

Dihydrobis(4-cyano-3-phenylpyrazol-1-yl)borate: Homoleptic Mononuclear Cobalt(II) and Copper(II) Complexes with a Cyano-Substituted Scorpionate Ligand

Christopher J. Siemer,[†] Niranjan Goswami,^{†,‡}
Pawan K. Kahol,[§] Michael J. Van Stipdonk,[†] and
David M. Eichhorn^{*,†}

Departments of Chemistry and Physics,
Wichita State University, Wichita, Kansas 67260-0051

Received March 23, 2001

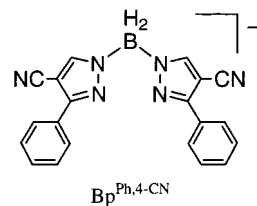
Introduction

Poly(pyrazolyl)borate ligands, or scorpionates, first developed by Trofimenko in the mid-1960s,¹ are bidentate (bis(pyrazolyl)-borate) or tridentate (tris(pyrazolyl)borate) monoanionic ligands, the growing popularity of which stems largely from the relative ease with which one can synthesize pyrazole rings bearing a wide range of substituents at the 3-, 4-, and 5-positions, allowing for the availability of scorpionate ligands with varied steric and electronic characteristics.² As such, scorpionate ligands have been used for a number of different purposes, including bioinorganic models of enzyme active sites,³ polymerization catalysts,⁴ and C–H activation.⁵ The vast majority of scorpionate ligands which have been prepared and studied over the past 35 years contain pyrazole rings with alkyl or aryl groups as substituents. It has been demonstrated that the use of sterically demanding substituents, especially at the 3-position of the pyrazole rings in tris(pyrazolyl)borate ligands, can affect not only the coordination geometry and the types of coordination complexes that can be formed but also the electronic characteristics of the coordinated metal ion.⁶

There are very few examples in the literature of scorpionate ligands incorporating electronically noninnocent substituents.

Included among these are the tris(4-halopyrazolyl)borates⁷ and the bis- and tris(pyrazolyl)borates bearing trifluoromethyl substituents.⁸ With this latter class of ligands, it has been shown that the strongly electron-withdrawing CF₃ substituents reduce the electron density on the coordinated metal ion.^{9,10} We are interested in a related and previously unreported class of scorpionate ligands, with cyano-substituted pyrazole rings. In addition to its strong electron-withdrawing properties, the cyano group, itself, can serve as a ligand to transition metals.¹¹ Thus, metal complexes of cyano-substituted scorpionate ligands can potentially be linked together via coordination of another metal ion to the nitrile groups of the complexes, with a fully conjugated pathway connecting the pyrazole- and nitrile-coordinated metals. Extension of this motif will ultimately result in a coordination polymer in which the intermetallic communication might be expected to yield materials which demonstrate useful bulk properties such as magnetism or conductivity.

During the preparation of this manuscript, a report appeared describing the synthesis of a cyano-substituted bis(pyrazolyl)-borate ligand, Bp^{4CN}, and some mixed-ligand metal complexes thereof.¹² In this report, the authors noted an inability to isolate monomeric homoleptic complexes of this ligand, apparently due to the formation of intractable polymeric species formed by cross-linking via coordination of the CN group to the metal atom of a neighboring (Bp^{4CN})M complex. In this paper, we report the synthesis of a related cyano-substituted scorpionate ligand containing an additional phenyl substituent in the 3-position, Bp^{Ph,4CN}. Unlike the less-substituted Bp^{4CN}, this ligand is capable of forming homoleptic mononuclear complexes, and we report the synthesis and structural characterization of Co(II) and Cu(II) complexes.



Experimental Section

General Methods. All reagents were purchased from Aldrich Chemical Co. or Fisher Scientific and were used as received, unless

* To whom comments should be forwarded at the following address: Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051. Phone: (316) 978-7367. Fax: (316) 978-3431. E-mail: david.eichhorn@wichita.edu.

[†] Department of Chemistry.

[‡] Current address: Kaskaskia College, Centralia, IL 62801.

