Notes

Hydrotris(3,4-diphenyl-5-methylpyrazol-1-yl)borate: Control of Coordination Number via an Equatorial Substituent

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Introduction

The hydrotris(pyrazolyl)borate ligand, $[HB\{pz\}_3]^-$, is of proven usefulness in modeling metalloenzyme active sites. It has been employed in the study of blue copper and non-heme iron proteins, the zinc center of carbonic anhydrase, molybdopterin enzymes, and the polymanganese site of the photosystem II oxygen-evolving center.[1−8] In recent years several workers have explored the factors that control the coordination number of $[HB\{pz\}_3]_nM$ complexes.[9−16] Six-coordination (full-sandwich coordination), which yields $[HB\{pz\}_3]_2M$ complexes, is observed except where sufficiently bulky substituents, e.g., ᵗBu, phenyl, and isopropyl, at the 3-position of the pyrazole ring prevent the binding of a second equally hindered tridentate ligand. In complexes that incorporate the 3-phenyl-substituted ligand, $[HB\{3\text{-}Phpz\}_3]^-$, four-coordination is generally observed, with a single axial ligand. Full-sandwich complex formation, i.e. $[HB\{3\text{-}Phpz\}_3]_2M$, occurs only when the counterion is of low nucleophilicity, e.g. trifluoromethanesulfonate.[10] We discuss here the steric effects of pyrazole substitution at the 4-position on the orientation of a 3-phenylpyrazole substituent and the enforcement of half-sandwich, $[HB\{pz\}_3]M$, formation.

Experimental Section

All synthetic procedures were performed under a nitrogen atmosphere by Schlenk line techniques or in an inert-atmosphere glovebox. Methanol, acetonitrile, THF, and diethyl ether were distilled under nitrogen before use. All other reagents were purchased and used as received.

1,2-Diphenyl-1,3-butanedione, $C_6H_5COCH(C_6H_5)COCH_3$.[17] Deoxybenzoin, $C_6H_5CH_2COC_6H_5$ (145.31 g, 0.7404 mol), *p*-toluenesulfonic acid hydrate, $CH_3C_6H_4SO_3H{\cdot}H_2O$ (5.65 g, 0.0296 mol), and acetic anhydride (140.0 mL, 1.481 mol) were mixed in a 2 L round-bottom flask with stirring. After 2 h, all solids were dissolved and boron trifluoride−bis(acetic acid), $BF_3{\cdot}2CH_3COOH$ (176.9 mL, 1.27 mol), was introduced. The resulting dark brown solution was stirred for 20 h, following which a 1 L aqueous solution of sodium acetate trihydrate (403.01 g, 2.962 mol) was added. This solution was refluxed for 3 h and left to cool to room temperature. The product was extracted using petroleum ether (2 L, b.p. 35−60 °C), washed with 5% $NaHCO_3$ (1.5 L), and then washed with saturated aqueous NaCl solution (1.5 L), following which it was dried over $CaSO_4$. The resulting solution was filtered and the volatile components were removed on a rotary evaporator at 50 °C. The yellow oil which remained, when cooled to room temperature, formed light yellow crystals of 1,2-diphenyl-1,3-butanedione, which were collected by filtration, washed with 95% ethanol (100 mL), and dried in the air. Yield: 70.15 g, 39.76%. NMR (ppm) (DMSO-d_6): 2.24 (Me), 6.39 (−CHPh−), 7.05−8.045 (Ph).

3,4-Diphenyl-5-methylpyrazole. The diketone, $C_6H_5COCH(C_6H_5)COCH_3$ (44.0 g, 0.1847 mol), was added to a flask containing 200 mL of ethanol. Hydrazine hydrate, $NH_2NH_2{\cdot}H_2O$ (11.0 mL, 0.219 mol), was added dropwise to this slurry with stirring. The resulting solution was refluxed for 2 h, during which time all solids dissolved. After cooling, the product, a white precipitate, was collected by filtration, recrystallized from acetone, and dried in an oven (80 °C). Yield: 29.5 g, 68.17%. Bp: 178 °C. NMR (ppm) (DMSO-d_6): 2.23 (Me), 7.16−7.43 (Ph), 12.86 (−NH). MS: *m*/*e* 234.

