Do Poly(indazolyl)borates Have Abnormal Regiochemistry?

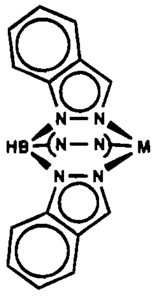
Arnold L. Rheingold,*,† Glenn Yap,† and Swiatoslaw Trofimenko*,‡

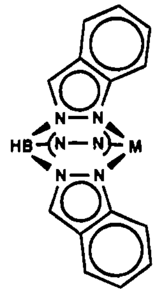
Department of Chemistry, University of Delaware, Newark, Delaware 19716-2522, and E. I. Du Pont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19880-0302

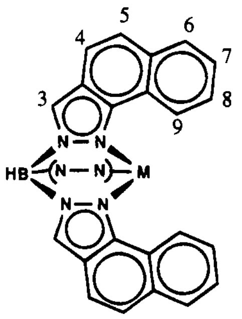
Received November 22, 1994

In the reaction of 3(5)-substituted pyrazoles with KBH_4 to form the homoscorpionate (tris(pyrazolyl)borate) ligands,[1] it had been always found that B–N bond formation occurred at the least hindered position (N1), yielding ligands of the type $[HB(3\text{-}Rpz)_3]^-$. This held true for R being methyl, isopropyl, *tert*-butyl, neopentyl, 2-thienyl, phenyl, *p*-tolyl, *p*-anisyl, *p*-chlorophenyl, mesityl, and 9-anthryl. Only with a few rather bulky substituents, such as mesityl, 9-anthryl, and neopentyl was there concurrent formation of the isomeric ligand $[HB(3\text{-}Rpz)_2(5\text{-}Rpz)]^-$. Even then, at least two pyrazolyl residues were bonded through the least hindered nitrogen. Furthermore, when different substituents were present in the 3- and 5-positions, the boron atom bonded invariably to the less sterically hindered nitrogen.

In contrast to this well-established empirical rule were reports claiming that in poly(indazolyl)borate ligands indazole (benzopyrazole) bonds to boron "abnormally" through the more hindered 1-nitrogen (by indazole numbering),[2] with the benzo group fused to the 4,5-positions of pyrazole, as in **a**. No reason was given for such assignment. Although this assertion was questioned in an older review,[3] it was also tentatively supported,[4] and the issue remained unresolved.







(-(N-N)- denotes the third, hidden, indazolyl ring)

a = (Tp^{4Bo}) **b** = (Tp^{3Bo}) Tp^{a*}

While expanding the scope of the scorpionate ligand system to include diversely substituted hydrotris(indazolyl)borates, we had to clarify the above apparent anomaly, especially since the hydrotris(2*H*-benz[*g*]indazol-2-yl)borate ([HB(naphthopyrazol-1-yl)$_3$] = Tp^{a*}) ligand was found to have the "normal" structure (**b**).[5] It was also important to establish the relative steric hindrance of a pyrazole-fused benzo ring, as compared with other 3-substituents. A priori, one would expect the indazolyl 7-CH to exert steric interference in the bond-forming step somewhere between that of a hydrogen atom and that of a methyl group.

The HB(indazolyl)$_3$ ligand (= Tp^{4Bo})[6] was synthesized from indazole and KBH_4. This K salt (BH 2415 cm^{-1}) was higher melting than the reported HB(indazolyl)$_3$K (256–258 °C, versus 230–232 °C).[2] It was characterized as the Tl salt, Tp^{4Bo}Tl,[7] which was a regiochemically pure, single isomer of C_{3v} symmetry but whose NMR gave no clue as to whether the structure was **a** or **b**. The ligand Tp^{4Bo} readily formed an octahedral Tp$^{4Bo}{}_2$Co complex,[8] as well as the heteroleptic complex Tp^{4Bo}CoTp^{Np},[9] none of which provided crystals suitable for X-ray crystallography. Still, an accurate diagnosis of the mode of B–N bonding in these complexes could be deduced from their NMR spectra. As had been shown earlier,[10–12] in octahedral homo- and heteroleptic Co(II) scorpionates the pyrazolyl 3-H (as in **a**) is in the minus 90–100 ppm range, while the 5-H (as in **b**) is around plus 60–80 ppm. The complex Tp$^{4Bo}{}_2$Co had the pyrazolyl hydrogen at –100 ppm, while Tp^{4Bo}CoTp^{Np} had it at –96 ppm, both results strongly suggesting the "abnormal" structure **a**. By contrast, in the heteroleptic complex Tp^{a*}CoTp^{Np},[13] where the ligand structure is known from X-ray crystallography, the pyrazolyl proton in Tp^{a*} was at plus 68 ppm, as befits a pyrazolyl 5-H (3-H in the indazole numbering system).