[§] Department of Physics.

- (1) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842. (b) Trofimenko, S.; *Chem. Rev.* **1993**, *93*, 943. (c) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
- (2) According to the protocol developed by Trofimenko in ref 1c, the bis(pyrazolyl)borate ligands will be referred to as Bp^R, where R represents the substituent in the 3-position (closest to the metal-coordinating nitrogen atom) of the pyrazole. If the pyrazole is disubstituted in the 3- and 5-positions, the ligand will be denoted as Bp^{R2}. A substituent, R', in the 4-position is identified as Bp^{4-R'}.
- (3) (a) Xiao, Z.; Young, C. G.; Enemark, J. H.; Wedd, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 9194. (b) Hikichi, S.; Komatsuzaki, H.; Kitajima, N.; Akita, M.; Mukai, M.; Kitagawa, T.; Moro-oka, Y. *Inorg. Chem.* **1997**, *36*, 266. (c) Kimblin, C.; Parkin, G. *Inorg. Chem.* **1996**, *35*, 6912. (d) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653. (e) Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1995**, *34*, 1632.
- (4) Bloesch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066.
- (5) (a) Ghosh, C. K.; Rodgers, D. P. S.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 1511. (b) Fernandez, M. J.; Rodriguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073.

- (6) (a) Oliver, J. D.; Mullica, D. F.; Hutchinson, B. B.; Milligan, W. O. *Inorg. Chem.* **1980**, *19*, 165. (b) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3158. (c) Eichhorn, D. M.; Armstrong, W. H. *Inorg. Chem.* **1990**, *29*, 3607.
- (7) (a) Trofimenko, S.; Calabrese, P. J.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *29*, 1091. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288. (c) Lobbia, G. G.; Bovio, B.; Santini, C.; Cecchi, P.; Pettinari, C.; Marchetti, F. *Polyhedron* **1998**, *17*, 17.
- (8) (a) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 11408. (b) Han, R.; Ghosh, P.; Desrosiers, P. J.; Trofimenko, S.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1997**, 3713. (c) Rodriguez, V.; Full, J.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *New J. Chem.* **1997**, *21*, 847. (d) Dias, H. V. R.; Huai, L.; Jin, W.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1973. (e) Dias, H. V. R.; Gordon, J. D. *Inorg. Chem.* **1996**, *35*, 318. (f) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **2000**, *39*, 2246. (g) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1997**, *36*, 6205.
- (9) Dias, H. V. R.; Lu, H. *Inorg. Chem.* **1995**, *34*, 21.
- (10) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724.
- (11) (a) Johnson, A.; Taube, H. *J. Indian Chem. Soc.* **1989**, *66*, 503. (b) Angelici, R. J.; Quick, M. H.; Kraus, G. A.; Plummer, D. T. *Inorg. Chem.* **1982**, *21*, 2178.
- (12) Rheingold, A. R.; Incarvito, C. D.; Trofimenko, S. *Inorg. Chem.* **2000**, *39*, 5569.

Table 1. Crystallographic Parameters for **I** and **II**

param	I	II
formula	C ₄₀ H ₂₈ N ₁₂ B ₂ Cu·2CH ₂ Cl ₂	C ₄₀ H ₂₈ N ₁₂ B ₂ Co
fw	931.77	757.29
cryst system	monoclinic	triclinic
space group	P2 ₁ /n (No. 14)	P1̄ (No. 2)
a, Å	9.665(2)	10.434(2)
b, Å	14.009(4)	11.261(2)
c, Å	16.26(1)	18.597(2)
α, deg		74.71(2)
β, deg	104.83(4)	89.84(2)
γ, deg		63.71(2)
V, Å ³	2128(1)	1873.3(8)
Z	2	2
2θ range (deg)	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50
no. reflns	4142	6987
unique reflns (R _{int})	3954 (0.041)	6592 (0.068)
obsd reflns (I > 2σ(I))	3005	4360
temp, °C	−110	−110
λ, Å	0.710 73	0.710 73
ρ _{calc} , g/cm ³	1.454	1.342
μ, cm ^{−1}	8.12	5.06
R ^a	0.039	0.049
R _w ^b	0.039	0.043

