Synthesis and Characterization of Fluorinated Tris(pyrazolyl)borate Complexes. Observation of an (η^5-Pyrazole)−K^+ Interaction in the Solid State

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Received August 1, 2000

Cyclopentadienyl (Cp) ligands have received considerable attention mainly because of their π six-electron donation capability. Tris(pyrazolyl)borate ligands (Tp) are often compared with Cp because of their identical charge, number of donated electrons, and similar facial coordinating geometry. Their six-electron donation, however, is formally σ-type. The X-ray structure of the $[Tp^{CF_3,CH_3}CuK(\mu_4\text{-}CO_3)KTp^{CF_3,CH_3}]_2$ aggregate, **1**, reveals for the first time an unprecedented η^5-Tp^{CF_3,CH_3} potassium bonding interaction. **1** crystallizes in the triclinic space group $P\bar{1}$ with $a =$ 12.0411(2) Å, $b =$ 14.9791(2) Å, $c =$ 16.0567(3) Å, $\alpha =$ 71.301(1)°, $\beta =$ 69.785(1)°, $\gamma =$ 66.539(1)°, and $Z =$ 2. Both K−F and K−μ_4-CO_3^{2-} interactions stabilize the aggregate, as suggested by the lack of hexanuclear aggregation and K incorporation in the absence of fluorine groups or when $O{=}CO_2^{2-}$ is replaced by $CH_3{-}CO_2^-$. In the latter case we have isolated the complex $[CuTp^{CF_3,CH_3}(CH_3CO_2)]$, **2**, which retains a Cu coordination sphere similar to that encountered in the $Tp^{CF_3,CH_3}Cu$ subset of **1**. The mononuclear complex **2** crystallizes in the monoclinic space group $P2(1)/c$ with $a =$ 14.1474(2) Å, $b =$ 14.1474(2) Å, $c =$ 19.0456(6) Å, $\beta =$ 99.012(2)°, and $Z =$ 4. The novel η^5-coordination mode revealed in **1** suggests that Tp ligands might function not only as σ donors but also as Cp-like π donors. The η^5-coordination mode might therefore constitute a new potential common denominator of these two important classes of ligands.

Introduction

Since the discovery 100 years ago[1] of the first cyclopentadienylmetal complex, CpNa, alkali metal−aromatic π interactions have received considerable attention.[2] The location of a metal cation above the plane of the anionic Cp ring has been unequivocally demonstrated early on by NMR, IR, and X-ray diffraction studies.[3] K^+ can bind arenes in anionic solids[4a] and, in the gas phase, even neutral π systems, such as benzene; in the latter case the binding is at least as strong as that to water.[4b] Very recently π-binding to heteroaromatic side chains of tryptophan[5] and tyrosine[6] has been demonstrated. Interestingly, in the case of the indole side chain of tryptophan, the alkali metals (Na^+, K^+) are located above the N-containing five-membered pyrrolo subunit, in contrast to theoretical predictions of favorable binding to the benzo subunit.[7] The π-interaction of K^+ with another N−heterocycle (a Zr porphyrinogenato complex) has been proven by X-ray diffraction.[8] In both this and an the indole case, the K^+ π-binding is entropically favored by its additional coordination to a Zr-linked enolate or tethered crown ether, respectively. Pyrazolato rings also exhibit a variety of coordination modes. Sterically induced Tl interactions with p orbitals of a single N atom of a pyrazole ring,[9a,b] unique η^3-coordination,[9c] and overall η^5-coordination[9d] modes have been observed. The last, however, is viewed[9d] as a sum of η^2-(N2) and η^3-(C3) coordination modes due to the differences between the Tl−N and Tl−C distances. Recently, the first η^5-coordination mode of free pyrazole was observed in a kinetically stabilized, mixed CpRuTp complex.[9e]

Tris(pyrazolyl)borate ligands (Tp) have often been compared with Cp because of their identical charge, facial coordination, and formal σ six-electron donation.[10] To our knowledge, however, pyrazolyl borates have not been recognized to display η^5 hapticity. Herein we report the synthesis and structural characterization of the polynuclear complex $[Tp^{CF_3,CH_3}CuK(CO_3)KTp^{CF_3,CH_3}]_2$, **1**, which represents the first example of the η^5 Tp-binding mode.

