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Organo-Tricyanoborates as Tectons: Illustrative Coordination Polymers Based on Copper(I) Derivatives

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The first systematic study on the use of tricyanoborates as ligands is presented. The tricyanoborates $[RB(CN)_3]^-$ (R = oct and Ph) can be prepared by direct cyanation of $RBCl_2$ precursors as well as by thermolysis of the corresponding isocyanides $[RB(NC)_3]^-$. The first organo-cyanogallates $[RGa(CN)_3]^-$ (R = Bu, C_6H_2-2,4,6-Me_3) were prepared from the corresponding dichloride, the structure of $Et_4N[mesGa(CN)_3]$ being confirmed crystallographically. The reaction of equimolar $[RB(CN)_3]^-$ (R = oct, Ph) and $[Cu(MeCN)_4]^+$ afforded two-dimensional polymers $[RB(CN)_3Cu(NCMe)]$. The sheets arise via conjoined hexagonal $B_3Cu_3(CN)_6$ rings with chair conformations. The reaction of excess $[PhB(CN)_3]^-$ and $[Cu(MeCN)_4]^+$ gives the polymer $[K(18\text{-crown-}6)]\{Cu[PhB(CN)_3]_2\}$. Treatment of $[PhB(CN)_3]^-$ with $[Cu(PCy_3)_2(NCMe)_x]PF_6$ gave the one-dimensional polymer $[PhB(CN)_3Cu(PCy_3)_2]$, wherein two of the three BCN substituents are coordinated.

Introduction

Of perennial interest for the design of molecular cages are modular precursors—tectons or building blocks—that have geometrically well-defined linking tendencies.[1] Systematic modification of these subunits promises to enable the synthesis of molecules with tailored host−guest behavior. Within the context of host−guest behavior, cyanometalates have been heavily studied.[2,3] For example, the Hoffmann salts $Ni(NH_3)_2Ni(CN)_4$, derived from $[Ni(CN)_4]^{2-}$, are amine-pillared two-dimensional sheets, which selectively bind aromatic guests (Figure 1A).[4] Similarly, various Prussian Blue analogues, which commonly have defects and vacancies, have been employed for K^+/Cs^+ and CH_4/CO_2 separations.[2,5] Less studied but relevant to this work are the layered cyanocuprates $[Cu_2(CN)_3]^-$.[6] Mixed-ligand cyanometalates generate interesting coordination polymers, some of which

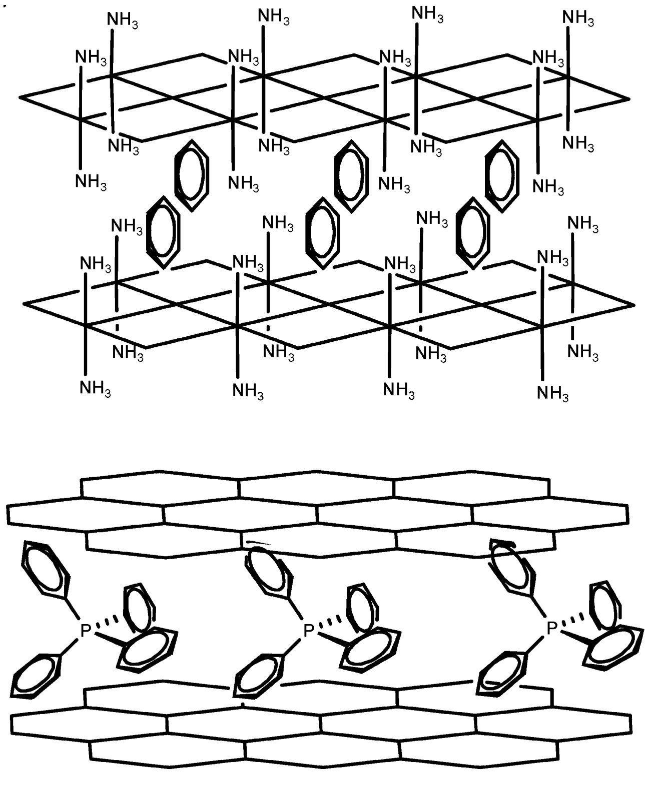

Figure 1. Schematic views of the Hoffmann-benzene clathrate $[Ni(NH_3)_2Ni(CN)_4]$ (top) and of $PPh_4[Cu_2(CN)_3]$ (bottom). The vertexes represent metal atoms (Ni^{2+}, Cu^+), and the lines represent μ-CN groups.