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}.$$

otherwise stated. When dry solvents are specified, they were prepared by distillation from Na (THF, toluene, hexanes) or CaH₂ (CH₂Cl₂). NMR spectra were obtained on a Varian Inova 300 MHz or a Varian Inova 400 MHz spectrometer. IR spectra were obtained on a Nicolet Avatar 360 FTIR. EPR spectra were obtained on a Bruker EMX 6/1 spectrometer. Room-temperature magnetic susceptibility data were obtained using a Johnson-Matthey Mb-1 balance, and variable-temperature magnetic susceptibility data were obtained on a force magnetometer built in-house. UV/visible spectra were obtained on a Hitachi U-2010 spectrophotometer. Electrospray mass spectra were obtained on a Finnigan LCQ DECA spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. X-ray data were collected using a Nonius CAD4 diffractometer controlled by a SGI O2 computer, and the structures were solved using the TeXsan package.¹³ X-ray data collection parameters are given in Table 1, and further details are available in the Supporting Information.

Potassium Dihydrobis(4-cyano-3-phenylpyrazolyl)borate (KBp^{Ph,4CN}). A modification of the method of Tupper and Bray was used for the synthesis of 4-cyano-3-phenylpyrazole.¹⁴ A 1.54 g portion of 4-cyano-3-phenylpyrazole (9.11 mmol) was mixed with 246 mg (4.56 mmol) of KBH₄ in a mortar and pestle. The mixture was placed in a round-bottom flask equipped with a water-cooled condenser and heated slowly to 150 °C. As the pyrazole melted, hydrogen evolution was detected. Heating for 2–3 h resulted in the evolution of ≈180 mL of hydrogen and the appearance of a solid residue, which was dissolved in acetonitrile and filtered to remove any unreacted KBH₄. Removal of the solvent by rotary evaporation yielded a viscous yellow oil, which was suspended in boiling toluene to give KBp^{Ph,4CN} as a white powder (1.09 g, 2.82 mmol, 61.6%). Mp: 221 °C. ¹H NMR (acetone-*d*₆, ppm): 8.11 (s, 1H), 7.9–8.0 (m, 2H), 7.2–7.4 (m, 3H). IR (KBr disk, cm^{−1}): 2421 (ν_{BH}, w), 2225 (ν_{CN}, vs). ESI-MS (positive detection, *m/z*): 427, (KBp)K⁺. To 100 mg of KBp^{Ph,4CN} in 2 mL of THF was added a solution of 140 mg of TiNO₃ in 2 mL of H₂O. Extraction into CH₂Cl₂ followed by removal of solvent and washing with Et₂O produced TiBp^{Ph,4CN} as a white powder (80.5 mg, 0.15 mmol, 56%). ¹H NMR (acetone-*d*₆, ppm): 8.22 (s, 1H), 7.8–7.9 (m, 2H), 7.4–7.5 (m, 3H). IR (KBr disk, cm^{−1}): 2464 (ν_{BH}, w), 2388 (ν_{BH}, w), 2330, 2258, 2225 (ν_{CN}, s), 2210 (ν_{CN}, vs).

Bis{dihydrobis(4-cyano-3-phenylpyrazolyl)borato}copper(II) [I, (Bp^{Ph,4CN})₂Cu]. To a solution of KBp^{Ph,4CN} (200 mg, 0.52 mmol) in