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10.1021/ic000860g CCC: $20.00

Experimental Section

All solvents and chemicals were of reagent grade. The ligands, potassium hydrotris(3-trifluoromethyl-5-methylpyrazol-2-yl)borate (KTp$^{\mathrm{CF_3,CH_3}}$) and potassium dihydrobis(3-trifluoromethyl-5-methylpyrazol-2-yl)borate (KBp$^{\mathrm{CF_3,CH_3}}$) were synthesized according to a modified literature procedure.[11] ^{1}H, ^{19}F, ^{13}C, and ^{11}B NMR were performed. Carbonate ions were not detected by IR in the starting materials.

Preparation of [Tp$^{\mathrm{CF_3,CH_3}}$CuK(CO$_3$)KTp$^{\mathrm{CF_3,CH_3}}$]$_2$ (1). A total of 80 mg CuCl (0.8 mmol) was added under Ar to a 15 mL CH_2Cl_2 solution of 100 mg of KTp$^{\mathrm{CF_3,CH_3}}$ (0.2 mmol) and 70 mg of KBp$^{\mathrm{CF_3,CH_3}}$ (0.2 mmol); the mixture was stirred overnight and filtered. The colorless filtrate turned dark-blue upon exposure to air and deposited a purple crystalline material [Cu$^{\mathrm{II}}$(Bp$^{\mathrm{CF_3,CH_3}}$)$_2$],[11] which was filtered out. Aerobic evaporation of the solution gave 12 mg (11% yield based on Tp$^{\mathrm{CF_3,CH_3}}$) of **1** as blue, X-ray quality crystals. IR (KBr, cm^{-1}): 2560 (br, B−H), 1587 and 1329 (s, CO_3^{2-}). Anal. Calcd for $C_{62}H_{52}B_4N_{24}F_{36}Cu_2K_4O_6$: C, 33.25; H, 2.34; N, 15.01. Found: C, 33.32; H, 2.38; N, 15.12.

Preparation of [CuTp$^{\mathrm{CF_3,CH_3}}$(O$_2$CCH$_3$)] (2). A total of 15 mL of CH_3CN solution containing 54 mg of anhydrous [Cu(OAc)$_2$] (0.3 mmol) and 150 mg of KTp$^{\mathrm{CF_3,CH_3}}$ (0.3 mmol) was stirred for 20 min and filtered and the solvent removed via rotoevaporation. The blue solid was recrystallized from CH_3CN to give 143 mg of X-ray quality crystals (82% yield). IR (KBr, cm^{-1}): 2564 (s, B−H), 1518, 1471 (s, bidentate CH_3COO^-). Anal. Calcd for $C_{17}H_{16}BN_6F_9CuO_2$: C, 35.10; H, 2.77; N, 14.45. Found: C, 35.02; H, 2.90; N, 14.53.

Preparation of [Tp$^{\mathrm{CF_3,CH_3}}$K(μ-CH$_3$CN)$_2$KTp$^{\mathrm{CF_3,CH_3}}$] (3). A total of 15 mL of CH_3CN solution containing 150 mg of KTp$^{\mathrm{CF_3,CH_3}}$ was stirred in air for 1 h and allowed to evaporate. Single crystals appeared overnight.

X-ray Crystallography of [Tp$^{\mathrm{CF_3,CH_3}}$CuK(CO$_3$)KTp$^{\mathrm{CF_3,CH_3}}$]$_2$ (1). A 0.4 × 0.4 × 0.55 mm^3 blue block was mounted with epoxy cement at the end of a quartz fiber. X-ray data collection was carried out using a Siemens P4 single-crystal diffractometer equipped with a CCD area detector and controlled by SMART version 4.1 software. A total of 23 850 reflections was obtained, 9718 of them unique. Data reduction was carried out by SAINT version 4.1 and included profile analysis; this was followed by absorption correction using SADABS.