Potassium Hydrotris[3(5),4-diphenyl-(3)5-methylpyrazolyl]-borate. 3,4-Diphenyl-5-methylpyrazole (28.57 g, 0.1219 mol) and KBH_4 (2.157 g, 0.0400 mol) were combined in anhydrous anisole (150 mL). The yellow solution was refluxed for 10 days, following which it was filtered and solvent was removed under vacuum on a hot water bath. The resulting glassy white solid was loosened by the addition of heptane (200 mL) and then dissolved in acetone (200 mL). The acetone solution was filtered to remove unreacted KBH_4, and the solvent was removed under vacuum. Excess pyrazole was removed by sublimation at 140 °C under vacuum. The product, a white crystalline powder (yield: 26.5 g, 86.9%) was used directly in the synthesis of the metal complexes without further purification. During a later stage in this research, we were able to obtain the pure salt $KHB[3,4\text{-}diphenyl\text{-}5\text{-}methylpyrazol\text{-}1\text{-}yl]_3$ by recrystallization from toluene/pentane in 54% yield based on KBH_4. NMR (ppm) (DMSO-d_6): 2.11 (Me), 7.10−7.40 (Ph). IR (cm^{-1}) (KBr): 2467.8, ν(BH).

$CoI[BH(3,4\text{-}Ph_2\text{-}5\text{-}Mepz)_3]$ (1). CoI_2 (0.166 g, 0.533 mmol) and $KBH[3(5),4\text{-}Ph_2\text{-}(3)5\text{-}Mepz]_3$ (0.401 g, 0.533 mmol) were stirred in THF (30 mL) overnight. The solution was then filtered, and the solvent was removed under vacuum, leaving a dark green powder, which was washed with ether (80 mL). The resulting green powder was recrystallized from toluene at −40 °C to form green crystals of X-ray diffraction quality (yield: 0.140 g, 29.3%). IR (cm^{-1}) (KBr): 2552.1, ν(BH). UV−vis (nm) (THF): 624, 656, 684. Anal. Calcd for $C_{48}H_{40}CoBIN_6{\cdot}0.9CH_3C_6H_5$: C, 66.52; H, 4.85; N, 8.66. Found: C, 66.71; H, 4.91; N, 9.28.

$Co[BH(3,4\text{-}Ph_2\text{-}5\text{-}Mepz)_3][BH(3,4\text{-}Ph_2\text{-}5\text{-}Mepz)_2(3\text{-}Me\text{-}4,5\text{-}Ph_2\text{-}pz)]$ (2). CoI_2 (0.116 g, 0.374 mmol) was added to a THF solution (50 mL) of a 2-fold excess of $KBH[3(5),4\text{-}Ph_2\text{-}(3)5\text{-}Mepz]_3$ (0.562 g, 0.748 mmol), and the mixture was stirred for 30 h. The pink solution

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Table 1. Crystallographic Data for CoI[BH(3,4-Ph_2-5-Mepz)$_3$]·C_7H_8 (**1**) and Co[BH(3,4-Ph_2-5-Mepz)$_3$][BH(3,4-Ph_2-5-Mepz)$_2$-(3-Me-4,5-Ph_2pz)] (**2**)

	1	2
chem formula	$C_{90}H_{88}BCoIN_6$	$C_{102}H_{86}B_2CoN_{12}$
fw	1450.3	1560.4
space group	$R3$	Cc
a, Å	26.032(4)	17.288(5)
b, Å		22.611(8)
c, Å	10.082(2)	22.052(10)
b, deg		93.70(3)
v, Å^3	5915(2)	8602(6)
Z	3	4
T, K	238	293
λ, Å	0.710 73	0.710 73
ϱ_{calcd}, g·cm^{-3}	1.222	1.205
μ, cm^{-1}	0.0649	0.0255
$R(F)$, %^{a}	5.76	7.87
$R_w(F)$, %^{b}	6.72	8.93

