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Dihydrobis(4-cyanopyrazol-1-yl)borate, [Bp^{4CN}], a Functionalized Heteroscorpionate Ligand with Cross-Linking Potential[†]

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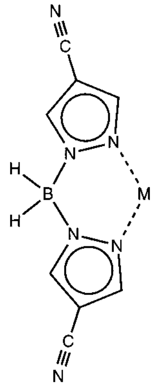
Among the numerous scorpionate ligands known,[1] differing in the number and nature of substituents (R, Ar, R_F, and halogen) on the pyrazolyl carbons and on boron, there are very few examples of scorpionates containing organic functional groups as substituents. The only homoscorpionate example is Tp^{cpd} (cpd = carboxypyrrolidido), which is capable of both N_3O_3 hexadenticity and N_2O_2 tetradenticity.[2] Other heteroscorpionate examples include the octahedral complex $Ni[(pz^{4CN})Bp]_2$, which was prepared from 4-cyanopyrazole and the square-planar $Ni(Bp)_2$.[3] Both cyano substituents in $Ni[(pz^{4CN})Bp]_2$ were converted by alkaline hydrolysis to the dicarboxylic acid and to its further derivatives. Additional examples of scorpionates containing cyano groups on pyrazolyl carbon atoms are the 2,6-dicyano-4,4,8,8-R_4-pyrazaboles, $R_2B(\mu\text{-}pz^{4CN})_2BR_2$, with R being H or Et, which could be regarded as complexes of the $[R_2B(4\text{-}CNpz)_2]^-$ ligand with a $[R_2B]^+$ cation.[4,5] In fact, asymmetric pyrazaboles were prepared in precisely this fashion: $[R_2B(pz)_2]^- + R'_2BX$, where X^- was a good leaving group.[6]

Since the powerfully electron-withdrawing 4-CN group in pyrazoles can not only coordinate to metal ions, provided its coordinating ability is not compromised by the presence of sterically interfering 3- and 5-substituents, but can also be transformed into other functionalities, such as −COOH or CH_2NH_2, the effect of a 4-CN substituent in scorpionate ligands on their coordination chemistry was explored. We are reporting now the synthesis of dihydrobis(4-cyanopyrazol-1-yl)borate, [Bp^{4CN}], the simplest member of this ligand family, and of several of its complexes, the structures of which were established by X-ray crystallography.

Experimental Section

Tl[Bp^{4CN}]. A mixture of 4-cyanopyrazole[7] and KBH_4 in 2.5:1 mole ratio was stirred and refluxed in DMF, with the hydrogen evolved being measured by a wet-test-meter. After the theoretical amount had been evolved, the solution was cooled under nitrogen and concentrated under vacuum. The concentrated solution was added with rapid stirring to an excess of aqueous $TlNO_3$, and the precipitated Tl[Bp^{4CN}] was filtered off and washed with water and with a small amount of acetone to remove excess 4-cyanopyrazole. It was obtained, when dried, in 73% yield. This compound is very soluble in polar solvents such as DMF and MeCN, moderately soluble in methanol and acetone, very sparingly soluble in dichloromethane and chloroform, and insoluble in hydrocarbons. Mp 228−229 °C. IR (cm^{-1}): BH_2, 2468, 2384; CN, 2236. ^1H NMR (in DMSO-d_6): 7.78, 8.06 ppm. Anal. Calcd for $C_8H_6BN_6Tl$: C, 23.9; H, 1.50; N, 21.0. Found: C, 24.1; H, 1.63; N, 20.6.



M[Bp^{4CN}]

Rh[Bp^{4CN}](COD). This complex was prepared by stirring an equimolar mixture of Tl[Bp^{4CN}] and $[Rh(COD)Cl]_2$ in methylene chloride for 1 h, filtering off the TlCl, and evaporating the filtrate. The yellow residue was obtained in 78% yield, and it was recrystallized from a heptane/toluene mixture. Mp 236−237 °C, dec. IR (cm^{-1}): BH_2, 2451, 2422; CN, 2237. Anal. Calcd for $C_{16}H_{18}BN_6Rh$: C, 47.1; H, 4.41; N, 20.6. Found: C, 47.5; H, 4.58; N, 20.2.

