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Notes

Copper(I) Chemistry of Bis(pyrazolyl)diphenylborate Ligands: Formation of a Heterocycle by Cu-Mediated Acetonitrile Addition

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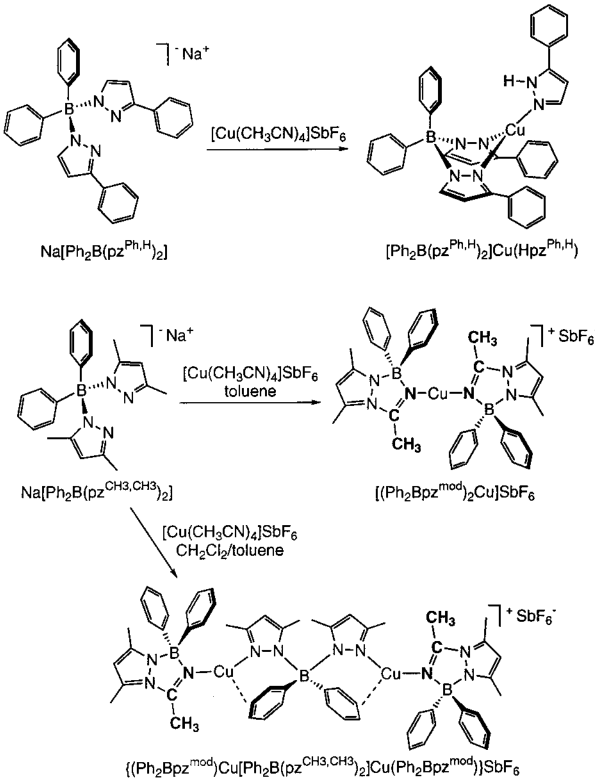
Important insights into the binding and activation of small molecules such as O_2 and NO by copper sites in proteins have been obtained through studies of the reactivity of Cu(I) complexes supported by facially binding tris(pyrazolyl)hydroborate ligands,[1] the properties which may be modified readily by pyrazolyl substituent variation.[2] Reasoning that lower coordinate Cu(I) complexes with enhanced or otherwise divergent reactivity might be accessible by using an analogous, yet bidentate bis(pyrazolyl)borate frame that lacks B−H groups known to interact with metal centers,[3] we targeted for synthesis Cu(I) complexes of $Ph_2B(pz^{R,R'})_2^-$ (R = Ph, R′ = H and R = R′ = CH_3, Scheme 1). These ligands are new derivatives of the $Ph_2B(pz)_2^-$ type.[4] Herein we report that the course of their complexation reactions with Cu(I) depends on the pyrazolyl substitution pattern and that an unusual ligand modification occurs for the case where R = R′ = CH_3, in which Cu-mediated cycloaddition of CH_3CN to a pyrazolyl unit yields a novel heterocyclic ring system.

Experimental Section

General Procedures. Unless otherwise noted, all reagents, solvents and gases used were obtained commercially and were of analytical grade. When necessary, solvents were dried according to published procedures[5] and distilled under N_2 immediately prior to use. All air-sensitive reactions were performed either in a Vacuum Atmospheres inert-atmosphere glovebox under a N_2 atmosphere or by using standard Schlenk and vacuum line techniques. The compounds 3,5-dimethylpyrazole (Hpz^{CH_3,CH_3}),[6] 3-phenylpyrazole ($Hpz^{Ph,H}$),[7] and $[Cu(CH_3CN)_4]SbF_6$[8] were prepared according to published procedures. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA. NMR and FTIR spectroscopic, and FAB-MS data were collected as described previously.[9]

Scheme 1



$Na[Ph_2B(pz^{Ph,H})_2]$. A mixture of $Hpz^{Ph,H}$ (7.00 g, 48.5 mmol) and $NaBPh_4$ (2.08 g, 6.06 mmol) was heated gradually to 220 °C for 4.5 h during which time benzene (∼1 mL) was removed by distillation through a short distillation apparatus. The molten mixture was cooled to ∼70 °C, poured into boiling CH_2Cl_2 (∼100 mL), and cooled to room temperature. Pentane (100 mL) was added to the solution and it was allowed to stand at −20 °C. A white precipitate formed above a tan oil after several days. The white precipitate was manually separated from the oil and then heated under vacuum (0.05 Torr) to distill away the excess $Hpz^{Ph,H}$, leaving the product as a white powder (0.285 g, 10%). The product was >90% pure by NMR spectroscopy and was used directly for complexation reactions. ^1H NMR (300 MHz, CD_3OD)