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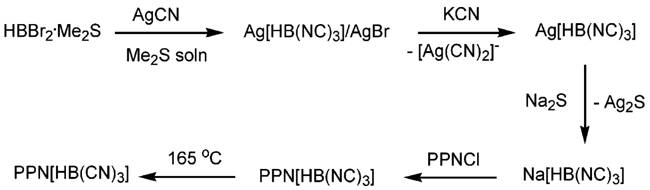
also exhibit host−guest behavior.[7] Mixed-ligand cyanometalates also form discrete cages,[8,9] which can exhibit highly selective host−guest behavior reminiscent of the parent solid-state materials.[10,11]

Previous work on molecular tricyanometalates has emphasized cuboidal cages.[9,10,12] These box-like structures are a natural consequence of the ∼90° NC−M−CN angles of the tricyanometalate precursors. In an effort to develop new structural families of cyanometalate cages, we sought tricyano building blocks with NC−M−CN angles > 90°. Such building blocks could, for example, stabilize adamantanoid cages. Our attention was drawn to the recently reported coordination solid {Ag[FB(CN)$_3$]}, formed from the reaction of AgNO$_3$, NaF, and K[B(CN)$_4$].[13] We decided to examine the coordination chemistry of a range of [RB(CN)$_3$]$^-$ precursors, which we envisioned could be synthesized with diverse substituents (H, alkyl, aryl) for use as building blocks. The promise of this approach is illustrated by our recent synthesis of the hexagonal prism {[PhB(CN)$_3$]$_6$[RhCp*]$_6$}$^{6+}$.[14] Although salts of [B(CN)$_4$]$^-$ have been well-studied,[15−18] fewer of the tricyanoborates are known; these include Na[HB(CN)$_3$],[18] M[BF(CN)$_3$] (M = Li, K),[17] and Me$_3$SiNCBF(CN)$_3$.[17] Only limited coordination chemistry has been reported for the tricyanides.

Results and Discussion

Synthesis of [RB(CN)$_3$]$^-$ and [RB(NC)$_3$]$^-$. The basic chemistry of [HB(CN)$_3$]$^-$ has been developed by Györi et al., who synthesized this anion via a multistep process that begins with the reaction of HBBr$_2$ and AgCN.[18,19] Conversion of the resulting coordination polymer Ag[HB(NC)$_3$][18] into the more soluble Na$^+$ salt via reduction with metallic Na proved difficult to reproduce. We found, however, that sodium sulfide smoothly and quantitatively converted Ag[HB(NC)$_3$] into the desired Na[HB(NC)$_3$]. This sodium salt was transformed into the air-stable salt PPN[HB(NC)$_3$] (PPN = [N(PPh$_3$)$_2$]$^+$), which, in refluxing Bu$_2$O, rearranged into PPN[HB(CN)$_3$] (Scheme 1).

Scheme 1



The previously rare[20] *organo*cyanoborates can be prepared by the AgCN route via the organo-triisocyanoborate, Et$_4$N[PhB(NC)$_3$], which was fully characterized. Direct cyanation with KCN is easier, however. Thus, [K(18-crown-6)][PhB(CN)$_3$] was synthesized via the reaction of PhBCl$_2$ and 3 equiv of KCN in the presence of the crown ether in a THF solution. This air-stable colorless salt was purified chromatographically and characterized by electrospray ionization mass spectrometry (ESI-MS) as well as by ^{1}H and ^{11}B NMR spectroscopy. The octyl analogue, [K(18-crown-6)][octB(CN)$_3$], was prepared and characterized similarly.

Characterization of Et$_4$N[PhB(CN)$_3$] and Et$_4$N[PhB(NC)$_3$]. To further distinguish the isomeric boron tricyanides and triisocyanides, we examined the Et$_4$N$^+$ salts of the Ph derivatives of both. Regarding the IR spectra, ν_{CN} for Et$_4$N[PhB(CN)$_3$] is weak but occurs at a higher frequency than Et$_4$N[PhB(NC)$_3$] (Figure 2), consistent with the literature,[18,19] and as also seen for PPN[HB(CN)$_3$] and PPN[HB(NC)$_3$]. The ^{13}C NMR spectrum of Et$_4$N[PhB(CN)$_3$] showed a ^{11}B-coupled quartet (J = 66 Hz) at δ 130 assigned to B*C*N. For comparison, J(B,C) coupling in [BF$_n$(CN)$_{4-n}$]$^-$ ranges from 71 to 90 Hz,[17] but no such coupling was observed for Et$_4$N[PhB(N*C*)$_3$]. These two compounds are further distinguished by their ^{11}B NMR spectra, the cyanide and isocyanide displaying singlets at δ −28.6 and −13.4, respectively.