Co[Bp^{4CN}][Tp^{Np}]. An equimolar mixture of Co[Tp^{Np}]Cl, prepared by the literature method,[8] and Tl[Bp^{4CN}] was stirred in methylene chloride until the blue color changed to wine-red. The slurry was filtered and chromatographed on alumina, producing a wine-red eluate, which produced a red solid on evaporation. It was recrystallized from a toluene/heptane mixture yielding dark garnet-colored crystals. Mp: 192−194 °C, dec. IR (cm^{-1}): BH_2, 2468, 2384; CN, 2236. Anal. Calcd for $C_{32}H_{46}B_2CoN_{12}$: C, 56.9; H, 6.73; N, 24.6. Found: C, 57.3; H, 6.92; N, 24.2.

Co[Bp^{4CN}][Tp^{Cy}]. This complex was prepared as above, but instead of Co[Tp^{Np}]Cl, Co[Tp^{Cy}]Cl was used.[9] The red solution yielded a yellow solid on evaporation. Mp 254−258 °C, dec, with prior turning red from about 146 °C but without melting. IR (cm^{-1}): BH_2, 2453; CN, 2235, 2262. Anal. Calcd for $C_{35}H_{46}B_2CoN_{12}$: C, 58.7; H, 6.43; N, 23.5. Found: C, 59.1; H, 6.62; N, 23.1.

Upon the coordination of DMF, the IR spectrum had the following peaks: BH_2, 2455; CN, 2231; and CO, 1649 cm^{-1}. This compound decomposed at 157−160 °C.

Zn[Bp^{4CN}]$_2$(DMF)$_2$. To a solution of Tl[Bp^{4CN}] in methylene chloride containing enough DMF to dissolve all of the Tl salt was added half an equivalent of $Zn(OAc)_2$. After stirring for 1 h, Celite was added and the slurry was filtered. The colorless filtrate was evaporated, resulting in the growth of large colorless crystals. Mp 121−123 °C. IR (cm^{-1}): BH_2, 2427; CN, 2230; DMF, 1633. Calcd for $C_{22}H_{26}B_2N_{14}O_2Zn$: C, 43.6; H, 4.30; N, 32.4. Found: C, 43.8; H, 4.62; N, 32.0.

Co[Bp^{4CN}]$_2$(DMF)$_2$. This complex was prepared as above, using $CoCl_2$ instead of $Zn(OAc)_2$, and it was isolated as large orange crystals. Mp 194−198 °C dec. IR (cm^{-1}): BH_2, 2425; CN, 2232; DMF, 1649. Calcd for $C_{22}H_{26}B_2CoN_{14}O_2$: C, 44.1; H, 4.34; N, 32.7. Found: C, 44.5; H, 4.62; N, 32.3.

The related Fe(II) and Ni(II) complexes were obtained in similar fashion, as colorless and pale-violet crystals, respectively, and they had IR spectra essentially identical to those of the above cobalt and zinc complexes.

[†] Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday.

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Table 1. Crystallographic Data for Zn[Bp^{4CN}]$_2$(DMF)$_2$·2DMF (**2**), Rh[Bp^{4CN}](COD) (**4**), and Co[Bp^{4CN}][Tp^{Np}] (**5**)