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(1) Representative examples: (a) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277−1291. (b) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079−12080. (c) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 11285−11298. (d) Ruggiero, C. E.; Carrier, S. M.; Tolman, W. B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 895−897. (e) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 11408−11418. (f) Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. M. *J. Am. Chem. Soc.* **2000**, *122*, 3556−3557.

(2) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *34*, 419−531. (d) Parkin, G. *Adv. Inorg. Chem.* **1995**, *34*, 291−393.

(3) Recent examples in Cu(I) compounds: (a) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357−366. (b) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **2000**, *39*, 2246−2248.

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10.1021/ic000637j CCC: $20.00

Table 1. Crystallographic Data

	$[Ph_2B(pz^{Ph,H})_2]Cu(pz^{Ph,H})$ CH_2Cl_2	$[(Ph_2Bpz^{mod})_2Cu]SbF_6$ C_7H_8	$\{(Ph_2Bpz^{mod})Cu\ [Ph_2B(pz^{CH_3,CH_3})_2]$ $Cu(Ph_2Bpz^{mod})\}SbF_6$
chemical formula	$C_{40}H_{34}BCl_2CuN_6$	$C_{45}H_{48}B_2CuF_6N_6Sb$	$C_{61}H_{66}B_3Cl_2Cu_2F_6N_{10}Sb$
formula weight	743.98	993.80	1405.40
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	9.8701(2)	12.3249(5)	12.9617(10)
b (Å)	14.0583(2)	22.6703(13)	35.929(3)
c (Å)	26.1718(3)	16.2777(9)	14.1137(11)
β (deg)	99.692(1)	93.521(3)	93.619(2)
V (Å^3)	3579.7(1)	4539.6(4)	6559.6(9)
Z	4	4	4
T (°C)	−122(2)	−100(2)	−100(2)
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.380	1.454	1.423
μ (mm^{-1})	0.798	1.127	1.195
$R1$ [F^2, $I > 2\sigma(I)$][a]	0.0361	0.0765	0.0607
w$R2$ [F^2, $I > 2\sigma(I)$][b]	0.0784	0.1783	0.1469

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$, and A and B varied among the different structures (see CIF files).

δ 6.64 (d, J = 2.4 Hz, 2 H), 6.90 (tt, J = 7.5 and 1.4 Hz, 2 H), 7.04 (t, J = 7.2 Hz, 4 H), 7.29 (tt, J = 7.5 and 1.5 Hz, 2 H), 7.38 (dd, J = 7.5 and 1.5 Hz, 4H), 7.44 (dt, J = 7.7 and 1.5 Hz, 4 H), 7.63 (d, J = 2.1 Hz, 2 H), 7.74 (dd, J = 7.2 and 1.5 Hz, 4 H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD) δ 101.8, 123.3, 125.3, 125.7, 127.5, 128.4, 134.2 ppm; FAB-MS *m/z* (relative intensity) 397 ($M^+ - Ph$, 5), 375 ($M^+ -$ Ph-Na+H, 35), 309 ($M^+ -$ Na-$pz^{Ph,H}$+H, 25).