A conclusive proof of the regiochemistry in Tp^{4Bo} was obtained from the X-ray crystallographic structure[14] determination of Tp^{4Bo}Mo(CO)$_2$(η^3-methallyl),[15] which confirmed the results obtained from the NMR spectra of Tp$^{4Bo}{}_2$Co and Tp^{4Bo}CoTp^{Np}, thus underscoring again the usefulness of that

---

[†] University of Delaware.

[‡] Du Pont.

(1) Trofimenko, S. *Chem. Rev.* **1991**, *93*, 943–980 and references cited therein.

(2) (a) Siddiqi, K. S.; Neyazi, M. A.; Zaidi, S. A. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 253–265. (b) Siddiqi, K. S.; Neyazi, M. A.; Siddiqi, Z. A.; Majid, S. J.; Zaidi, S. A. A. *Indian J. Chem.* **1982**, *21A*, 932–933.

(3) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 147.

(4) Lalor, F. J.; Miller, S. M.; Garvey, N. *Polyhedron* **1990**, *9*, 63–68.

(5) Rheingold, A. L.; Haggerty, B. S.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1973.

(6) The abbreviation Tp^{Bo} for hydrotris(indazolyl)borate is intended to convey its relationship to the pyrazole-derived Tp-class of ligands, with "3Bo" and "4Bo" signifying 3,4- and 4,5-fusion of the benzo ring, respectively. The Tp^{Bz} abbreviation is reserved for the, still unknown, hydrotris(3-benzylpyrazol-1-yl)borate.

(7) Tp^{4Bo}Tl: mp 254–256 °C; IR 2450 cm^{-1}; ^{1}H NMR d 8.12 (3 H), s 8.00 (3 H), d 7.62 (3 H), t 7.38 (3 H), t 7.02 (3 H) ppm; ^{13}C NMR 112.7, 120.3, 120.5, 123.2, 126.3, 132.9, 144.3 ppm. Anal. Calcd for $C_{21}H_{16}BN_6Tl$: C, 44.4; H, 2.82; N, 14.8. Found: C, 44.7; H, 2.96; N, 14.5.

(8) Tp$^{4Bo}{}_2$Co: mp 446 °C (by DSC); IR 2470 cm^{-1} (BH); ^{1}H NMR 115 (1 H, BH), 51.1 (3 H, H7), 20.2 (3 H, H6), 10.4 (3 H, H5), –10.4 (3 H, H4), –102 (3 H, H3) ppm. Anal. Calcd for $C_{42}H_{32}B_2CoN_{12}$: C, 64.2; H, 4.08; N, 21.1 Found: C, 64.3; H, 4.13; N, 20.9.

(9) Tp^{4Bo}CoTp^{Np}: mp 268–270 °C; IR 2508, 2463 cm^{-1}; ^{1}H NMR 111.4 (1 H, BH), 107.6 (1 H, BH), 79.0 (3 H, Tp^{Np} H5), 48.4 (3 H, Tp^{Np} H4), 46.9 (3 H, H7), 20.2 (3 H, H6), 10.6 (3 H, H5), –9.4 (3 H, H4), –20.6 (27 H, *t*-Bu), –95.6 (6 H, CH_2), –96.0 (3 H, H3) ppm. Anal. Calcd for $C_{45}H_{56}B_2CoN_{12}$: C, 63.9; H, 6.63; N, 19.9 Found: C, 64.2; H, 6.71; N, 19.6.