5 mL of THF was added a solution of Cu(NO₃)₂·2.5H₂O (60 mg, 0.26 mmol) in 5 mL of THF, resulting in a yellow-brown solution and a white precipitate of KNO₃, which was removed by filtration. Removal of the solvent by rotary evaporation yielded a brown oil. Dissolution in ≈1 mL of THF and addition of 25 mL of CH₂Cl₂ resulted in a yellow solution, leaving behind a small amount of green material. Removal of the solvent from the yellow solution and recrystallization from diethyl ether at −4 °C yielded [(Bp^{Ph,4CN})₂Cu] as yellow crystals (21 mg, 0.028 mmol, 11%).¹⁵ Mp: 186 °C (dec). Anal. Found (calcd for C₄₀H₂₈N₁₂B₂Cu·2CH₂Cl₂): C, 62.88 (63.06); H, 4.00 (3.70); N, 21.92 (22.06). IR (KBr disk, cm^{−1}): 2454 (ν_{BH}, w), 2415 (ν_{BH}, w), 2232 (ν_{CN}, vs). ESI-MS (positive detection, *m/z*): 800, (Bp₂Cu)K⁺; 784, (Bp₂Cu)Na⁺. EPR (CH₂Cl₂/toluene, 121 K): *g*_{||} = 2.23, *g*_⊥ = 2.05, *A*_{||}^{Cu} = 587 MHz, *A*_⊥^N = 51 MHz. Magnetic susceptibility (room temperature, μ_B): 2.15. UV/visible (CH₂Cl₂, nm (M^{−1} cm^{−1})): 250 (7530), 328 (256).

Bis{dihydrobis(4-cyano-3-phenylpyrazolyl)borato}cobalt(II) [II, (Bp^{Ph,4CN})₂Co] and Aquobis{dihydrobis(4-cyano-3-phenylpyrazolyl)borato}cobalt(II) [III, (Bp^{Ph,4CN})₂(H₂O)Co]. To a solution of KBp^{Ph,4CN} (200 mg, 0.52 mmol) in 5 mL of THF was added a solution of Co(NO₃)₂·6H₂O (75 mg, 0.26 mmol) in 5 mL of THF, resulting in a deep blue solution and a white precipitate (KNO₃), which was removed by filtration. Removal of solvent by rotary evaporation yielded a blue oil, which upon dissolution in 40 mL toluene produced a blue solution. Addition of 40 mL of hexanes and cooling to −4 °C overnight resulted in the isolation of [(Bp^{Ph,4CN})₂Co] as blue crystals (64 mg, 0.84 mmol, 33%). Mp: 290 °C. Anal. Found (calcd for C₄₀H₂₈N₁₂B₂Co): C, 63.39 (63.44); H, 3.90 (3.73); N, 21.97 (22.19). IR (KBr disk, cm^{−1}):

2473 (ν_{BH}, w), 2448 (ν_{BH}, w), 2234 (ν_{CN}, vs). ESI-MS (positive detection, *m/z*): 815, (Bp₂Co)Co⁺. Magnetic susceptibility (room temperature, μ_B): 4.29. UV/visible (CH₂Cl₂, nm (M^{−1} cm^{−1})): 252 (27 200), 584 (786). Addition of more hexanes and continued cooling at −4 °C for 1 month resulted in the deposition of red crystals of [(Bp^{Ph,4CN})₂(H₂O)Co]. IR (KBr disk, cm^{−1}): 2485 (ν_{BH}, w), 2418 (ν_{BH}, w), 2229 (ν_{CN}, vs).

Results and Discussion

Syntheses. Synthesis of KBp^{Ph,4CN} was accomplished by heating a mixture of the pyrazole and KBH₄ in a 2:1 ratio at a temperature slightly higher than the melting point of the pyrazole (138 °C) and was confirmed by the presence of a B–H stretch in the IR spectrum as well as the loss of the N–H resonance in the ¹H NMR spectrum. The metal complexes were synthesized by combining THF solutions of the ligand (as either the K or Tl salt) and M(NO₃)₂·*x*H₂O in a 2:1 molar ratio. Isolation and purification of the M(Bp^{Ph,4CN})₂ complexes was accomplished by recrystallization, yielding golden crystals of [Cu(Bp^{Ph,4CN})₂] (**I**) and dark blue crystals of [Co(Bp^{Ph,4CN})₂] (**II**). Attempts to isolate a second crystalline batch of [Co(Bp^{Ph,4CN})₂] by the addition of more heptane resulted not only in the desired crystals but also in the deposition of a red compound, identified by X-ray crystallography as [Co(Bp^{Ph,4CN})₂(H₂O)] (**III**).