$[Ph_2B(pz^{Ph,H})_2]Cu(Hpz^{Ph,H})$. $[Cu(CH_3CN)_4]SbF_6$ (0.109 g, 0.235 mmol) dissolved in CH_2Cl_2 (∼2 mL) was added to $Na[Ph_2B(pz^{Ph,H})_2]$ (0.122 g, ∼0.258 mmol) in CH_2Cl_2 (∼2 mL) under N_2 at ∼24 °C and stirred for 1.5 h. The mixture was filtered through Celite, the filtrate was concentrated under reduced pressure to ∼1.5 mL, and pentane (∼10 mL) was layered on the solution which was then placed in a −20 °C freezer. After several days, an oil and colorless X-ray quality crystals deposited. After washing with pentane and drying under reduced pressure, the product was obtained in bulk form (>90% pure by NMR spectroscopy) as a white powder (0.035 g, 22%). ^1H NMR (300 MHz, CD_2Cl_2) δ 6.46 (d, J = 2.1 Hz, 1 H), 6.51 (d, J = 2.4 Hz, 2 H), 7.07−7.10 (m, 4 H), 7.22−7.42 (m, 18 H), 7.59 (d, J = 2.4 Hz, 2 H), 7.82−7.85 (m, 4 H), 9.50 (br. s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 101.9, 103.5, 126.1, 126.5, 127.3, 127.7, 128.3, 128.9, 129.2, 134.7, 137.6 ppm; FAB-MS *m/z* (relative intensity) 577 ($M^+ - Hpz^{Ph,H} +$ CH_3CN−H+Na, 25), 515 ($M^+ - Hpz^{Ph,H}$+H, 20), 154 ($M^+ - Hpz^{Ph,H} -$ $pz^{Ph,H}$−Cu−2Ph, 100).

$Na[Ph_2B(pz^{CH_3,CH_3})_2]$. A mixture of Hpz^{CH_3,CH_3} (3.00 g, 31.2 mmol) and $NaBPh_4$ (2.14 g, 6.24 mmol) was heated gradually to 220 °C under N_2 over 4 h during which time benzene (∼1.1 mL) was removed by distillation through a short distillation apparatus. The system was cooled slightly before applying a vacuum (0.05 Torr) to sublime away the excess Hpz^{CH_3,CH_3}. The remaining off-white solid was boiled in CH_2Cl_2 (50 mL) and filtered hot, leaving the product as a white powder (1.69 g). The product was contaminated with variable amounts of $NaBPh_4$ (5−40%) as shown by NMR spectroscopy but was used directly for complexation reactions. Several attempts to cleanly separate the desired product from $NaBPh_4$ were unsuccessful, and correct elemental analyses (CHN) were not obtained. ^1H NMR (300 MHz, CD_3OD) δ2.19 (s, 12 H), 5.80 (s, 2 H), 6.92 (tt, J = 7.2 and 1.2 Hz, 2 H), 7.05 (t, J = 7.2 Hz, 4 H), 7.47 (dd, J = 7.8 and 1.2 Hz, 4 H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD) δ 12.03, 104.80, 122.77, 124.88, 126.45 (q, $J_{C,B}$ = 2.6 Hz), 127.22, 133.92, 137.39 ppm; FAB-MS *m/z* (relative intensity) 357 ($M^+ -$ Na+H, 12) 261 ($M^+ -$ Na− pz^{CH_3,CH_3}, 52).

$[(Ph_2Bpz^{mod})_2Cu]SbF_6 \cdot C_7H_8$. A mixture of $Na[Ph_2B(pz^{CH_3,CH_3})_2]$ (0.500 g, 1.32 mmol) and $[Cu(CH_3CN)_4]SbF_6$ (0.612 g, 1.32 mmol) was stirred in toluene (∼18 mL) under N_2 at ∼24 °C for 2.5 h. The cloudy, colorless mixture was filtered through Celite using CH_2Cl_2 (10 mL) to wash the precipitate. As the solvent from the filtrate was removed under reduced pressure, crystals deposited. Pentane (3−4 mL) was added to the filtrate until it was just turbid, and the solution was placed in a −20 °C freezer. A second batch of crystals was isolated from this mixture. The two batches of crystals were slurried in CH_2Cl_2 (3.5 mL) and filtered through Celite. Toluene (3.5 mL) and pentane (∼5 mL) were added to the filtrate until it became turbid, whereupon it was cooled to −20 °C to induce deposition of colorless X-ray quality crystals (0.190, 32%). ^1H NMR (300 MHz, CD_2Cl_2) δ 2.17 (s, 6 H), 2.36 (s, 3 H), 2.42 (s, 6 H), 2.60 (s, 6 H),6.38 (s, 2 H), 7.18−7.28 (m, 25 H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 12.6, 12.7, 20.5, 21.6, 114.3, 125.7, 127.9, 128.5, 128.6, 129.5, 133.5, 139.6, 143.0 (br m), 149.8, 151.6 ppm; FAB-MS *m/z* (relative intensity) 665 ($M^+ - SbF_6$, 20); FTIR (KBr) 3071, 3048, 3009, 2932, 2917, 1649, 1562, 1491, 1433, 1389, 1367, 1299, 1194, 1154, 1129, 1097, 1034, 1000, 937, 880, 765, 749, 743, 708, 656 cm^{-1}. Anal. Calcd for $C_{38}H_{40}N_6B_2CuSbF_6 \cdot 0.5C_7H_8$: C, 52.59; H, 4.67; N, 8.86. Found: C, 52.10; H, 4.81; N, 8.59.