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w^{-1} = \sigma^2(F_o) + gF_o^2$.

was then filtered and the solvent removed under vacuum, leaving a light red powder (yield: 0.35 g, 63.1%). Crystals suitable for X-ray and elemental analysis were grown by the slow diffusion of ether into its saturated benzene solution. IR (cm^{-1}) (KBr): 2553.8, ν(BH). UV-vis (nm) (THF): 506, 534. Anal. Calcd for $C_{96}H_{80}CoBN_{12}$: C, 77.78; H, 5.45; N, 11.34. Found: C, 77.35; H, 5.62; N, 10.97.

IR data were collected from KBr pellets at a resolution of 4 cm^{-1} by the use of a Nicolet 5DXB spectrometer. UV-visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Proton NMR data were acquired on a Varian Gemini-200 and a General Electric QE 300 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

X-ray Structure Determinations

Crystallographic data for **1** and **2** are listed in Table 1. For data collection, crystals were mounted on a glass fiber with epoxy cement. Unit-cell parameters were determined by a least-squares fit of 25 reflections. In both cases, the space groups were initially chosen from expected unit-cell compositions and the distribution of normalized structure factors. Subsequently, the space groups were verified by the outcomes of structure solution and refinement. The structures were solved by direct methods and completed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were treated as idealized, updated isotropic contributions. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

In many recent reports pseudotetrahedral (half-sandwich) coordination involving hydrotris(pyrazolyl)borate ligands was enforced by placing sterically demanding groups at the 3-position of each of the three pyrazole rings which surround the entrance to the metal-binding pocket of the ligand.[9,11-13,16] The complete occupation of these positions by phenyl groups has been shown to enforce half-sandwich coordination for all but the weakest apical ligands in 4-coordinate hydrotris(pyrazolyl)-borate complexes.[10] Our strategy for the synthesis of a half-sandwich-forming ligand was to manipulate the conformation of the 3-phenyl groups so as to further disfavor the formation of symmetric full-sandwich complexes. We achieved this by placing a moderately bulky substituent, a phenyl group, at the 4-position of the pyrazole ring. We expected that the 4-phenyl group would restrict the rotation of the 3-phenyl group and block its coplanarity with the pyrazole ring.