The structure was solved in the space group $P\bar{1}$ using direct methods and then refined on F^2. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. Hydrogen atoms, with the exception of B−H, were placed at their calculated positions and subject to a riding refinement; each was refined with an isotropic temperature factor 20−50% greater than that of the ridden atom; the B−H hydrogen was refined freely. The CF_3 groups are 2-fold rotationally disordered. They were refined as two geometrically restrained interpenetrating tetrahedra with their sum of occupancy factors set to 1.0. The final distribution of the two-site populations was 40:60. The refinement converged with R1 = 0.0464 and wR2 = 0.1156; GOF = 1.038. The five highest residual electron density peaks are found near either the metals or the CH_3 groups (suggesting some rotational disorder) but not in the vicinity of the CF_3 groups. The largest peak and hole in the last difference Fourier map are 0.395 and − 0.329 eÅ^{-3}, respectively. Crystallographic data is reported in Table 1.

X-ray Crystallography of [CuTp$^{\mathrm{CF_3,CH_3}}$(O$_2$CCH$_3$)] (2). A 0.44 × 0.34 × 0.22 mm^3 blue block was mounted with epoxy cement at the end of a quartz fiber. X-ray data collection and processing was carried out using the same procedures and equipment employed for **1**. A total of 17 447 reflections was collected, 3395 of them unique. The structure was solved by direct methods in space group $P1$, then refined on F^2 in the true space group $P2(1)/c$. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. Hydrogen atoms, with the exception of B−H, were placed at their calculated positions and subject to a riding refinement; each was refined with an isotropic temperature factor 20−50% greater than that of the ridden atom. Only one CF_3 group exhibited significant rotational disorder and was therefore refined as two interpenetrating, restrained tetrahedra with site occupancy factors of 30 and 70%. The refinement converged with R1 = 0.0415 and wR2 = 0.1116; GOF = 1.042. The largest peak and hole in the last difference Fourier map are 0.408 and − 0.265 eÅ^{-3}, respectively. Crystallographic data is reported in Table 1.

Table 1. Crystallographic Data for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{31}H_{26}B_4CuF_{18}$-$K_2N_{12}O_3$	$C_{17}H_{16}BCuF_9$-N_6O_2	$C_{17}H_{16}BF_9KN_7$
fw	1120.0	581.71	539.28
space group (No.)	$P\bar{1}$ (No. 2)	$P2(1)/c$ (No. 14)	$P\bar{1}$ (No. 2)
temp, °C	25	25	25
λ, Å	0.710 73	0.710 73	0.710 73
a, Å	12.0411(2)	14.1474(2)	10.7152(2)
b, Å	14.9791(2)	8.8856(3)	11.1235(2)
c, Å	16.0567(3)	19.0456(6)	12.2161(2)
α, deg	71.301(1)	90	73.765(1)
β, deg	69.785(1)	99.012(2)	83.073(1)
γ, deg	66.539(1)	90	64.846(1)
V, Å^3	2436.01(7)	2364.6(1)	1265.41(4)
Z	2	4	2
d_{calc}, g cm^{-3}	1.527	1.634	1.415
μ, mm^{-1}	0.733	1.021	0.294
R1[a]	0.0464	0.0415	0.0554
wR2[a,b]	0.1156	0.1116	0.1266

[a] $R1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for 6563 reflections with $I > 2\sigma(I)$ for **1**, 3369 for **2**, and 3392 for **3**. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$; $a = 0.0678$ for **1**, 0.0578 for **2**, and 0.0598 for **3**; $b = 0.71$ for **1** and 0.00 for **2** and **3**.