	(**2**)·2DMF	(**4**)	(**5**)
formula	$C_{28}H_{40}B_2N_{16}O_4Zn$	$C_{16}H_{18}BN_6Rh$	$C_{32}H_{46}B_2CoN_{12}$
fw	751.75	408.08	679.36
space group	$C2/c$	$P2_1/c$	$C2/c$
a, Å	12.9031(15)	16.606(11)	33.801(6)
b, Å	15.6057(18)	7.615(5)	10.9292(18)
c, Å	19.498(2)	14.990(9)	20.488(3)
β, deg	104.763(2)	114.70(4)	103.545(3)
V, Å^3	3796.6(8)	1722(2)	7358(4)
Z, Z'	4, $^1/_2$	4, 1	8, 1
D(calc), g cm^{-3}	1.315	1.574	1.226
μ(MoKα), cm^{-1}	7.02	10.01	5.06
temp, K	173(2)	243(2)	173(2)
radiation	Mo Kα (λ = 0.71073 Å)		
$R(F)$,%^{a}	6.72	4.23	7.05
$R(wF^2)$, %^{a}	19.00	12.78	17.97

^{a} Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$.

Results and Discussion

The Bp^{4CN} ligand was prepared by the reaction of 4-cyanopyrazole with KBH_4, and it was isolated as the Tl salt, the low solubility of which in halocarbon solvents, in contrast to other Tl scorpionate salts, suggested a polymeric structure.

The special nature of the Bp^{4CN} ligand became dramatically apparent when we tried to prepare the simple monomeric bis-complexes, M[Bp^{4CN}]$_2$, with first-row transition metals by the reaction of Tl[Bp^{4CN}], **1**, with MX_2 (X = Cl, OAc, ClO_4) in methylene chloride. Instead of the typical organic-soluble deep purple tetrahedral cobalt(II) complexes, or orange-red square-planar nickel(II) ones, which were obtained with all known Bp^x ligands, except for those containing coordinating substituents in the 3-position such as pyridyl,[10] bipyridyl,[11] or 2,4-(dimethoxy)-phenyl,[12] insoluble materials were obtained, with colors characteristic of octahedral structures. However, these products were readily extracted with DMF, from which large crystals were obtained, the structures of which turned out to be M[Bp^{4CN}]$_2$(DMF)$_2$, as was shown by X-ray crystallography for the zinc complex, **2** (Figure 1). The analogous cobalt complex, **3**, had the same structure. Identical products were also obtained when DMF was added to methylene chloride before the reaction. In these structures, the two DMF molecules were cis to one another, the remaining coordination sites being occupied by the two [Bp^{4CN}] ligands. The infrared spectra of these, as well as of the nickel(II) and iron(II) analogues, were essentially superimposable. While the preference for octahedral coordination by cobalt and nickel may be understandable, it was surprising that zinc, which is often content with being four-coordinate and tetrahedral, still opted for the octahedral, bis-DMF structure. The M[Bp^{4CN}]$_2$ complexes prior to addition of DMF had two nitrile bands at 2232 and 2262 cm^{-1}, as did Co[Tp^{Cy}][Bp^{4CN}], being assigned to the uncoordinated and coordinated 4-CN, respectively. This is in agreement with previous observations that the CN stretch in coordinated benzonitrile appears at a higher frequency than that of uncoordinated benzonitrile.[13-15] In the M[Bp^{4CN}]$_2$(DMF)$_2$ complexes, as well as in Rh[Bp^{4CN}](COD) and in Co[Bp^{4CN}][Tp^{Np}], only one peak in the 2232−2237 cm^{-1} range was observed.