The isolation of monomeric homoleptic complexes of Bp^{Ph,4CN} parallels results obtained with Bp ligands bearing only alkyl or aryl substituents^{8e,16} but differs markedly from the reports with Bp^{4CN} in which monomeric complexes could only be isolated by the addition of ancillary ligands such as COD, DMF, or substituted Tp ligands.¹² Apparently, the sterically demanding

(13) TeXsan: Crystal Structure Analysis Package; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.

(14) Tupper, D. E.; Bray, M. R. *Synthesis* **1997**, 337. In this report, the first step was followed by an extraction into water. We found that an extraction into 0.2 M NaOH solution gives increased yields.

(15) This compound can also be crystallized from mixtures of THF/toluene/heptane or CH₂Cl₂/toluene/heptane. The latter solvent system was used to obtain the material used for crystallographic and elemental analyses. A crystal isolated from THF/toluene/heptane mixture was also examined by X-ray crystallography. The structure, although it resisted complete refinement, showed a copper complex which is identical to that in the reported crystal structure, along with a toluene molecule of crystallization instead of CH₂Cl₂. The crystallographic parameters for this crystal were the following: monoclinic P2₁/c; *a*, 11.921 Å; *b*, 17.005 Å; *c*, 23.637 Å; β, 93.40°; *V*, 4783 Å³.