(10) (a) Jesson, J. P. *J. Chem. Phys.* **1967**, *47*, 579–581. (b) Jesson, J. P. *J. Chem. Phys.* **1967**, *47*, 582–591. (c) McGarvey, B. R. *J. Chem. Phys.* **1970**, *53*, 86–91. (d) Lamar, G. N.; Jesson, J. P.; Meakin, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5392–5393.

(11) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091–1101.

(12) Calabrese, J. C.; Trofimenko, S. *Inorg. Chem.* **1992**, *31*, 4810–4814.

(13) Tp^{a*}CoTp^{Np}: mp 284–286 °C; IR 2473, 2452 cm^{-1} (BH); ^{1}H NMR 75 (3 H, Tp^{Np} H5), 68 (3 H, H3 = pyrazolyl H5), 51 (3 H, Tp^{Np} H4), 27 (3 H, H4), 6.5 (3 H, H6), –0.1 (3 H, H7), –3.2 (3 H, H8), –3.6 (3 H, H5), –17 (27 H, *t*-Bu), –53 (3 H, H9), –89 (6 H, CH_2) ppm. Anal. Calcd for $C_{57}H_{64}B_2CoN_{12}$: C, 68.6; H, 6.42; N, 16.9. Found C, 68.5; H, 6.36; N, 16.5.

0020-1669/95/1334-0759$09.00/0

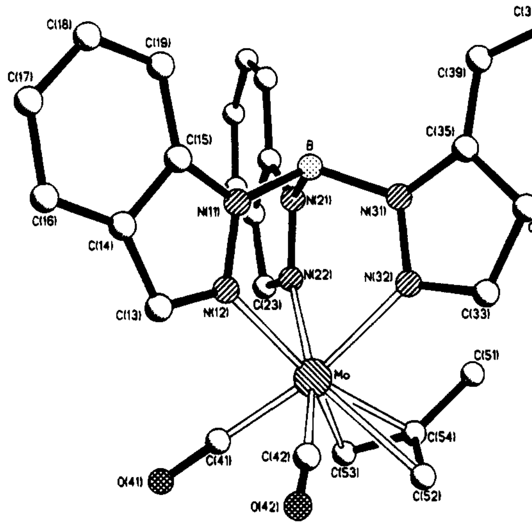


Figure 1. PLUTO drawing and labeling scheme for Tp^{4Bo}Mo(CO)$_2$(η^3-methallyl). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo−N(12) 2.232(15), Mo−N(22) 2.277(12), Mo−N(32) 2.256(16), Mo−C(41) 1.916(22), Mo−C(42) 1.922(17), Mo−C(52) 2.327(18), Mo−C(53) 2.333(22), Mo−C(54) 2.243(21), N(12)−Mo−N(22) 79.7(5), N(12)−Mo−N(32) 78.1(5), N(22)−Mo−N(32) 85.3(5), N(12)−Mo−C(41) 89.3(8), N(22)−Mo−C(41) 92.8(6), N(32)−Mo−C(41) 167.4(8), N(12)−Mo−C(42) 84.9(7), N(22)−Mo−C(42) 164.2(8), N(32)−Mo−C(42) 95.2(8), C(41)−Mo−C(42) 83.4(8). Selected bond distances (Å) and angles (deg) for the second molecule in the unit cell: Mo′−N(12′) 2.207(17), Mo′−N(22′) 2.298(16), Mo′−N(32′) 2.287(11), Mo′−C(41′) 1.899(19), Mo′−C(42′) 1.947(26), Mo′−C(52′) 2.335(21), Mo′−C(53′) 2.331(24), Mo′−C(54′) 2.248(22), N(12′)−Mo′−N(22′) 77.6(6), N(12′)−Mo′−N(32′) 77.7(5), N(22′)−Mo′−N(32′) 86.8(5), N(12′)−Mo′−C(41′) 87.6(8), N(22′)−Mo′−C(41′) 94.6(8), N(32′)−Mo′−C(41′) 164.6(8), N(12′)−Mo′−C(42′) 90.6(9), N(22′)−Mo′−C(42′) 168.1(9), N(32′)−Mo′−C(42′) 92.6(7), C(41′)−Mo′−C(42′) 82.8(9).

diagnostic method. The structure, shown in Figure 1, is very similar to that of the complex derived from the parent Tp, TpMo(CO)$_2$(η^3-methallyl).[16] The Mo−N bond lengths were essentially identical. However, the carbonyl Mo−C bonds were 0.04 Å longer and C−O bonds 0.03 Å shorter in the Tp analog, implying a higher Mo−C bond order in the Tp^{4Bo} derivative. Still, these results suggest that the cone and wedge angles for Tp^{4Bo} should also be very close to those of the parent Tp ligand.