Synthesis of [RGa(CN)$_3$]$^-$ (R = Bu, C$_6$H$_2$-2,4,6-Me$_3$). Both Ga(CN)$_3$ and salts of [Ga(CN)$_4$]$^-$ are known,[21] but otherwise, no work has been reported on the organic derivatives. We attempted to prepare [BuGa(CN)$_3$]$^-$ using [K(18-crown-6)]CN and BuGaCl$_2$. ESI-MS analysis showed,

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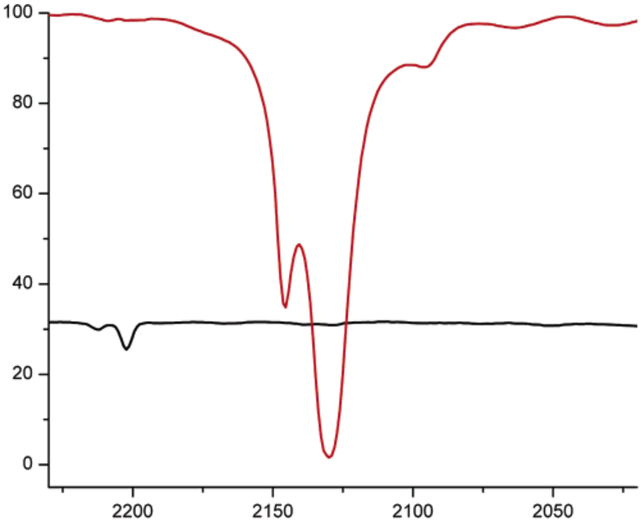

Figure 2. IR spectra of $[Et_4N][PhB(NC)_3]$ (top, red) and $[Et_4N][PhB(CN)_3]$ (bottom, black) (0.1M sample of MeCN solution).

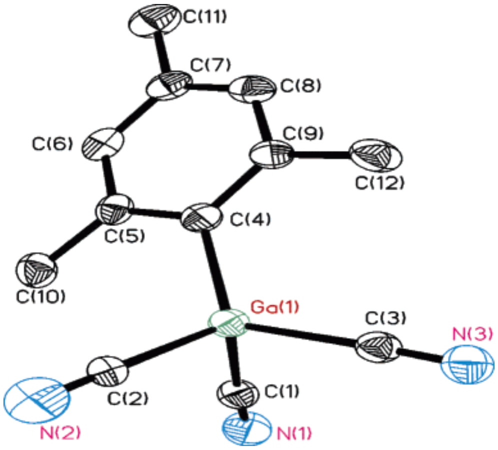

Figure 3. Molecular structure of the anion in $Et_4N[mesGa(CN)_3]$. Thermal ellipsoids are drawn at the 35% level (N = blue, C = gray, and Ga = green). Selected distances and angles: C4−Ga1−C1, 111.24(8); C4−Ga1−C2, 118.82(8); C2−Ga1−C1, 101.47(9); C4−Ga1−C3, 116.22(9); C2−Ga1−C3, 101.30(9); C1−Ga1−C3, 106.03(9); N1−C1−Ga1, 176.0(2); N2−C2−Ga1, 177.5(2); N3−C3−Ga1, 178.1(2). Ga−C1, 1.997(2); Ga1−C2, 1.996(2); Ga1−C3, 2.019(2); Ga1−C4, 1.971(2); C1−N1, 1.139(3); C2−N2, 1.130(3); C3−N3, 1.074(3).

however, that even after 10 days in a refluxing THF solution, the mixture consisted mainly of the chlorides $[BuGaCl_3]^-$, $[BuGa(CN)Cl_2]^-$, and $[BuGa(CN)_3Cl]^-$, together with $[BuGa(CN)_3]^-$. The butyl and mesityl (mes) derivatives could be more readily prepared using Et_4NCN in a THF solution. The pure cyanogallates are relatively air-stable, although the purification of these salts required an anaerobic technique. Solutions of $Et_4N[BuGa(CN)_3]$ in MeCN are sensitive to H_2O.

The organo-tricyanogallium salts displayed the expected IR, ESI-MS, and ^1H and ^{13}C NMR spectroscopic signatures. Crystallographic characterization of $Et_4N[mesGa(CN)_3]$ confirmed that the gallium is tetrahedral (Figure 3) with an average Ga−CN distance of 2.003(2) Å, which is shorter than that in $[Cs(PhMe)_2\{CN(GaMe_3)_2\}]$ [2.086(6) Å].[22]