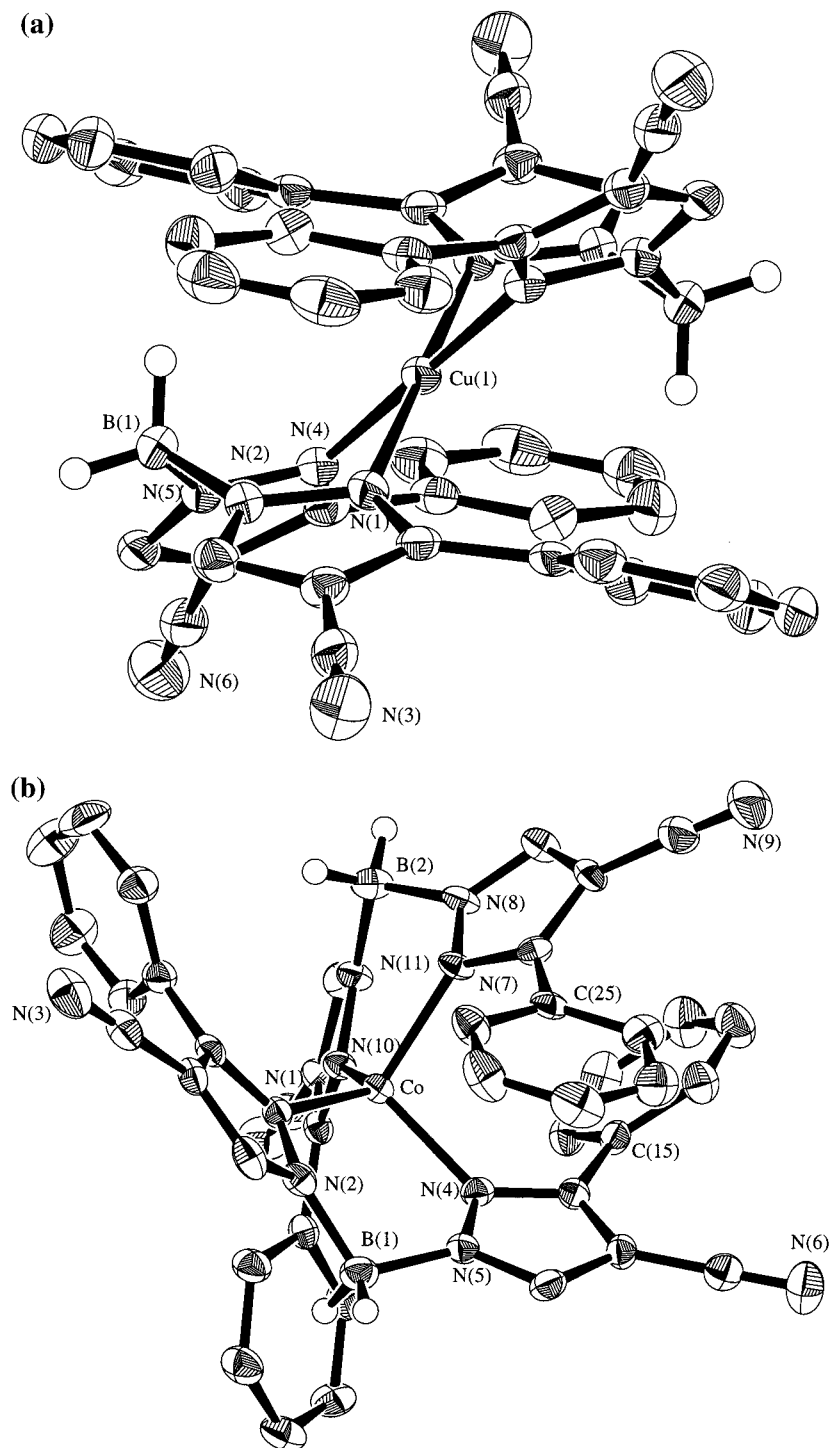


Figure 1. ORTEP diagrams of (a) (Bp^{Ph,4CN})₂Cu (I) and (b) (Bp^{Ph,4CN})₂Co (II) showing 50% thermal ellipsoids. Hydrogen atoms, except B–H hydrogens, have been omitted for clarity.

phenyl substituent blocks the coordination of a cyano group on one complex to the metal atom of a neighboring complex and allows for the isolation of the monomeric Bp₂M complexes.

Structure Descriptions. ORTEP diagrams of compounds I and II are shown in Figure 1, with data collection and refinement parameters in Table 1 and important bond lengths and angles in Table 2. Compound I crystallizes on an inversion center in

the monoclinic space group $P2_1/n$ and was found to contain one CH₂Cl₂ molecule in the asymmetric unit.¹⁵ Each of the ligands is bidentate, forming a six-membered Cu–(N–N)₂–B chelate ring. The chelate rings adopt a boat configuration with a “V-angle” of 124° (180° represents coplanar pyrazole rings). The plane of the four pyrazole N atoms on a single ligand makes a “step angle” of 43.9° with the square-planar CuN₄ coordination sphere. This “stepped square-planar” geometry results in a B–H hydrogen atom from each ligand being situated above and below the CuN₄ plane but at a distance (Cu⋯H = 2.90 Å) too large to be considered bonding. The only other structurally characterized Bp₂Cu complex is Bp^{(CF₃)₂}₂Cu,^{8e} which displays essentially

(16) (a) Guggenberger, L. J.; Prewitt, C. T.; Meakin, P.; Trofimenko, S.; Jesson, J. P. *Inorg. Chem.* **1973**, *12*, 508. (b) Kokusen, J.; Sohrin, Y.; Matsui, M.; Hata, Y.; Hasegawa, H. *J. Chem. Soc., Dalton Trans.* **1996**, 195. (c) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **I** and **II**

I		II	
Cu–N(1)	2.003(3)	Co–N(1)	2.002(3)
Cu–N(4)	2.004(3)	Co–N(4)	2.004(3)
Cu···H(16)	2.902	Co–N(7)	2.029(3)
N(1)–Cu–N(4)	89.67(9)	Co–N(10)	1.980(3)
N(1)–Cu–N(4)*	90.33(9)	N(1)–Co–N(4)	101.2(1)
		N(1)–Co–N(7)	111.1(1)
		N(1)–Co–N(10)	121.4(1)
		N(4)–Co–N(7)	101.0(1)
		N(4)–Co–N(10)	119.6(1)
		N(7)–Co–N(10)	100.8(1)