$\{(Ph_2Bpz^{mod})Cu[Ph_2B(pz^{CH_3,CH_3})_2]Cu(Ph_2Bpz^{mod})\}SbF_6$. A mixture of $Na[Ph_2B(pz^{CH_3,CH_3})_2]$ (0.212 g, 0.56 mmol) and $[Cu(CH_3CN)]SbF_6$ (0.260 g, 0.56 mmol) was stirred in 1:1 CH_2Cl_2-toluene (∼8 mL) under N_2 at ∼24 °C for 30 min. The yellow-brown mixture was filtered through Celite using CH_2Cl_2 (∼5 mL) to wash the precipitate. The solvent from the filtrate was removed under reduced pressure and the resulting pale yellow residue was slurried in CH_2Cl_2 (3−4 mL) and filtered through Celite. Toluene (∼0.5 mL) and pentane (4 mL) were added to this filtrate until the solution became turbid, and it was cooled to −20 °C. Colorless and yellow-orange crystals deposited. The colorless crystals were manually separated, dissolved in 1:1 CH_2Cl_2-toluene (∼1−2 mL), and pentane was allowed to diffuse into this solution at −20 °C, yielding colorless crystals (0.060 g). The ^1H NMR spectrum indicated that these crystals were a mixture of $[(Ph_2Bpz^{mod})_2Cu]SbF_6 \cdot C_7H_8$ (13%) and $\{(Ph_2Bpz^{mod})Cu[Ph_2B(pz^{CH_3,CH_3})_2]Cu(Ph_2Bpz^{mod})\}SbF_6$ (87%). Therefore, the yield of desired product was 0.052 g (21%). ^1H NMR (300 MHz, CD_2Cl_2) δ 1.52 (s, 6 H), 1.59 (s, 6 H), 2.00 (s, 12 H), 2.53 (s, 6 H), 5.85 (s, 2 H), 6.27 (s, 2 H), 6.49 (t, J = 7.5 Hz, 4 H), 6.72 (t, J = 7.2 Hz, 2 H), 6.90 (d, J = 6.9 Hz, 4 H), 7.01−7.30 (m, 20 H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 12.3, 12.7, 13.2, 14.1, 20.8, 107.9, 113.8, 126.3, 127.6, 128.1, 129.0, 132.6, 133.7, 138.6, 143.0 (br m), 147.9, 148.5, 148.5, 149.29 ppm; FAB-MS *m/z* (relative intensity) 1085 ($M^+ - SbF_6$, 2), 785 ($M^+ - SbF_6 - pz^{mod}$, 5), 665 ($M^+ - SbF_6$, 7, where M = $[(Ph_2Bpz^{mod})_2Cu]SbF_6$), 481 ($M^+ - SbF_6 - 2pz^{mod}$, 65), 323 ($M^+ - SbF_6 - 2pz^{mod}$−Cu−$pz^{CH_3,CH_3}$, 100).