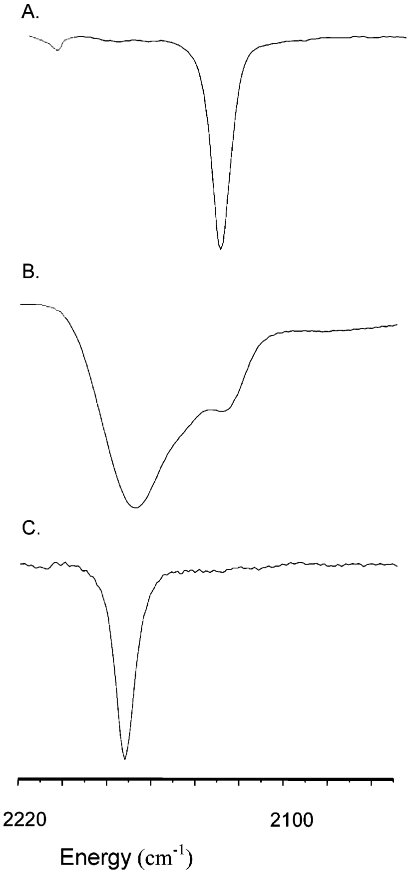

Figure 4. IR spectra of $[K(18\text{-crown-}6)][PhB(CN)_3]$ (A), $[PhB(CN)_3Cu(PCy_3)_2]$ (B), and $[PhB(CN)_3Cu(NCMe)]$ (C), all in KBr.

Reaction of $[RB(CN)_3]^-$ (R = H, octyl, Ph) and $[Cu(NCMe)_4]^+$. Reaction of $PPN[HB(CN)_3]$ with $[Cu(NCMe)_4]PF_6$ in MeCN solution gave an insoluble precipitate from which single crystals could not be obtained. For this reason, we focused on the organoborate derivatives.[23]

Treatment of a MeCN solution of $[Cu(NCMe)_4]PF_6$ with 1 equiv of $[K(18\text{-crown-}6)][PhB(CN)_3]$ gave a white solid, which indeed proved slightly soluble in MeCN. The IR spectrum of this solid features a single ν_{CN} band at 2173 cm^{-1}, which is shifted to higher energy by 38 cm^{-1} versus $[K(18\text{-crown-}6)][PhB(CN)_3]$, consistent with the coordination of cyanide ligands (Figure 4). Note that in such species, the ν_{CN} band for MeCN is usually weak and often not observed. Single crystals, obtained by cooling a hot MeCN extract, were characterized by X-ray diffraction. The solid has the formula $[PhB(CN)_3Cu(NCMe)]\cdot 0.5MeCN$ and adopts a two-dimensional sheetlike structure. The sheets are formed by conjoining $B_3Cu_3(CN)_6$ hexagons, where the cyanides form the edges and the copper and boron are alternating vertexes (Figure 5). The hexagons adopt a shallow chair conformation, reflecting the tetrahedral nature of the boron and copper sites, the latter also bearing a MeCN ligand. A comparable chair conformation is adopted also by the $Rh_3B_3(CN)_3$ rings in

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(23) General comments on metrical data: bond angles and distances are supplied in the Supporting Information but reveal normal N−Cu (1.96−2.07 Å), B−C (1.56−1.60 Å), and Cu−P (2.30 Å) distances. Correspondingly, the N−Cu−N and C−B−C angles reflect the tetrahedral geometry (99−118°) for the boron and copper(I) centers.

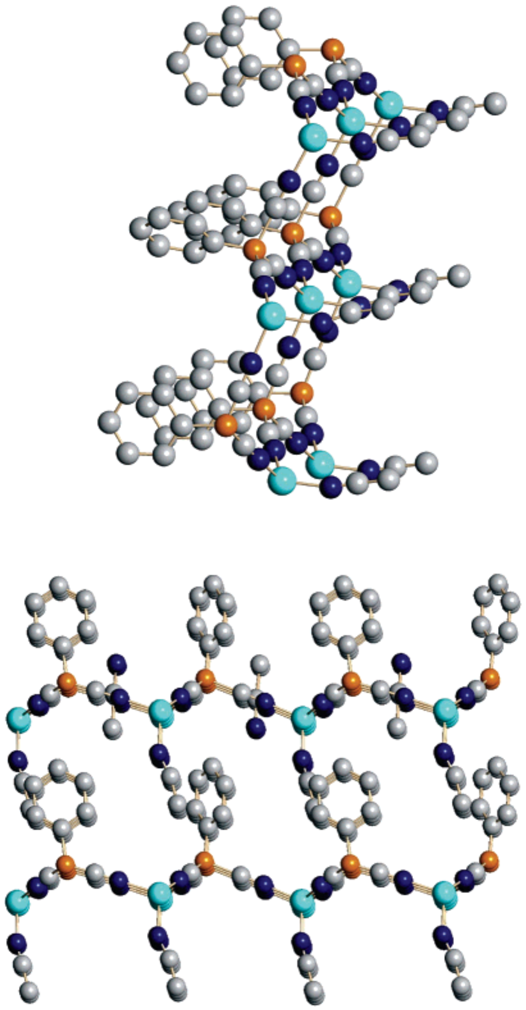

Figure 5. Top: Fragment of the two-dimensional sheet of [PhB(CN)$_3$Cu(NCMe)] (MeCN of solvation not shown). Bottom: the extended structure of [PhB(CN)$_3$Cu(NCMe)]. MeCN molecules of solvation are included in the top layer but are omitted from the bottom sheet for clarity. N = blue, C = gray, Cu = light blue, and B = orange.