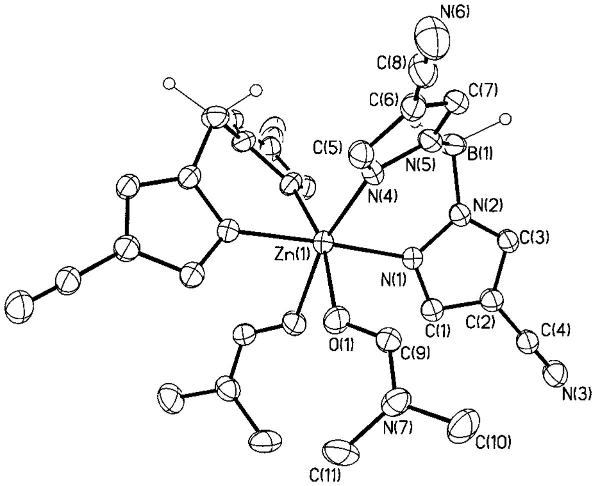

Figure 1. The structure of Zn[Bp^{4CN}]$_2$(DMF)$_2$, **2**. Bond lengths (Å) and angles (deg): Zn−O(1), 2.167(3); Zn−N(1), 2.147(3); Zn−N(4), 2.142(3); 2.164; O(1)−Zn−N(1), 93.96(12); O(1)−Zn−N(4), 90.04(13); N(1)−Zn−N(4), 87.55(12);

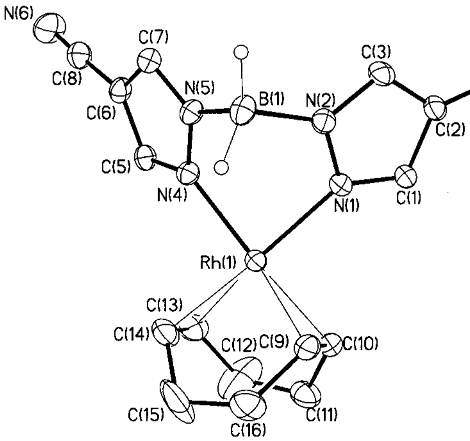

Figure 2. The structure of Rh[Bp^{4CN}](COD), **4**. Bond lengths (Å) and angles (deg): Rh−N(1), 2.127(5); Rh−N(4), 2.107(4); Rh−C(9), 2.112(5); Rh−C(10), 2.128(5); Rh−C(13), 2.131(6); Rh−C(14), 2.118(6); N(1)−Rh−N(4), 87.98(15); N(1)−Rh−C(9), 92.33(19); N(4)−Rh−C(9), 155.79(19); N(1)−Rh−C(10), 91.71(17); N(4)−Rh−C(10), 166.25(18).

These results show clearly the intermolecular coordinating ability of the 4-CN group which, in the absence of competing donors, leads to octahedral, cross-linked structures, as the two open coordination sites are occupied by the 4-CN donors from a neighboring M[Bp^{4CN}]$_2$ complex. At the same time, such bonds are relatively labile, permitting their cleavage by DMF.

To avoid any complication from additional coordination by the 4-CN groups, the complex Rh[Bp^{4CN}](COD), **4**, was prepared by the reaction of **1** with [Rh(COD)Cl]$_2$. Its structure (Figure 2) shows the presence of a symmetry plane, and the distance to Rh of the pseudoaxial B−H is about 2.9 Å and thus not in the agostic bonding range. This structure shows clearly that the CN groups are quite unhindered and should be capable to coordinate to other metals. Although Rh(COD) complexes with Bp and Bp* have been reported before[16,17] and several

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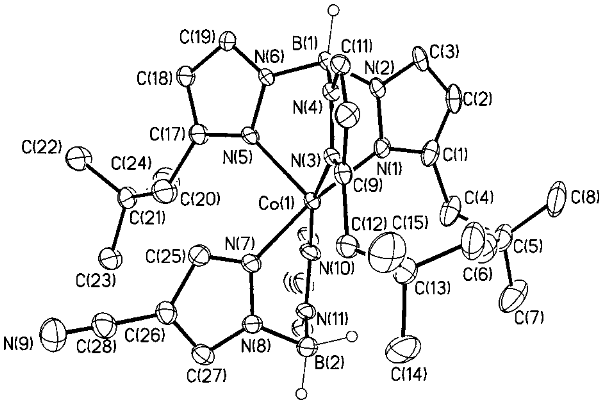