X-ray Crystallography of [Tp$^{\mathrm{CF_3,CH_3}}$K(μ-CH$_3$CN)$_2$KTp$^{\mathrm{CF_3,CH_3}}$] (3). A total of 0.35 × 0.38 × 0.42 mm^3 colorless irregular block was mounted with epoxy cement, then coated with more cement to prevent loss of solvent. X-ray data collection and processing was carried out using the same procedures and equipment employed for **1**. A total of 12 134 reflections was collected, 4932 of them unique. The structure was determined by direct methods in space group $P1$, then refined on F^2 in the true space group $P\bar{1}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Two sets of three fluorine atoms on each carbon atom were assigned variable site occupancy factors constrained to sum to unity. The refinement converged with R1 = 0.0554 and wR2 = 0.1266; GOF = 1.049. The largest peak and hole in the last difference Fourier map are 0.206 and −0.137 eÅ^{-3}, respectively. Crystallographic data is reported in Table 1.

Results and Discussion

Synthesis. While searching for reversible dioxygen copper complexes using fluorinated ligands,[12] we observed that the reaction of [KTp$^{\mathrm{CF_3,CH_3}}$] with CuCl in the presence of KBp$^{\mathrm{CF_3,CH_3}}$ produces a complex formulated as [(KTp$^{\mathrm{CF_3,CH_3}}$)$_2$(CuCO$_3$)]$_2$, **1**. Since the starting materials lack the relevant IR bands, the CO_3^{2-} must originate from atmospheric CO_2. A similar transformation has been noted previously.[13] The detailed mechanism of formation of **1** is incompletely understood and is likely to involve several species because of its low yield. We noted, however, that the omission of KBp$^{\mathrm{CF_3,CH_3}}$ results in the exclusive formation of the previously reported complex (CuTp$^{\mathrm{CF_3,CH_3}}$)$_2$.[12] Considering the 2:1 K/Tp stoichiometry found in **1**, the KBp$^{\mathrm{CF_3,CH_3}}$ ligand might supply the remaining potassium ions and/or help solubilize the copper ions because CuCl is only sparingly soluble in acetone. Consistent with this view, the Bp$^{\mathrm{CF_3,CH_3}}$ anion is found quantitatively in Cu(Bp$^{\mathrm{CF_3,CH_3}}$)$_2$. The

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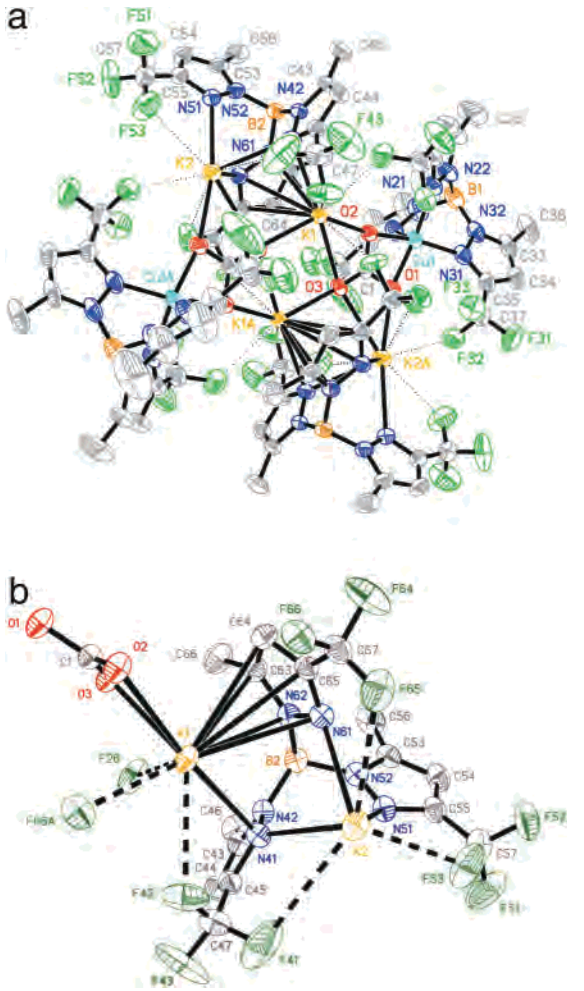

Figure 1. ORTEP plots (40% thermal probability ellipsoids, hydrogen atoms omitted for clarity) of (a) the complete structure of **1**; (b) the K1 environment. Only one set of the 2-fold rotationally disordered CF_3 groups is shown. Symmetry-related atoms are labeled with "A".

potassium ions of the ligand are thus available for complexation and may help the formation of the carbonate ions from CO_2 in the presence of traces of water. The above explanation for the formation of **1**, however, is only tentative because its low yield requires the presence in solution of a significant amount of unreacted reagents and/or other unidentified species.