the molecular prism $\{[\mathrm{PhB(CN)_3}]_6[\mathrm{RhCp^*}]_6\}^{6+}$.[14] Examination of the extended unit cell reveals that the $Cu_3B_3(CN)_6$ hexagons are eclipsed with respect to the other sheets, resulting in hexagonal channels. These channels are occupied with noncoordinated molecules of MeCN (Figure 6). The structure is polar in the sense that the phenyl groups project from the same relative side of the sheets along the *a* axis. Heating a slurry of [PhB(CN)$_3$Cu(NCMe)] in refluxing PhCN produced [PhB(CN)$_3$Cu(NCPh)], characterized by the appearance of a new ν_{CN} band at 2234 cm^{-1}. A single $\nu_{\mathrm{B}CN}$ band at 2173 cm^{-1} was observed for [PhB(CN)$_3$Cu(NCPh)], as in [PhB(CN)$_3$Cu(NCMe)].

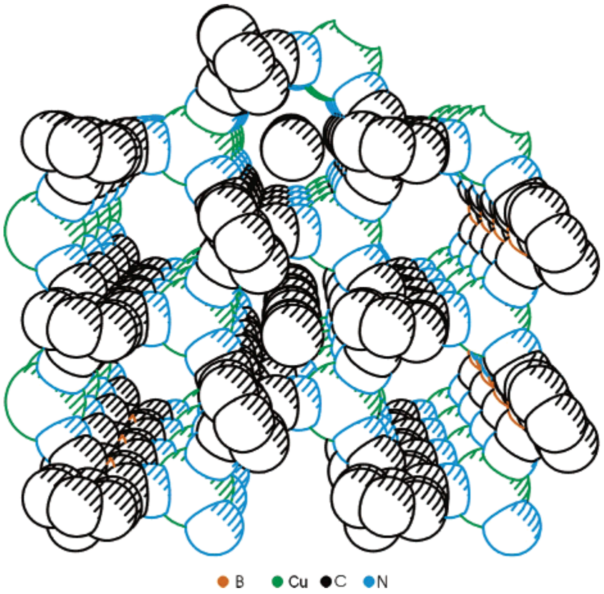

Figure 6. Space-filling model for [PhB(CN)$_3$Cu(NCMe)]·0.5MeCN. The MeCN solvate molecules are omitted from half of the channels for clarity. Hydrogen atoms are not shown.

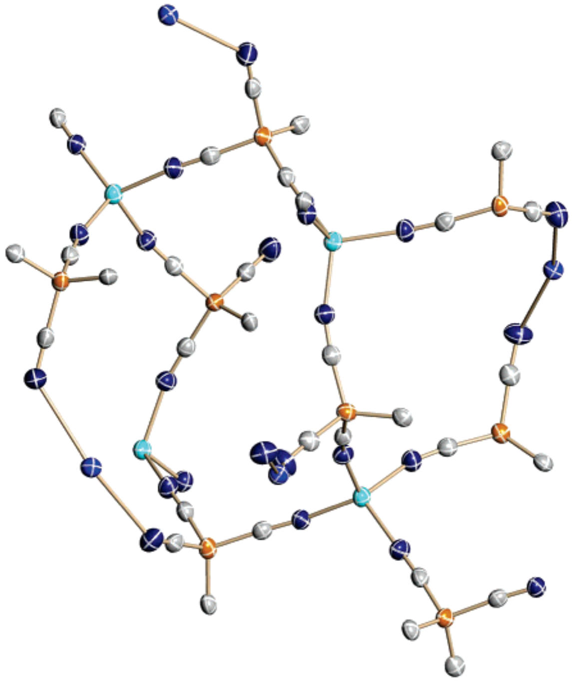

Figure 7. Extended structure of Cu[PhB(CN)$_3$]$_2$[K(18-crown-6)]·MeCN showing the $B_4Cu_4(CN)_8$ pseudo-octagons. MeCN solvate, 18-crown-6, and phenyl rings are omitted for clarity; N = blue, C = gray, B = orange, Cu = light blue, and K = light blue.

The product of the reaction of [Cu(NCMe)$_4$]PF$_6$ and [K(18-crown-6)][PhB(CN)$_3$] proved sensitive to stoichiometry. When the Cu/B ratio > 1, only the aforementioned [PhB(CN)$_3$Cu(NCMe)] precipitated from the solution; however, at Cu/B = 0.5, we obtained a colorless homogeneous solution. The ^{1}H NMR spectrum showed the presence of one crown ether for two Ph groups, consistent with the crystallographically established formula {[K(18-crown-6)][PhB(CN)$_3$]$_2$Cu}·MeCN. One of the three C*N* units on each boron is bound to K$^+$, which is 8-coordinated, which explains the observation of a single ν_{CN} band (2164 cm^{-1}) in the IR spectrum of [PhB(CN)$_3$Cu(NCMe)]. The remaining B(C*N*)$_2$ units link tetrahedral Cu centers to give a three-dimensional network formed by conjoined $B_4Cu_4(CN)_8$ pseudo-octagons (Figure 7).