X-ray Crystallography. Single crystals of $[Ph_2B(pz^{Ph,H})_2]Cu(Hpz^{Ph,H}) \cdot CH_2Cl_2$, $[(Ph_2Bpz^{mod})_2Cu]SbF_6 \cdot C_7H_8$, and $\{(Ph_2Bpz^{mod})Cu[Ph_2B(pz^{CH_3,CH_3})_2]Cu(Ph_2Bpz^{mod})\}SbF_6$ were attached to glass fibers and mounted on the Siemens SMART system for a data collection at 173 (2) K. Selected crystallographic data are listed in Table 1. An initial set of cell constants was calculated from reflections harvested from 3 to 8 sets of 25−30 frames oriented such that orthogonal wedges of reciprocal space were surveyed; orientation matrixes were determined from 50 to 300 reflections. Final cell constants were calculated from a set that did not exceed 8192 strong reflections from the actual data collection. Data were collected via the hemisphere collection method, surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å.

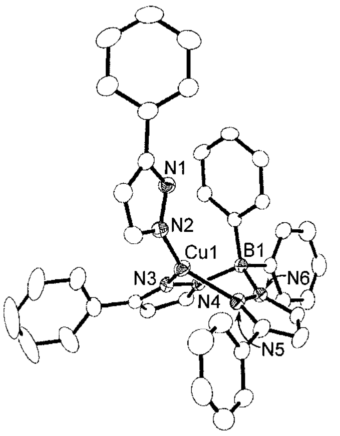


Figure 1. Representation of the X-ray crystal structure of $[Ph_2B(pz^{Ph,H})_2]Cu(Hpz^{Ph,H})\cdot CH_2Cl_2$ as 50% thermal ellipsoids (hydrogen and solvent atoms not shown). Selected interatomic distances (Å) and angles (deg) are as follows: Cu−N2, 1.927(2); Cu−N5, 2.022(2); Cu−N3, 2.006(2); N5−Cu−N2, 128.57(7); N3−Cu−N2, 137.23(7); N3−Cu−N5, 93.98(7).

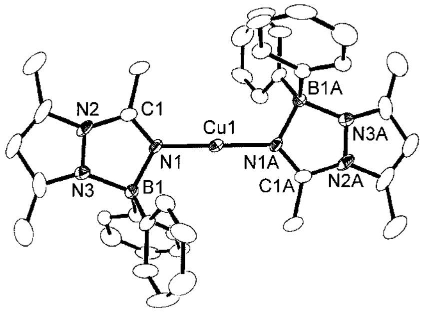
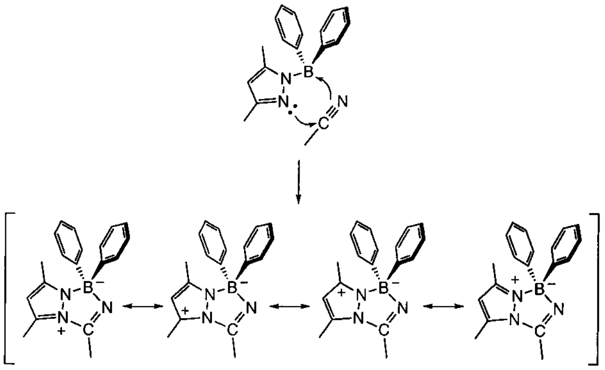


Figure 2. Representation of the cationic portion of the X-ray crystal structure of $[(Ph_2Bpz^{mod})_2Cu]SbF_6\cdot C_7H_8$ as 50% thermal ellipsoids (hydrogen and solvent atoms not shown). Selected interatomic distances (Å) are as follows: Cu−N1, 1.848(6); N1−C1, 1.280(9); N2−N3, 1.357(9); N2−C1, 1.394(9); N3−B1, 1.606(10); N1−B, 1.557(10).

Scheme 2



Three major swaths of frames with 0.30° steps in ω were collected. Space groups for the structures were determined on the basis of systematic absences and intensity statistics, and successful direct-methods solutions were calculated which provided most non-hydrogen atoms. The remaining non-hydrogen atoms were located by several least-squares/difference Fourier cycles. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All calculations were performed with an SGI INDY R4400−SC or a pentium computer using the SHELXTL V5.0 suite of programs.[10] Crystallographic data, details of the handling of disorder, solvation, and/or twinning issues (for the nonmerohedral twin of the dicopper complex specimen using UNTWIN[11]), as well as full tables of bond lengths, bond angles, and thermal and positional parameters are provided as Supporting Information.