Description of the Structures and Investigation of Their Assembly. The full X-ray structure of **1**, shown in Figure 1a, reveals a novel μ_4-CO_3 bridged Cu_2K_4 aggregate ($n = 2$), which appears to be the first example of a structurally characterized mixed main group−transition metals Tp aggregate.[14a] The coordination environment of the K^+ ions is shown in Figure 1b, while selected bond distances and angles are listed in Table 2.

The aggregate contains $\mathrm{CuTp}^{\mathrm{CF_3,CH_3}}$ and $\mathrm{KTp}^{\mathrm{CF_3,CH_3}}$ subunits related by an inversion center. Each Cu is facially coordinated by one $\mathrm{Tp}^{\mathrm{CF_3,CH_3}}$ ligand and two CO_3^{2-} oxygen atoms. The latter, O1 and O2 (C−O distances 1.300 ± 0.002 Å) link the Cu to K1 and K2, respectively. The third (carbonyl) oxygen (C−O3 = 1.249(3) Å) links asymmetrically both K1 and K1A to K2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1b**[a]

O(1)−C(1) 1.303(3)	O(2)−C(1) 1.300(3)
O(3)−C(1) 1.249(3)	O(3)−C(1)−O(2) 123.3(3)
O(3)−C(1)−O(1) 123.6(3)	O(2)−C(1)−O(1) 113.1(2)
K(1)−O(3A) 2.571(2)	K(1)−O(2) 2.658(2)
K(1)−O(3) 2.830(2)	K(1)−F(26) 2.84(2)
K(1)−F(66A) 2.88(1)	K(1)−F(42) 3.08(1)
O(3A)−K(1)−O(2) 138.50(7)	O(3A)−K(1)−O(3) 91.51(6)
O(2)−K(1)−O(3) 48.14(5)	K(2A)−O(1) 2.628(2)
K(2A)−O(3) 2.898(2)	O(1)−K(2A)−O(3) 47.70(6)
K(1A)−O(3)−K(1) 88.49(6)	K(1A)−O(3)−K(2A) 95.03(6)
K(1)−O(3)−K(2A) 154.48(9)	

[a] Symmetry transformations used to generate equivalent atoms. #1: $-x, -y + 1, -z + 1$.

Table 3. Bond Distances (Å) and Angles (deg) for the First Coordination Sphere of Copper in **1** and **2**

1	
Cu(1)−O(1) 1.951(2)	Cu(1)−O(2) 1.944(2)
Cu(1)−N(31) 2.003(3)	Cu(1)−N(21) 2.015(3)
Cu(1)−N(11) 2.302(3)	
O(2)−Cu(1)−O(1) 67.77(8)	O(2)−Cu(1)−N(31) 166.6(1)
O(1)−Cu(1)−N(31) 102.6(1)	O(2)−Cu(1)−N(21) 97.6(1)
O(1)−Cu(1)−N(21) 161.1(1)	N(31)−Cu(1)−N(21) 89.5(1)
O(2)−Cu(1)−N(11) 105.8(1)	O(1)−Cu(1)−N(11) 103.8(1)
N(31)−Cu(1)−N(11) 85.2(1)	N(21)−Cu(1)−N(11) 91.5(1)
2	
Cu−O(1) 2.025(3)	Cu−O(2) 1.991(3)
Cu−N(1) 2.295(3)	Cu−N(3) 1.988(3)
Cu−N(5) 1.994(3)	
N(3)−Cu−O(2) 99.7(1)	O(2)−Cu−O(1) 65.2(1)
O(2)−Cu−N(5) 165.5(1)	N(3)−Cu−N(5)−89.1(1)
N(5)−Cu−O(1) 103.9(1)	N(3)−Cu−O(1) 162.0(1)
O(2)−Cu−N(1) 103.3(1)	N(3)−Cu−N(1) 90.9(1)
O(1)−Cu−N(1) 101.9(1)	N(5)−Cu−N(1) 87.9(1)

