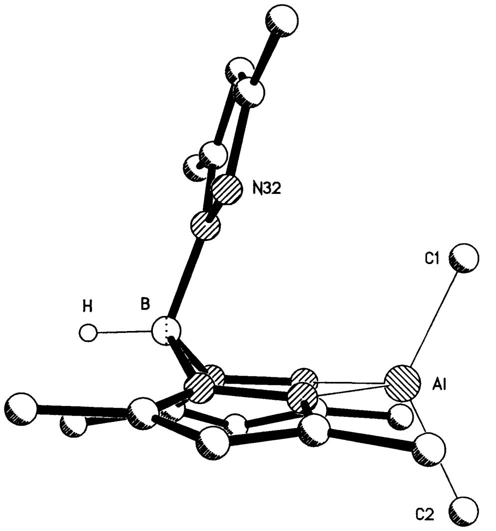


Figure 2. A side view of $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$ (hydrogen and fluorine atoms on carbons have been removed for clarity).

The X-ray crystal structure of $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$, however, shows that the tris(pyrazolyl)borate ligand coordinates to the aluminum center in κ^2-fashion (Figure 1).[22] The uncoordinated pyrazole ring plane is nearly perpendicular to the C2−Al−C1 plane (∼100°, see Figure 2). The Al···N32 distance is 3.76 Å. The aluminum center adopts a distorted-tetrahedral geometry, and the C−Al−C angle is large at 128.5(2)°, but not as large as the C−In−C angle in $[HB(3,5-(CF_3)_2Pz)_3]InMe_2$ (146.0(2)°).[23] Significant deviations from typical tetrahedral angles have been observed in other related group 13 metal adducts.[24,25] For comparison, the Al−N distances and C−Al−C angle of the κ^2-bonded

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(18) $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$: mp 114−116 °C; ^1H NMR (C_6D_6) δ −0.57 (s, 6H, CH_3), 6.25 (s, 3H, CH); ^{19}F NMR (C_6D_6) δ −58.44 (d, $^5J = 3.4$ Hz), −61.14 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −9.94 (br, CH_3), 109.04 (s, CH), 118.96 (q, $^1J(C,F) = 271$ Hz, CF_3), 119.83 (q, $^1J(C,F) = 271$ Hz, CF_3), 142.33 (q, $^2J(C,F) = 45$ Hz, CCF_3), 145.38 (q, $^2J(C,F) = 41$ Hz, CCF_3).

(19) $[HB(3,5-(CF_3)_2Pz)_3]ZnEt$: mp 171−173 °C; ^1H NMR (C_6D_6) δ 1.26 (q, 2H), 1.88 (t, 3H), 6.01 (s, 3H, CH); ^{19}F NMR (C_6D_6) δ −58.74 (d, $^5J(F,H) = 3.4$ Hz), −60.80; $^{13}C\{^1H\}$ NMR (C_6D_6) δ −1.90 (s, $ZnCH_2$), 11.28 (s, CH_3), 107.36 (s, CH), 119.00 (q, $^1J(C,F) = 270$ Hz, CF_3), 119.56 (q, $^1J(C,F) = 272$ Hz, CF_3), 140.60 (br), 144.90 (q, $^2J(C,F) = 41$ Hz, CCF_3).

(20) Fackler, J. P., Jr. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1987; Vol. 7, pp 3829−3834.

(21) Looney, A.; Parkin, G. *Polyhedron* **1990**, *9*, 265−276.

(22) X-ray crystallographic data for $[HB(3,5-(CF_3)_2Pz)_3]AlMe_2$: $T = 183(2)$ K, triclinic, $P\bar{1}$, $a = 9.284(2)$ Å, $b = 11.788(2)$ Å, $c = 12.604(1)$ Å, $\alpha = 76.055(10)°$, $\beta = 69.300(12)°$, $\gamma = 85.176(13)°$, $V = 1252.4(3)$ Å^3, $Z = 2$, R1 = 0.0450, wR2 = 0.1002.

(23) $[HB(3,5-(CF_3)_2Pz)_3]InMe_2$ also features a κ^2-bonded tris(pyrazolyl)borate ligand, In−C 2.088(5), 2.096(5) Å; In−N 2.320(4), 2.337(4) Å; N−In−N 84.1(1)°; C−In−C 146.0(2)°. Dias, H. V. R.; Jin, W. Unpublished results.

tris(pyrazolyl)borate adduct [HB(3-(*t*-Bu)Pz)$_3$]AlEt$_2$ are 1.990(3) Å, 1.990(4) Å, and 127.6(2)°, respectively.[25]

The crystal structure also shows that there are two fluorine atoms (F16C and F26C) pointed toward the aluminum center at a distance of 2.845 and 2.886 Å (for comparison, sum of van der Waals radii of Al and F = 3.40 Å).[26,27] These observations suggest the presence of weak Al···F−C interactions. Such bonding interactions are of interest[28] and may contribute to the reduced reactivity at the aluminum center toward molecules like O$_2$. Steric effects may also account for such stability as in the oxygen stable, alkylaluminum compounds like Me$_2$Al(3,5-(Me)$_2$Pz)$_2$AlMe$_2$.[25,29] Comparison of solid-state features of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AlMe$_2$ to room-temperature solution NMR spectroscopic data suggests that it is fluxional on the NMR time scale. Both fluxional and nonfluxional tris(pyrazolyl)boratoaluminum complexes have been reported in the literature.[21,25]