Figure 3. The structure of Co[Tp^{Np}][Bp^{4CN}], **5**. Bond lengths (Å) and angles (deg): Co−N(1), 2.117(4); Co−N(11), 2.073(3); Co−N(21), 2.077(3); Co−N(31), 2.075(4); Co−N(41), 2.072(4); Co−H(2), 3.104; N(1)−Co−N(11), 84.89(13); N(1)−Co−N(21), 90.96(14); N(1)−Co−(N31), 170.75(14); N(1)−Co−N(41), 92.51(14); N(11)−Co−N(21), 91.66(14); N(11)−Co−N(31), 92.19(14); N(11)−Co−N(41), 166.79(14); N(21)−Co−N(31), 97.91(14); N(21)−Co−N(41), 101.35(15); N(31)−Co−N(41), 88.34(14).

homoscorpionate Rh(COD) complexes have been synthesized and had their structures determined,[18−20] complex **4** seems to be the first instance of a structurally characterized Rh[Bp^x](COD) species.

We also synthesized heteroleptic complexes of structure Co[Tp^x][Bp^{4CN}] by the reaction of Co[Tp^x]Cl with **1** and found that CN coordination to cobalt depended on the structure of Tp^x. Thus, Co[Tp^{Np}][Bp^{4CN}], **5**, prepared from Co[Tp^{Np}]Cl and **1**, had a wine-red color, typical of five-coordinate cobalt scorpionate complexes, in solution and in the solid state. Its structure (Figure 3) showed that the cobalt ion was indeed five-coordinate, with the pseudoaxial B−H−Co distance of 3.103 Å and thus out of bonding range. The Co−N distances for [Bp^{4CN}] averaged 2.074 Å, being about 0.1 Å longer than in Co[Bp]$_2$, where they averaged 1.967 Å,[21] but shorter than in the related complex, Co[Tp^{iPr,4Br}][Bp^{Ph}], where an agostic B−H−Co bond (2.26 Å) was present and where the C−N distances for the Bp^{Ph} ligand averaged 2.131 Å.[22] In **3**, the Co−N bonds averaged 2.125 Å, consisting in each Bp^{4CN} ligand of one short and one long Co−N bond, the short bond being trans to the coordinated DMF.

A different situation prevailed with the rather similar heteroleptic complex Co[Tp^{Cy}][Bp^{4CN}], synthesized from Co[Tp^{Cy}]Cl and **1**. Its solution had the same wine-red color as that of **5**. However, upon evaporation of the solvent, the crystallizing solid was yellow. Upon the dissolving of the solid, the wine-red solution was regenerated. This pointed to the existence of a five-coordinate structure in solution but of a six-coordinate one in the solid state. It also indicated that the intermolecular CN−Co bond, present in the solid state, was rather weak. Accordingly, this compound added DMF readily to yield an octahedral complex characterized by a strong CO band at around 1650 cm^{-1}.

The Bp^{4CN} ligand is fairly flexible, as can be seen from the angle between the pyrazolyl planes, expanding or contracting to accommodate the rest of the molecule. This angle was 121.5° in **5**, 128.0° in **2,** and 112.1° in **4**. The coordination behavior of Bp^{4CN} depends on the presence of other ligands. In complexes with divalent metals, M[Bp^{4CN}]$_2$, the presence of two CN donor functionalities, plus two open coordination sites, leads to intractable polymeric structures. However, the CN−M bonds can be broken up by DMF, leading to well-defined, isolable M[Bp^{4CN}]$_2$(DMF)$_2$ species. In heteroleptic complexes which are not too hindered, such as Co[Tp^{Cy}][Bp^{4CN}], the CN groups can still coordinate to the metal ion of a neighboring molecule, leading to oligomeric or polymeric structures in the solid state, but such bonds are so weak that only a five-coordinate species exists in solution. In more sterically hindered heteroleptic complexes, such as **5**, the five-coordinate structure is also retained in the solid state. Finally, in heteroleptic complexes, such as **4**, where the metal is content to remain four-coordinate, the CN groups of the Bp^{4CN} ligand are not involved in coordination at all.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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