To investigate the effect of the organic substituents on the coordination properties of the organo-tricyanoborates, we examined the interaction of [K(18-crown-6)][octB(CN)$_3$] and [Cu(NCMe)$_4$]PF$_6$. Predictably, this condensation produced a poorly soluble solid analyzing as [octB(CN)$_3$Cu(NCMe)]-

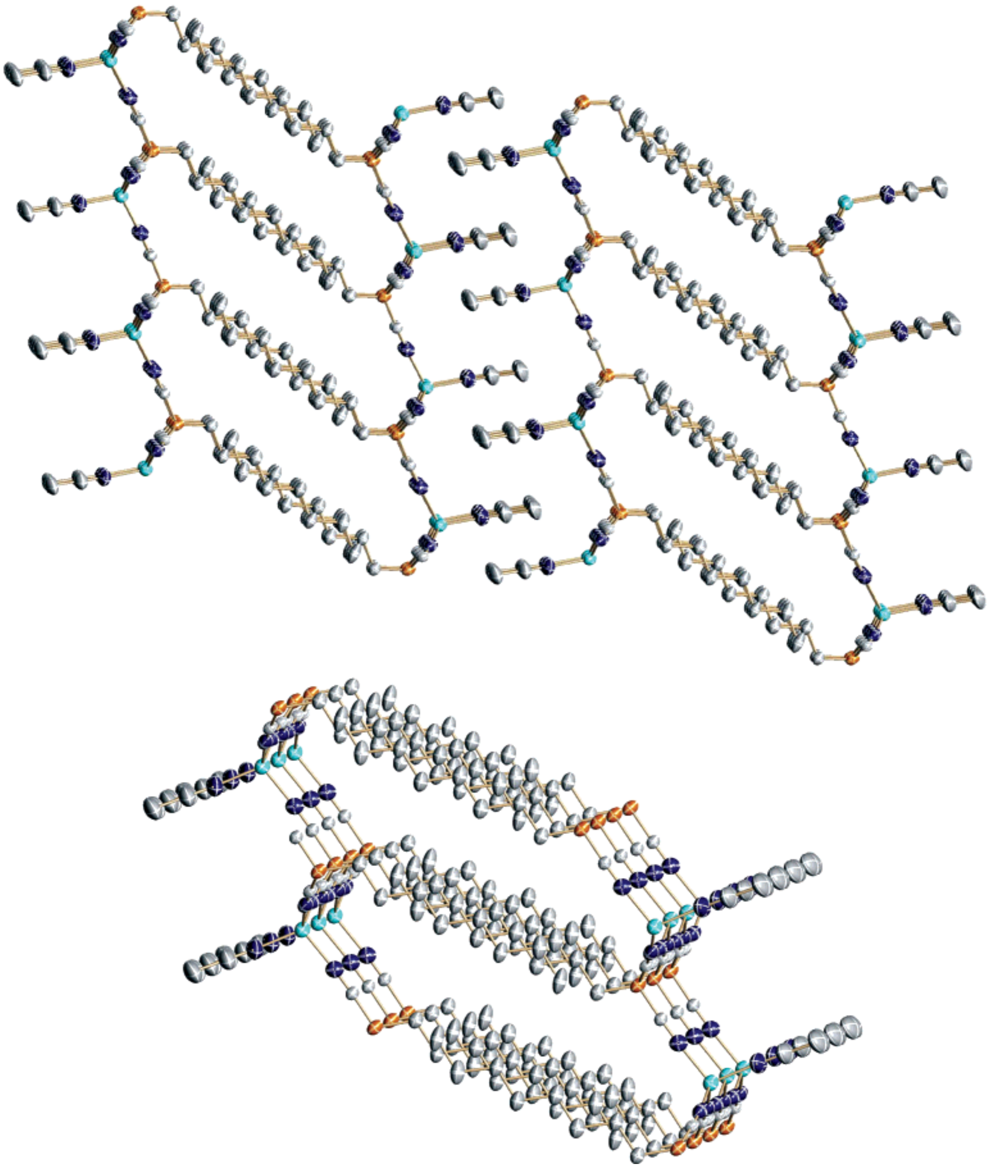

Figure 8. Two views of the structure of [octB(CN)$_3$Cu(NCMe)] highlighting the interdigitation of the octyl substituents. Thermal ellipsoids are drawn at the 50% level (N = blue, C = gray, Cu = light blue, and B = orange).