Results and Discussion

The ligands $Na[Ph_2B(pz^{R,R'})_2]$ (R = Ph, R′ = H and R = R′ = CH_3) were synthesized by heating neat mixtures of pyrazole and $NaBPh_4$ until a desired amount of benzene was removed by distillation, a method similar to that reported for the preparation of the parent $Na[Ph_2B(pz)_2]$.[4a] While ^1H and $\{^1H\}^{13}C$ NMR spectral and FAB-MS data for the ligands corroborated their formulations, elemental analyses indicated the presence of contaminants. For example, ^1H NMR spectra of samples of $Na[Ph_2B(pz^{CH_3,CH_3})_2]$ clearly showed the presence of varying amounts of $NaBPh_4$ (5−40%). Nevertheless, the ligands were used directly for the synthesis of Cu(I) complexes.

Treatment of $Na[Ph_2B(pz^{Ph,H})_2]$ with $[Cu(CH_3CN)_4]SbF_6$ afforded $[Ph_2B(pz^{Ph,H})_2]Cu(Hpz^{Ph,H})$ (Scheme 1), which was characterized by NMR spectroscopy, FAB-MS, and X-ray diffraction (Figure 1). In addition to the expected bidentate coordination of the bis(pyrazolyl)borate ligand, the trigonal Cu(I) ion is bound to a monodentate pyrazole derived either from the crude starting material or from precedented Cu-mediated cleavage of the pyrazolylborate.[12] Bulk samples were contaminated with small amounts of $[Ph_2B(pz^{Ph,H})_2]Cu(CH_3CN)$ according to ^1H NMR spectroscopy and FAB-MS. Interestingly, the plane of the $Hpz^{Ph,H}$ group in $[Ph_2B(pz^{Ph,H})_2]Cu(Hpz^{Ph,H})$ is perpendicular to the plane of a B-phenyl ring, indicating an edge-face aromatic−aromatic interaction.[13] Consistent with this arrangement in solution, the N−H hydrogen resonance at 9.5 ppm in the ^1H NMR spectrum (CD_2Cl_2) is significantly upfield from its position at 12.5 ppm in free $Hpz^{Ph,H}$ ($CDCl_3$).

In contrast to the reactivity seen for the phenyl-substituted bis(pyrazolyl)borate, treatment of $Na[Ph_2B(pz^{CH_3,CH_3})_2]$ with $[Cu(CH_3CN)]SbF_6$ did not yield the anticipated Cu(I) complex with an η^2-$[Ph_2B(pz^{CH_3,CH_3})_2]^-$ ligand. When toluene was used, the major isolated product instead contained two new N-donor ligands bound to a single Cu(I) ion that adopts a linear coordination geometry (Cu−N = 1.848(6) Å; Figure 2). In the new ligands (pz^{mod}), one pyrazolyl ring is missing from each boron center. In its place, a new heterocycle is present that apparently derives from a cycloaddition of CH_3CN to a B-pyrazolyl unit (Scheme 2). As implied by the indicated resonance structures, we consider the newly formed five membered ring system to be zwitterionic with a negative charge on the boron atom and a positive charge delocalized through the pyrazolyl ring system. In agreement with this bonding description, the N1−C1 [1.280(9) Å] and N2−C1 [1.394(9) Å] bonds reflect double and single bond character, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectral data for the complex in solution are consistent with retention of the structure determined by X-ray crystallographic analysis.

When the synthesis was performed in CH_2Cl_2/toluene (1:1), a mixture of the aforementioned complex $[(Ph_2Bpz^{mod})_2Cu]SbF_6\cdot C_7H_8$ and a second new product was isolated as confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectral and FAB-MS data. An X-ray diffraction analysis revealed that the latter complex,

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(10) *SHELXTL-Plus V5.0*; Siemens Industrial Automation, Inc.: Madison, WI.

(11) *UNTWIN*, V. G. Young, Jr. University of Minnesota, 1997.

(12) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, *32*, 4889−4899.

(13) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23 and references therein.

