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Synthesis and Structure of [Hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]potassium

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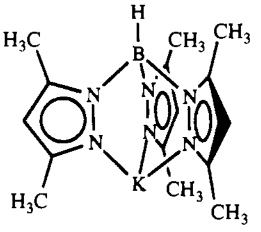
Metal complexes of the hydridotris(pyrazolyl)borate (Tp) ligand have been used widely in inorganic, organometallic, and bioinorganic chemistry.[1,2] However, most of these studies involve either the parent tris(pyrazolyl)borate or alkylated analogs such as hydridotris(3,5-dimethylpyrazolyl)borate, **1**.[1,3,4] Very little has been done on Tp systems bearing electron-withdrawing substituents such as trifluoromethyl groups.[1,5] In this communication, we report the synthesis and characterization of a Tp compound containing six CF_3 groups. Compound **2** was isolated as the dimethylacetamide (DMAC) adduct. This represents the perfluoromethyl analog of one of most widely used tris(pyrazolyl)borate ligands **1**.



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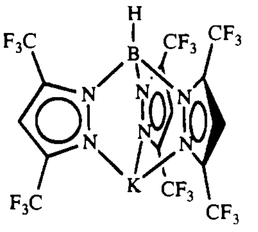

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[Hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]potassium, **2**, could be synthesized by treating KBH_4 with 3,5-bis(trifluoromethyl)pyrazole[6] in DMAC as described for certain tris(pyrazolyl)borates.[7,8] Compound **2** is an air- and moisture-stable colorless solid and has been characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and by elemental analysis. The elemental analysis data suggest the presence of one DMAC molecule for each molecule of **2**. This is also apparent from the ^{1}H and ^{13}C NMR spectroscopic data. The ^{13}C chemical shifts of CF_3 carbons (δ 120.17, 121.50) are very close to that of starting pyrazole (δ 120.5).[9] The ^{19}F NMR spectrum consists of two singlet resonances. These ^{19}F NMR chemical shifts are in the expected region for CF_3 groups. The melting point of the DMAC adduct of **2** (146−148 °C) is considerably lower than that of **1** (298−300 °C dec).[4]

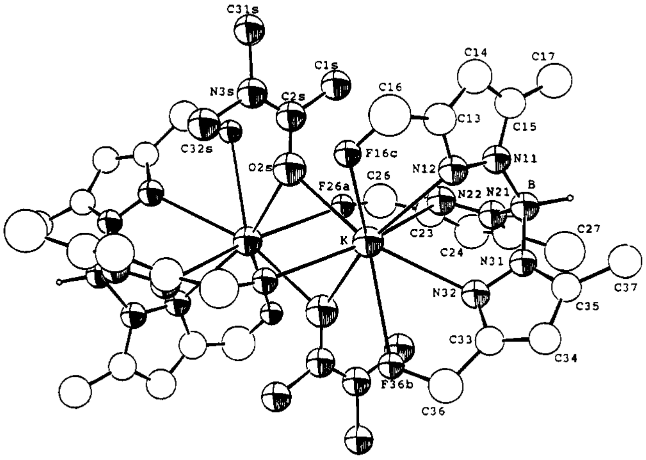

Figure 1. View of [**2**·DMAC]$_2$ showing the atom-labeling scheme. For clarity, noncoordinating fluorines are omitted, and the solvent molecule is shown with spheres of arbitrary size. Selected bond lengths (Å): K−O2s, 2.704(6); K−O2s′, 2.662(6); K−F16c, 3.07(1); K−F26a′, 2.82(1); K−F36b, 3.111(6); K−N12, 2.811(9); K−N22, 2.99(1); K−N32, 2.854(7).

The structure of **2** was confirmed by X-ray crystallography (Figure 1).[10] It crystallizes as dimeric units in the monoclinic space group $P2_1/n$, with the center of the dimer residing upon a center of inversion. The two Tp units are held together mainly by the bridging DMAC molecules. In addition, one of the fluorines of the CF_3 substitutents of each Tp ligand aids the