·MeCN. Single crystals of this solid could be obtained by slowly cooling hot MeCN extracts. X-ray crystallographic analysis again revealed a sheetlike hexagonal sheet with a tiling pattern closely resembling that for [PhB(CN)$_3$Cu(NCMe)] (Figure 8). In contrast to the phenyl derivative, the octyl structure is nonpolar. The octyl substituents from adjacent sheets interdigitate. The packing of these octyl chains seals off the channels that are more accessible in the related [PhB(CN)$_3$]$^-$ derivative. On the opposite sides of these hexagonal sheets, the Cu−NCMe groups similarly interdigitate, although less deeply, with those on the adjacent CuB(CN)$_3$ sheet. Noncoordinated molecules of MeCN occupy sites between the nitrile ligands.

Attempts to prepare Cu$^+$ derivatives of [RGa(CN)$_3$]$^-$ were disappointing. Following the protocols described above, colorless precipitates were obtained from a MeCN solution, but the IR spectra of these solids exhibited several bands in the ν_{CN} region, suggesting that the Ga−CN bonds are not robust.

Interaction of [PhB(CN)$_3$]$^-$ and [Cu(PCy$_3$)$_2$(NCMe)$_x$]$^+$. Treatment of MeCN solutions of [K(18-crown-6)][PhB(CN)$_3$] with 1.33 equiv of [Cu(PCy$_3$)$_2$(NCMe)$_x$]PF$_6$ gave a colorless precipitate. The IR spectrum of this solid revealed ν_{CN} bands at 2173 and 2129 cm^{-1}, the latter of which is comparable to the ν_{CN} for [K(18-crown-6)][PhB(CN)$_3$] (2135 cm^{-1}, see Figure 4), indicative of noncoordination. The IR spectrum in this region was unchanged for the solid and THF solution. The ^{1}H NMR spectrum of this THF-soluble species features one set of phenyl signals and two distinct sets of cyclohexyl signals. The ^{31}P NMR spectrum also reveals two signals indicating inequivalent phosphine ligands.

Single-crystal X-ray analysis of [PhB(CN)$_3$Cu(PCy$_3$)$_2$] revealed a one-dimensional polymer (Figure 9). The proposed polymer model includes disordered positions for one phenyl and two cyclohexyl groups. Two cyanide substituents of [PhB(CN)$_3$]$^-$ are coordinated, the third being free, giving a linear polymer with a syndiotactic configuration. The Cu−N and B−C distances are typical bond lengths for Cu−N and

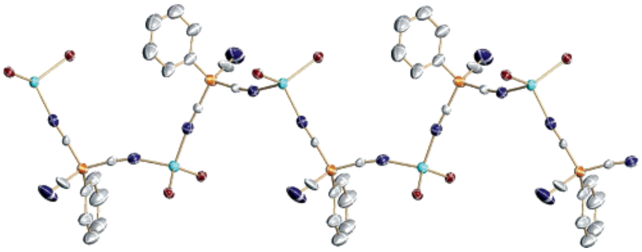

Figure 9. One-dimensional chain of $[PhB(CN)_3Cu(PCy_3)_2]$. Thermal ellipsoids are drawn at the 50% level. Cyclohexyl substituents are omitted for clarity; N = blue, C = gray, Cu = light blue, P = red, and B = orange.

B−C with distances of 2.05−2.07 and 1.59−1.62 Å, respectively.[24] Darensbourg et al. have described molecular rings based on cyanide coordination to Cu(I) phosphine centers.[25]

Interaction of $[RB(NC)_3]^-$ (R = H, Ph) and $[Cu(NCMe)_4]^+$. Reaction of MeCN solutions of $[Cu(NCMe)_4]PF_6$ with the isocyanide $Et_4N[PhB(NC)_3]$ resulted in the formation of a white solid. The reaction of $[Cu(NCMe)_4]PF_6$ with $PPN[HB(NC)_3]$ gave similar results. The IR spectrum of this product features a ν_{CN} band at 2158 cm^{-1}, which is shifted higher in energy relative to the anionic isonitrile (2128 cm^{-1}). Diffraction quality crystals could not be obtained. Refluxing the solid in Bu_2O for 10 h did not effect conversion of this Cu-triisocyanoborate into $[PhB(CN)_3Cu(NCMe)]$, as judged by IR spectroscopy. Thus, coordination inhibits the rearrangement of the BNC unit.