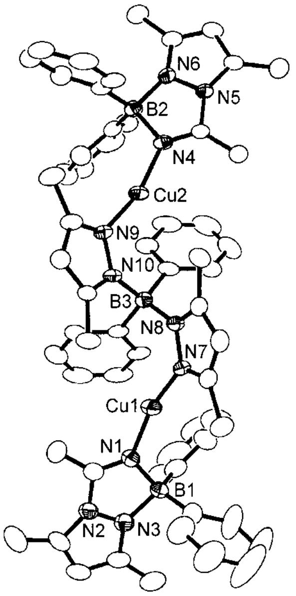

Figure 3. Representation of the cationic portion of the X-ray crystal structure of {(Ph_2Bpz^{mod})Cu[Ph2B(pz^{CH_3,CH_3})$_2$]Cu(Ph_2Bpz^{mod})}SbF_6 as 50% thermal ellipsoids (hydrogen atoms not shown). Selected interatomic distances (Å) and angles (deg) are as follows: Cu1−N1, 1.878(5); Cu1−N7, 1.884(4); Cu2−N4, 1.892(4); Cu2−N9, 1.901(5); N1−Cu1−N7, 159.4(2); N4−Cu2−N9, 160.6(2).

identifiable in the mixture by its different crystal morphology, contained two (pz^{mod})Cu units bridged by a [$Ph_2B(pz^{CH_3,CH_3})_2$]$^-$ ligand (Figure 3; the specimen was a nonmerohedral twin necessitating use of UNTWIN[11] for data correction). Here, the geometry about the two coordinate copper centers is bent [N1−Cu1−N7 = 159.4(2)° and N4−Cu2−N9 = 160.6(2)°], with typical Cu−N distances (avg 1.89 Å). The bent structure appears to be accompanied by weak bonding interactions of the Cu(I) centers with the phenyl rings of the central [$Ph_2B(pz^{CH_3,CH_3})_2$]$^-$ ligand.

To our knowledge, no other crystal structures with the bicyclic ring system found in pz^{mod} have been reported,[14] although related heterocycles with $BNCN_2$ ring systems have been described.[15] Mechanistic information on the formal cycloaddition reaction (Scheme 2) is unavailable, but analogous types of reactions involving additions of nitriles to unsaturated boron fragments provide some precedent.[16] In a test of the need for Cu(I) to mediate the formation of the pz^{mod} unit in the two new complexes, we stirred the starting ligand Na[$Ph_2B(pz^{CH_3,CH_3})_2$] in dry CH_3CN in the absence of added metal salt for 8 h. ^{1}H NMR spectroscopic monitoring showed that the ligand was unperturbed, indicating that Cu(I) is required for the pyrazole loss/cycloaddition reaction to occur. The possible utility of the pz^{mod} unit as a ligand or reagent and explorations of the potential generality of the synthetic route we have discovered are subjects for future research.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes [$Ph_2B(pz^{Ph,H})_2$]Cu($Hpz^{Ph,H}$)·CH_2Cl_2, [(Ph_2Bpz^{mod})$_2$Cu]SbF_6·C_7H_8, and {(Ph_2Bpz^{mod})Cu[$Ph_2B(pz^{CH_3,CH_3})_2$]Cu(Ph_2Bpz^{mod})}SbF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Cambridge Structural Data Base Version 5.1.7, July 1999.

(15) For example, see: (a) Wang, T.-T.; Niedenzu, K. *J. Organomet. Chem.* **1972**, *35*, 231−235. (b) Dewar, M. J. S.; Spanninger, P. A. *Tetrahedron* **1972**, *28*, 959−961. (c) Paetzold, P. I.; Maisch, H. *Chem. Ber.* **1968**, *101*, 2870−2873.

(16) For example, see: (a) Brauer, D. J.; Buchheim-Spiegel, S.; Bürger, H.; Gielen, R.; Pawelke, G.; Rothe, J. *Organometallics* **1997**, *16*, 5321−5330. (b) Witte, H.; Gulden, W.; Hesse, G. *J. Liebigs Ann. Chem.* **1968**, *716*, 1−10.