The role of the coordinating carbonyl oxygen, O3, and the CF_3 group in assembling the CuTp and KTp subunits to form the aggregate **1** was investigated. First, a literature survey revealed that carbonato copper complexes of Tp ligands lacking 3-CF_3 groups exhibit only μ_2-CO_3^{2-} groups, their nuclearity being thus limited to two copper ions.[13] Second, by formally replacing O3 by a hydrophobic CH_3 group, i.e., using $[Cu(CH_3COO)_2]$ as the copper source, we have obtained under aerobic conditions only the complex $[\mathrm{CuTp}^{\mathrm{CF_3,CH_3}}(O_2CCH_3)]$, **2** (Figure 2), which exhibits the same CuN3O2 chromophore as **1** (Table 3). Unlike **1**, however, **2** does not bind additional $\mathrm{KTp}^{\mathrm{CF_3,CH_3}}$ units.

It appears thus that both CO_3^{2-} and CF_3 groups are required for the assembly of **1** even if in both **1** and **2** the Cu⋯F contacts are too long to be considered bonding and thus not relevant. The CF_3⋯K interactions in **1**, on the other hand, are of interest.

Potassium K2 is coordinated by κ^3-bonded $\mathrm{Tp}^{\mathrm{CF_3,CH_3}}$, two CO_3^{2-} oxygens, and three CF_3 fluorine atoms. The F⋯K distances range from 3.06 to 3.15 Å (average 3.11 Å). Considering the 1.51 Å ionic radius[15] of eight-coordinated K^+ and the 1.75 Å van der Waals radius[16] of F in CF_4, these F⋯K contacts are slightly shorter than the 3.26 Å sum of K^+ and F van der Waals radii. Similar F⋯K stabilizing interactions have been observed in the dinuclear complex $[\mathrm{Tp}^{\mathrm{CF_3,R}}\mathrm{K}(\mu\text{-L})_2\mathrm{KTp}^{\mathrm{CF_3,R}}]$, **3** (R = CH_3, L = CH_3CN), shown in Figure 3, and a related complex with R = CF_3 and L = dimethylacetamido.[17]

The structure of **3** consists of two $\mathrm{KTp}^{\mathrm{CF_3,CH_3}}$ units related by an inversion center. Each K ion is facially coordinated by

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(14) Cambridge Crystallographic Database, April 2000: (a) none of the 1277 Tp structures contain both Tp(main group) and Tp(transition metal) subsets; (b) no μ-CF_3 structure was found.

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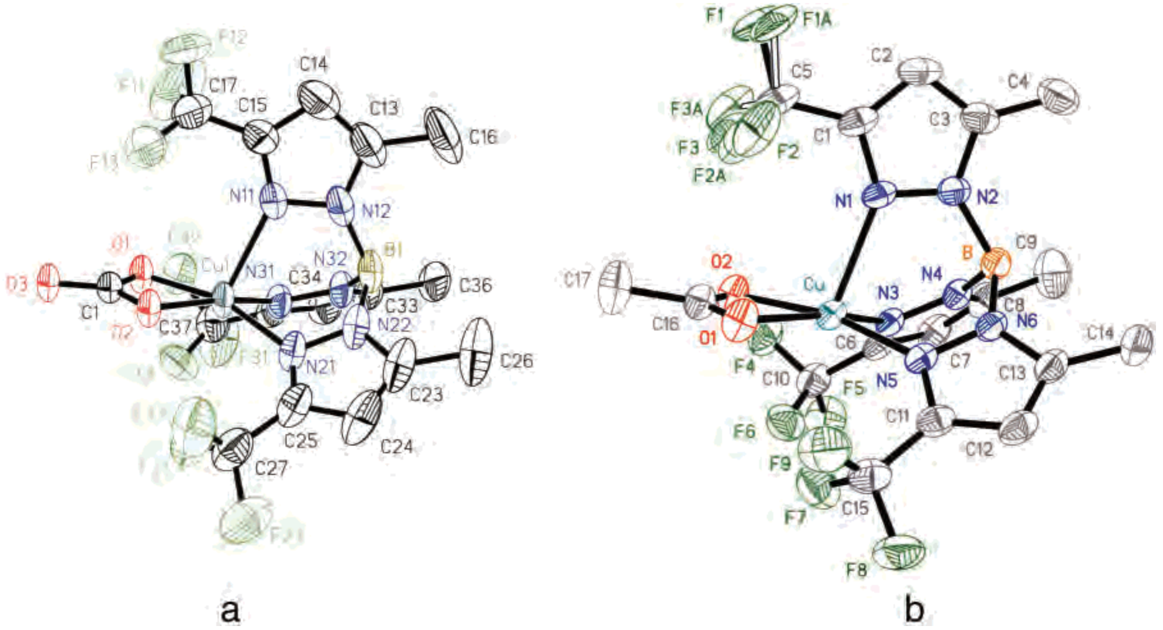