NMR spectroscopic features corresponding to the [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ moiety are very similar between the ethylzinc and dimethylaluminum adducts. Solid-state structures, however, are different. In contrast to the aluminum complex, the [HB(3,5-(CF$_3$)$_2$Pz)$_3$]ZnEt features a κ^3-N,N,N-bonded tris(pyrazolyl)borate ligand (Figure 3).[30] The zinc center is tetrahedral. The Zn−C bond length of 1.959(6) Å is not very different from those observed for the nonfluorinated analogues like [HB(3,5-(Me)$_2$Pz)$_3$]ZnMe (1.981(8) Å) or [HB(3-(Ph)Pz)$_3$]ZnMe (1.950(4) Å).[31] There are no significant Zn···F contacts (the closest Zn···F distance is 3.47 Å).

A large number of tris(pyrazolyl)boratozinc complexes have been investigated due to their importance in catalysis (e.g., lactide polymerization) and bioinorganic chemistry.[10,31−36] A few poly(pyrazolyl)boratoaluminum complexes are also known.[21,24,25,29,31,37,38] The synthesis of these zinc and aluminum compounds typically involves the use of alkali metal or thallium salts of tris(pyrazolyl)borates. This work represents the first successful use of silver tris(pyrazolyl)borate complexes as ligand transfer agents. We have reported the use of indium reagents for the synthesis of zinc adducts as well. New methods of ligand transfer such as those described in this paper are particularly important in weakly coordinating ligand chemistry since alkali metal salts often serve as poor ligand transfer agents.[11]

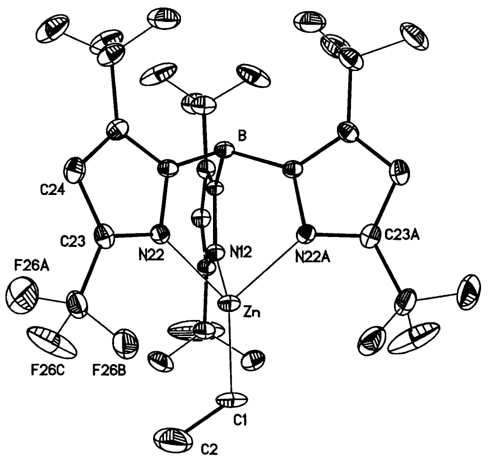

Figure 3. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]ZnEt (hydrogen atoms have been removed for clarity). Selected bond lengths (Å) and angles (deg): Zn−C(1) 1.959(6), Zn−N(12) 2.121(4), Zn−N(22)A 2.127(3), Zn−N(22) 2.127(3), N(11)−N(12) 1.377(6), N(11)−B 1.549(7), N(21)−N(22) 1.363(4), N(21)−B 1.555(5), B−N(21)A 1.555(5), C(1)−C(2) 1.442(14); C(1)−Zn−N(12) 126.5(2), C(1)−Zn−N(22)A 127.69(13), N(12)−Zn−N(22)A 87.06(11), C(1)−Zn−N(22) 127.69(13), N(12)−Zn−N(22) 87.06(11), N(22)A−Zn−N(22) 87.18(16), N(11)−B−N(21)A 108.6(3), N(11)−B−N(21) 108.6(3), N(21)A−B−N(21) 108.8(4), C(2)−C(1)−Zn 122.8(6).

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Supporting Information Available: X-ray crystallographic data (CIF) and synthetic details (PDF) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AlMe$_2$ and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]ZnEt. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Dowling, C. M.; Parkin, G. *Polyhedron* **1999**, *18*, 3567−3571 and the references therein.

(25) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C. *Inorg. Chem.* **1996**, *35*, 445−450.

(26) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998; pp 18 and 78.

(27) See for a discussion on directionality and weak bonds: Lewinski, J.; Zachara, J.; Justyniak, I. *Chem. Commun.* **2002**, 1586−1587.

(28) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363−3384 and the references therein.

(29) Lewinski, J.; Zachara, J.; Gos, P.; Grabska, E.; Kopec, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem. Eur. J.* **2000**, *6*, 3215−3227.

(30) X-ray crystallographic data for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]ZnEt: T = 183(2) K, orthorhombic, *Pnnm*, a = 19.156(2) Å, b = 9.0308(9) Å, c = 14.4970(19) Å, $\alpha, \beta, \gamma = 90°$, V = 2507.9(5) Å^3, Z = 4, R1 = 0.0414, wR2 = 0.1075.

(31) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288.

(32) Badura, D.; Vahrenkamp, H. *Inorg. Chem.* **2002**, *41*, 6013−6019.

(33) Bergquist, C.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 6322−6323.

(34) Bergquist, C.; Storrie, H.; Koutcher, L.; Bridgewater, B. M.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 12651−12658.

(35) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845−11854.

(36) Walz, R.; Vahrenkamp, H. *Inorg. Chim. Acta* **2001**, *314*, 58−62.

(37) Darensbourg, D. J.; Maynard, E. L.; Holtcamp, M. W.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 2682−2684.

(38) Han, R.; Looney, A.; Parkin, G. *J. Am. Chem. Soc.* **1989**, *111*, 7276−7278.