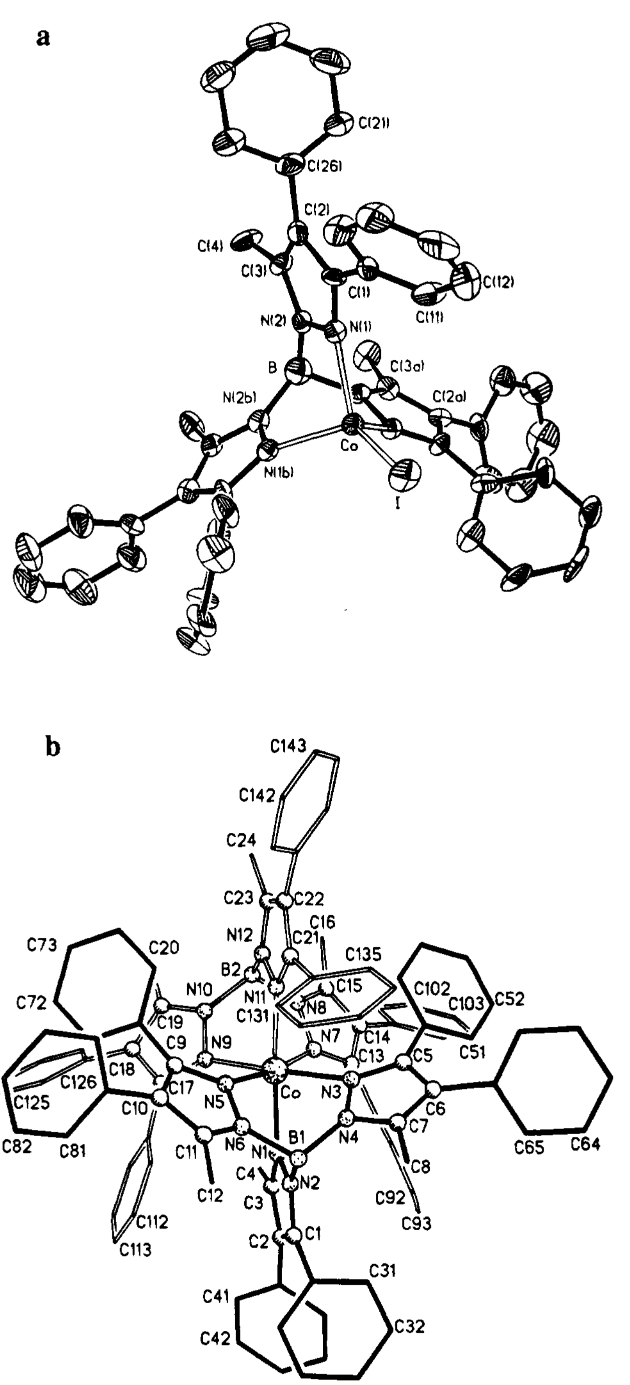
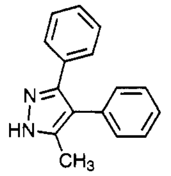


Figure 1. (a) ORTEP diagram of CoI[BH(3,4-Ph_2-5-Mepz)$_3$] (**1**) showing 30% probability ellipsoids. (b) PLUTO diagram of Co[BH-(3,4-Ph_2-5-Mepz)$_3$][BH(3,4-Ph_2-5-Mepz)$_2$(3-Me-4,5-Ph_2pz)] (**2**).

With deoxybenzoin as a starting material, we employed the method of Mao et al.[17] to synthesize 3,4-diphenyl-5-methyl pyrazole:



Ligand formation by reaction between pyrazole and KBH_4 was achieved in refluxing anisole. We isolated two ligands from this synthesis: (i) hydrotris(3,4-diphenyl-5-methylpyrazolyl)-borate, Tp; (ii) hydrobis(3,4-diphenyl-5-methylpyrazolyl)(3-

Table 2. Selected Bond Distances and Angles for $CoI[BH(3,4-Ph_2,5-Mepz)_3]{\cdot}C_7H_8$ (**1**)

Bond Distances (Å)			
Co−I	2.511(3)	N(1)−N(2)	1.395(14)
Co−N(1)	2.056(12)	B−N(2)	1.533(16)
Co−N(1A)	2.056(13)	N(1)−C(1)	1.324(20)
Co−N(1B)	2.056(11)	N(2)−C(3)	1.341(20)
B−N(2A)	1.533(16)	B−N(2B)	1.533(15)
Bond Angles (deg)			
I−Co−N(1)	121.6(3)	I−Co−N(1A)	121.6(3)
N(1)−Co−N(1A)	95.1(4)	I−Co−N(1B)	121.6(3)
N(1)−Co−N(1B)	95.1(4)	N(1A)−Co−N(1B)	95.1(4)
Co−N(1)−N(2)	108.7(8)	Co−N(1)−C(1)	142.8(9)
N(2)−N(1)−C(1)	107.1(11)	N(1)−N(2)−B	119.9(15)
N(1)−N(2)−C(3)	109.5(11)	B−N(2)−C(3)	130.5(15)
N(2)−B−N(2A)	110.6(11)	N(2)−B−N(2B)	110.6(12)
N(2A)−B−N(2B)	110.6(12)	N(1)−C(1)−C(2)	110.0(12)