Figure 2. Comparison of the Cu environments in **1** and **2**. ORTEP plots (40% thermal probability ellipsoids, hydrogen atoms omitted for clarity) of (a) the unique Cu subset of **1**, (b) complete structure of **2**. The second set of the rotationally disordered CF_3 (C5) is labeled "A".

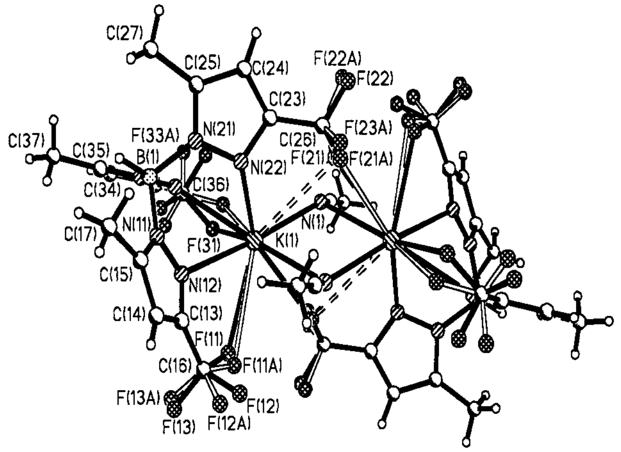

Figure 3. ORTEP plot (40% thermal probability ellipsoids) of **3**. Only the non-hydrogen atoms of the unique portion of the structure are labeled. The CF_3 groups are 2-fold rotationally disordered, the second set being labeled "A". Symmetry-related atoms are labeled "#1". K(1) is eight-coordinated by three Tp^{CF_3,CH_3} nitrogen atoms, two CH_3CN nitrogen atoms, and three fluorine atoms. The CF_3−K contacts shorter than 3.26 Å (sum of K^+ ionic and C−F fluorine van der Waals radii) are shown for both sets but with different bond types. Selected K−F distances (Å): K(1)−F(21)#1, 2.893(9); K(1)−F(31), 3.071(7); K(1)−F(11), 3.03(1).

three Tp^{CF_3,CH_3} nitrogen atoms, two fluorine atoms from two CF_3 groups bonded to the same ligand, and one fluorine from a CF_3 belonging to the symmetry-related Tp^{CF_3,CH_3}. In addition, two acetonitrile molecules bridge the metals, thus rendering the K eight-coordinated. F···K contacts range from 2.89 to 3.07 Å.

All the above contacts are within the 2.82−3.45 Å bonding range of the 38 CF_3−K contacts found in the 1999 Cambridge Crystallographic Database, calculated considering up to 105% the value of the sum of eight-coordinated potassium ionic radius and fluorine van der Waals radius. Tp^{CF_3,CH_3} is thus formally a hexadentate (3N plus 3F) chelating ligand for potassium K2 in **1** and the potassium ions in **3** but still only facially coordinating despite its high denticity.