Tp^{4Bo} represents thus the first structurally characterized example of a homoscorpionate ligand containing 4,5-substituents but unhindered at the pyrazolyl 3-position. This provides one with a useful variant of an HB(pz*)$_3$ ligand containing a protected B−H bond and yet with minimum steric hindrance, approaching that of the parent Tp, at the metal end.

Since in strictly steric terms the 7-CH grouping ought to be more bulky than a hydrogen atom, the exclusive formation of the "abnormal" product must be dictated by electronic considerations, such as those discussed for benzotriazole.[3] These electronic considerations do not have to be invoked for the regiospecific formation of **a**-type Tp^{4Bo} analogs containing an alkyl or aryl substituent in the 3-position, since even a methyl group is bulkier than the benzo CH. On the other hand, when an alkyl or aryl substituent is present in the 7-position, such group intrudes into close proximity to the metal, being sterically similar to the hydrotris(naphthopyrazolyl)borate ligand, Tp^{a*}. In this case, steric effects override the electronic ones, leading to structures of type **b**. For instance, the ligand based on 7-methylindazole (abbreviated as Tp^{3Bo,7Me}) has the "normal" structure of type **b**, as does the 7-*t*-Bu analog.[17]

In conclusion, unsubstituted hydrotris(indazolyl)borates do have "abnormal", in the sense of being contrary to steric considerations, regiochemistry. The same may hold true of 4-, 5-, or 6-substituted indazoles, where the substituents are sterically irrelevant. On the other hand, indazoles with substituents in either 3- or 7-positions form tris(indazolyl)borates with regiochemistry predictable in the same way as that of substituted tris(pyrazolyl)borates, i.e. with the least hindered nitrogen atom being attached to boron. Thus, in a strictly operational formalism, the benzo group fused to the pyrazole ring fits below the hydrogen atom in the steric hindrance hierarchy for poly(pyrazolyl)borates.

Supplementary Material Available: X-ray crystallographic data for Tp^{4Bo}Mo(CO)$_2$(η^3-methallyl), including experimental details and tables of crystal data, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles (12 pages). See any current masthead page for ordering information.

IC941343Z

---

(14) Crystal data for Tp^{4Bo}Mo(CO)$_2$(η^3-methallyl): $C_{26}H_{23}BMoN_{12}O_2$, monoclinic, $P2_1/c$, $a = 22.307(3)$ Å, $b = 12.057(2)$ Å, $c = 20.185(3)$ Å, $\beta = 111.38(1)°$, $V = 5055(1)$ Å^3, $Z = 8$, $D_c = 1.503$ g cm^{-3}. The unit cell contains two independent but chemically identical molecules. $R = 7.92\%$, $R_w = 8.02\%$, GOF = 1.22.

(15) Tp^{4Bo}Mo(CO)$_2$(η^3-methallyl): mp, darkens gradually from 265 °C, dec 310−312 °C; IR 2482 (BH), 1939, 1852 (CO) cm^{-1}; ^{1}H NMR 8.65 (very broad) (3 H), 7.92 (broad) (3 H), d 7.66 (3 H), t 7.39 (3 H), t 7.08 (3 H), s 3.71 (2 H), s 1.66 (2 H), s 1.55 (3 H) ppm. Anal. Calcd for $C_{26}H_{23}BMoN_{12}O_2$: C, 55.9; H, 4.12; N, 15.1. Found: C, 55.8; H, 4.09; N, 15.0.

(16) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1973**, 2444−2447.

(17) S. Trofimenko, unpublished results. Manuscript dealing with diverse substituted tris(indazolyl)borates in preparation.