methyl-4,5-diphenylpyrazolyl)borate, Tp*. The product ratio Tp:Tp* was 1:0.4, as determined by ^{1}H NMR, which revealed a 5-Me resonance of 2.157 ppm for Tp and 3-Me and 5-Me resonances at 2.013 and 2.232 ppm, respectively, for Tp*. The simultaneous formation of symmetric and asymmetric ligands Tp and Tp* is a common occurrence in hydrotris(pyrazolyl)borate compounds. It results from the isomerization in the attachment of pyrazole to borate during ligand formation at high temperature.[11] Two cobalt complexes were isolated from solutions containing both Tp and Tp*. The complexes comprised a half-sandwich compound, TpCoI (**1**), and a six-coordinate compound, TpTp*Co (**2**) (Figure 1, Table 1). A 1:1 ratio of CoI_2:Tp(Tp*) yielded TpCoI as the only isolable product from THF and ether. However, a 1:2 ratio of CoI_2:Tp(Tp*) yielded the asymmetric complex TpMTp*. The full-sandwich complex TpMTp does not form. This was confirmed by the addition of the potassium salt, KTp, to a THF solution of TpCoI. After 10 h, the UV−vis spectrum was unchanged from that of the starting material TpCoI.

In a recent paper by Trofimenko et al.,[18] full-sandwich formation was correlated with ligand cone and wedge angles defined as the N−B−N angles between the arms of the Tp ligand. It appears that a large cone angle and a small wedge angle ensured the formation of half-sandwich complexes. For **1** the ligand wedge and cone angles are 62 and 271°, respectively. Full-sandwich complexes have been reported with smaller wedge angles.[18] However, the largest cone angle reported for a full-sandwich complex is ~262°.[18] From this, we must presume that it is the large cone angle of Tp that prevents full-sandwich formation.

Table 3. Selected Bond Distances and Angles for $Co[BH(3,4-Ph_2\text{-}5\text{-}Mepz)_3][BH(3,4-Ph_2\text{-}5\text{-}Mepz)_2(3\text{-}Me\text{-}4,5\text{-}Ph_2pz)]$ (**2**)

Bond Distances (Å)			
Co−N(1)	2.106(12)	Co−N(3)	2.210(14)
Co−N(5)	2.151(14)	Co−N(7)	2.211(13)
Co−N(9)	2.172(15)	Co−N(11)	2.197(14)
Bond Angles (deg)			
N(1)−Co−N(3)	86.7(5)	N(1)−Co−N(5)	87.9(5)
N(1)−Co−N(7)	97.7(5)	N(1)−Co−N(9)	95.2(5)
N(1)−Co−N(11)	167.6(5)	N(3)−Co−N(5)	92.1(5)
N(3)−Co−N(7)	94.6(5)	N(3)−Co−N(9)	177.3(5)
N(3)−Co−N(11)	84.8(5)	N(5)−Co−N(7)	171.4(5)
N(5)−Co−N(9)	90.0(6)	N(5)−Co−N(11)	83.4(5)
N(7)−Co−N(9)	83.1(5)	N(7)−Co−N(11)	91.9(5)
N(9)−Co−N(11)	93.7(5)		

Conclusion

Abundant evidence shows that both cone and wedge angles influence the propensity of a ligand, $[HB(pz)_3]^-$, to support half- or full-sandwich complex formation. At present, the diversity of results does not allow the formulation of simple rules on this topic. Evidently the large cone angle in **1** accounts for the stability of half-sandwich coordination. This complex demonstrates the flexibility that can be achieved in the control of metal coordination by hydrotris(pyrazolyl)borate complexes. The presence of a bulky phenyl substituent at the 4-position evidently restricts the rotational freedom of the 3-phenyl group and therefore prevents symmetric full-sandwich formation.

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Supporting Information Available: For **1** and **2**, tables of complete data collection information, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and positional parameters of the H atoms (18 pages). Ordering information is given on any current masthead page.

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