The K1 coordination environment in **1**, Figure 1b, is more intriguing. Half of its coordination sphere is occupied by O2, O3, N41, and three fluorine atoms. The other half is occupied by the sixth pyrazole ring (atom labels: 6*b*, $b = 1-5$). K1 is located directly above the center of the sixth ring, the normal to the least-squares plane (labeled R_6) through this ring making only a 4° angle with the K−Z_6 (sixth ring centroid) vector (see Table 4). The K1 to sixth pyrazole ring atoms distances range from 3.277(2) to 3.424(4) Å (3.355 Å average). These values, expected because of the electron deficiency of the fluorinated pyrazole rings, are larger compared with the 3.033−3.081 Å (3.056 average) values[18] for CpK but comparable with 3.37 Å average η^6 K−arene interactions.[19] Importantly, they are shorter than the average 3.64 Å value observed for the K−π-contacts in indole.[5] The latter observation suggests a relatively stronger K···Tp π-interaction.

Table 4. Geometrical Parameters of $K^+-\sigma$ and π Interactions

K1 coordination	distance (Å) or angle (deg)	K2 coordination	distance (Å) or angle (deg)
K1−N61	3.339(3)	K2−N61	2.819(3)
K1−N62	3.277(2)	K2−R_6[a]	1.31(1)
K1−C63	3.339(3)	K2−N51	2.841(3)
K1−C64	3.424(4)	K2−R_5	1.18(1)
K1−C65	3.397(3)		
K1−Z_6[b]	3.150(4)		
K1−Z_6, the vector normal to R_6	4		
K1−N41	2.887(3)	K2−N41	2.873(3)
K1−R_4	2.48(1)	K2−R_4	1.43(1)
K1−N41−Z_4	121	K2−N41−Z_4	150

[a] R_a is the least-squares plane through ring "*a*", where "*a*" is the first digit of the ring atom label. [b] Z_a is the centroid of ring "*a*".

In summary, the position of K1 relative to the sixth pyrazole ring parallels that observed in CpK. The K1 to fourth pyrazole ring interaction is, in contrast, of the classical η^1-type, exhibiting reduced π-character as demonstrated by the short K1−N41 bond (2.887(3) Å) and the wide K1−N41−Z4 angle, which deviates by 31° from 90°.

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The η^5-coordination mode of K1 to Tp^{CF_3,CH_3} appears unusual, considering the conventional wisdom of the mostly electrostatic nature of K−Cp π-interactions and also the electron-withdrawing properties of CF_3. The favorable K coordination by CO_3^{2-} and especially by (well-recognized[20]) CF_3 likely play an additional stabilizing role. Indeed, in comparison with K2, the K1···CF_3 interactions are even stronger, ranging from 2.84 to 3.08 Å (average 2.98 Å). Furthermore, one of these interactions, F42−K1 is intramolecular and thus entropically favors the additional η^5 binding. Notably, the coordinating $C(47)F_3$ group exhibits an unprecedented bridging mode.[14b]

The observation of η^5 hapticity in **1** suggests that the large cone angle of Tp's (about 180° vs 100° for Cp) should perhaps no longer be considered an *a priori* limitation in envisioning sterically demanding transition states in Tp chemistry, for example, during oxidative additions and polymerizations. Furthermore, the fluorine atoms of the Tp ligands, by stabilizing C−F···metal interactions, could lead to unusual coordination modes in addition to enhancement of the metal electrophilicity. Such effects have been shown to be structurally significant[21] and catalytically relevant,[22] for example, in Ziegler−Natta type catalysts.[23]

In conclusion, the K1 to sixth pyrazole ring interactions in **1** represent a novel, π-bonding mode (η^5-type) of pyrazolyl(borate) ligands, favored by K^+···CF_3 and other interactions within a novel aggregate. This mode extends the known coordination versatility of Tp ligands. The detailed elucidation of the relative importance of electronic vs steric stabilization factors, however, must await a larger experimental database and detailed theoretical calculations.

Acknowledgment. The authors thank G. Carpenter for the X-ray structure of **3**. The X-ray equipment was purchased with assistance from NSF (CHE-8206423) and NIH (RR-06462).

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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