Table 3. Comparison of Bond Lengths for Co(Bp)₂ Complexes

	Co(Bp) ₂ ^a	Co(Bp ^{Me2}) ₂ ^b	II ^c	Co(Bp ^{Ph}) ₂ ^d
Co–N (Å)	1.97	1.99	2.00	2.01
N···N (Å)	2.95	3.00	3.09	3.13
Co···B (Å)	3.01	3.14	3.25	3.25

^a Reference 16a. ^b Reference 16b. ^c This work. ^d Reference 17.

the same structure with a less planar ligand (V-angle of 109°), a smaller step angle (36.4°), and a shorter (but still nonbonding) Cu···H distance (2.58 Å).

Compound **II** crystallizes on a general position in the triclinic space group *P* $\bar{1}$. This Co(II) complex adopts a tetrahedral geometry, as seen in the related complexes, [(Bp)₂Co]^{16a} and [(Bp^{Me2})₂Co].^{16b} Trofimenko and co-workers have reported the synthesis of [(Bp^{Ph})₂Co],^{16c} and we have completed a crystal structure of this complex for comparison.¹⁷ The metrical parameters of **I** and [(Bp^{Ph})₂Co] are very similar and, by comparison with those of the less highly substituted complexes, show the effect of the relatively bulky phenyl substituent. Although the Co–N bond lengths are not significantly affected, a noticeable lengthening is seen in the distance between the coordinated N atoms of one Bp ligand and in the Co–B distance (Table 3). The V-angle also shows the impact of the 3-substituent, as it increases from 122° in [(Bp)₂Co] to 131° in [(Bp^{Me2})₂Co] and ~150° in the 3-phenyl-substituted compounds.

Spectroscopic and Magnetic Properties. As with most scorpionate ligands, a convenient method by which to follow

the formation of the metal complexes of Bp^{Ph,4CN} is through the B–H stretching frequency in the infrared spectrum. In general, coordination of the scorpionate ligand to a metal ion results in a shift in this frequency. The B–H stretching band occurs at 2421 cm⁻¹ in KBp^{Ph,4CN} and is split and shifted to higher frequencies in the metal complexes. Room-temperature magnetic susceptibility data for **I** are consistent with an *S* = 1/2 system, and variable-temperature magnetic susceptibility data for **II** can be fit to a Curie–Weiss model for an *S* = 3/2 system with *g* = 2.14 and Θ = –6.62 K. The EPR spectrum of **I** is typical of Cu^{II} in a square-planar environment containing four nitrogen donors, displaying an axial spectrum with *g*_{||} > *g*_⊥ > 2 and *g*-values characteristic of stepped square-planar coordination.¹⁸

Conclusions

The two bis(pyrazolyl)borate ligands with cyano substituents, Bp^{4CN} and Bp^{Ph,4CN}, represent two extremes in their metal complexation behavior. While the former is unable to form homoleptic mononuclear complexes, such complexes of the latter ligand are easily isolated. The polymerization via the CN groups of Bp^{4CN} confirms the ability of this CN group to bind to metal ions. Without the protection of a substituent in the 3-position, polymerization proceeds in an uncontrolled manner. However, the ability to isolate homoleptic complexes with Bp^{Ph,4CN} will allow for a rational and controlled synthesis of polymeric materials by reacting these complexes with unhindered metal salts or metal complexes lacking bulky ligands. Preliminary modeling studies suggest that this should be possible, and we are currently investigating this reactivity.

Acknowledgment. We acknowledge the National Science Foundation (Grant No. EPS-9550 487 to D.M.E. and Grant No. EPS-9874 932 to M.J.V.) and matching funds from Wichita State University for funding of this research.

Supporting Information Available: Crystallographic data in CIF format and X-ray experimental details, an ORTEP drawing, and data collection and metrical parameters for **III**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC010316N

(17) Siemer, C. J.; Meese, F. A.; Armstrong, W. H.; Eichhorn, D. M. *Polyhedron*, in press.

(18) Herring, F. G.; Patmore, D. J.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1975**, 711.