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(8) [**2**·DMAC]: KBH_4 (0.331 g, 6.14 mmol) and 3,5-bis(trifluoromethyl)pyrazole (4.00 g, 19.61 mmol) were mixed in anhydrous DMAC, and the mixture was heated slowly under N_2 until reflux began. The refluxing was continued overnight, and the volatiles were removed under reduced pressure. The resulting oily residue was treated with hot toluene, and the mixture was cooled at 0 °C to obtain crystals of **2** as its DMAC adduct. These were isolated and dried under vacuum. The NMR of the supernatant solution showed the presence of more leftover sample, indicating considerable solubility of **2** in toluene. X-ray-quality crystals were grown from ether−hexane: 0.96 g, 21% yield; mp 146−148 °C; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ 1.96 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.95 (s, 3H, CH_3), 7.22 (s, 3H, CH); ^{13}C{^{1}H} NMR (75.47 MHz) δ 21.45 (s, CH_3), 34.61 (s, CH_3), 37.56 (s, CH_3), 106.20 (br s, C-4), 120.17 (q, ^{1}J(C,F) = 269 Hz, CF_3), 121.50 (q, ^{1}J(C,F) = 269 Hz, CF_3), 136.48 (q, ^{2}J(C,F) = 39 Hz, CCF_3), 140.75 (q, ^{2}J(C,F) = 38 Hz, CCF_3), 170.03 (s, CO); ^{19}F NMR (282.36 MHz, DMSO-d_6, 25 °C, $\delta(C_6F_6)$ −163) δ −59.3, −60.3; correct C,H,N analysis.

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(10) (a) The crystal used for measurements, 0.08 × 0.10 × 0.11 mm, was mounted under nitrogen in a Lindemann capillary: $C_{38}H_{26}B_2F_{36}K_2N_{14}O_2$, monoclinic, space group $P2_1/n$, $a = 10.847(3)$ Å, $b = 15.871(6)$ Å, $c = 17.666(4)$ Å, $\beta = 106.43(2)°$, $V = 2917(2)$ Å^3, $Z = 2$, $\varrho = 1.701$ g cm^{-3}. Data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo Kα, $\lambda = 0.71073$ Å, graphite monochromator, $\theta-2\theta$ scan mode, $T = 298$ K). Of 3955 reflections corrected for Lorentz and polarization effects, but not absorption ($2 < 2\theta < 44°$), 3737 were independent ($R_{merg} = 0.024$) and 1503 with $I > 3\sigma(I)$ were regarded as observed. Solution was by direct methods (SHELX86[10b]). Some disorder of the CF_3 groups was noted, and the occupancies were refined to a ratio of 2:1. All non-hydrogen atoms with the exception of the major-occupancy fluorine atoms were refined with isotropic thermal parameters, and hydrogen atoms were included in the model in calculated positions ($U(H) = 1.3[U(C)]$). Poor crystal quality precluded conversion of all non-hydrogen atoms to anisotropic, due to paucity of data. Refinement on F converged at $R = 0.0680$, $R_w = 0.0706$ ($w = [0.04F^2 + (\sigma F)^2]^{-1}$).[10c] (b) Sheldrick, G. M. SHELX86. In *Crystallographic Computing*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 184−189. (c) *MolEN: An Interactive Structure Solution Program*; Enraf-Nonius: Delft, The Netherlands, 1990.

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bridging by interacting strongly with the neighboring potassium centers (K···F distance 2.82(1) Å). Each potassium atom is coordinated to two oxygens, three fluorines (in which one comes from the CF_3 of adjacent Tp), and three nitrogens. All three K···F interactions, 2.82(1), 3.07(1), and 3.111(6) Å, are well within the sum of van der Waals radii of the two atoms (4.30 Å).[11,12] These values are similar to the distances observed for other perfluoromethyl systems with eight-coordinate potassium, $[K(OR)(thf)_2(\mu\text{-}thf)]_2$ or $[K(SR)(thf)]_x$, where R = 2,4,6-$(CF_3)_3C_6H_2$.[13] Surprisingly, despite the enormous amount of work done with alkali metal pyrazolylborate systems, very little information is available about their solid state structures.[14] Compound **2** represents a rare example of a structurally characterized potassium tris(pyrazolyl)borate.

Hydridotris(pyrazolyl)borate ligands (Tp) are often considered as cyclopentadienyl (Cp) analogs in that both classes are monoanionic, 6-electron donors capable of occupying three coordination sites around a metal center.[1] Cyclopentadienyl ligands involving CF_3 substituents are difficult to synthesize, and their metal complexes have been largely unexplored compared to the electron-rich alkylated analogs.[15-18] Therefore, ligands such as **2**, in addition to having their own unique properties and coordination chemistry, would also be valuable as reasonable models for CF_3-substituted Cp ligands. We are currently exploring the coordination chemistry of **2** and the synthesis of other CF_3-substituted Tp ligands.

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Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** (12 pages). Ordering information is given on any current masthead page.

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