Summary

Organo-tricyanoborates represent a promising family of ligands for the directed synthesis of coordination cages and solids. Unlike the tris(pyrazolyl)borates,[26] the tricyanoborates are incapable of chelation but instead promote the formation of polynuclear derivatives. These molecular tectons are readily prepared from $RBCl_2$, of which many examples are known or can be made by hydroboration.[27] Isomeric with the tricyanides are the triisocyanoborates, which have a fascinating chemistry in their own right,[18,19] but thus far, a limited coordination chemistry.[28] The second route to cyanoborates entails direct cyanation of $RBCl_2$ precursors. This methodology can be applied to the preparation of related gallium species, although in our hands, this species did not form well-defined complexes.[29]

The present work illustrates the use of the organoboron tricyanides as precursors to coordination polymers. The new polymers are two-dimensional, in contrast to $CuB(CN)_4$.[16]

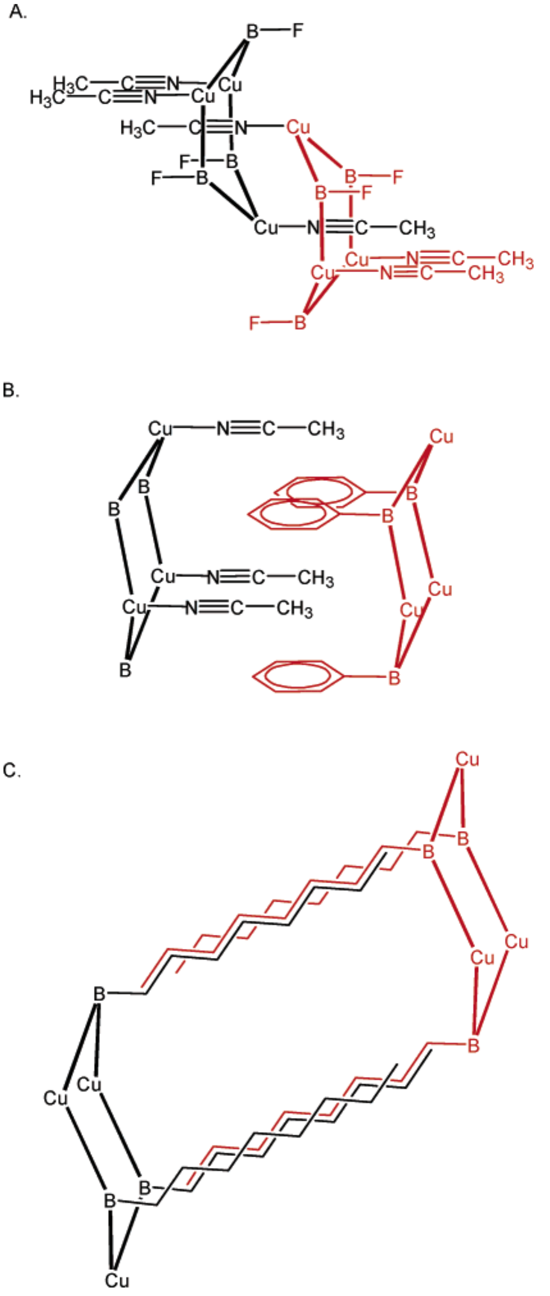

Figure 10. Schematic representation of the intersheet interactions in $[RB(CN)_3Cu(NCMe)]$ for R = F (A), Ph (B), and oct (C).

The small but significant solubility of these coordination polymers is attributed to the ability of MeCN to compete with the Cu···$NCBR_3$ interactions. Three related but differing structural motifs are exhibited for the Cu^+ derivatives of $[RB(CN)_3]^-$, for R = F, Ph, and octyl. In all three cases, sheetlike structures arise through edge-sharing of hexagonal $B_3Cu_3(CN)_6$ rings. Hexameric cyanometalates are precedented in $[Cu(CN)(PPh_3)_2]_6$.[6] In the $[PhB(CN)_3]^-$ and $[octB(CN)_3]^-$ derivatives, these hexagonal rings adopt chair conformations and, further, are eclipsed relative to the adjacent sheets. The previously reported $[FB(CN)_3Cu(NCMe)]$[13] is also best described as being two-dimensional (Figure 10). In contrast to the *organo*borates, the $B_3Cu_3(CN)_6$ rings in the *fluoro*borate adopt the boat conformation, and

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rings on one sheet are staggered with respect to the next, allowing the Cu−NCMe groups to penetrate the hexagonal rings.

Materials and Methods

General. Standard Schlenk techniques were employed in all syntheses. $PhBCl_2$, $octBCl_2$, $BuGaCl_2$,[30] $MesGaCl_2$,[31] $Me_2S{\cdot}BHBr_2$, and AgCN were prepared according to literature methods or purchased from Aldrich. The purity of the 18-crown-6 is important in reactions involving borane precursors. PPN[HB(CN)$_3$] was prepared by a modification of the published procedure. Other synthetic protocols have been previously described.[32] Elemental analyses were conducted by the School of Chemical Sciences Microanalytical Laboratory. ^{11}B, ^{13}C, and ^{1}H NMR spectra were acquired on Varian Unity 300, 400, and 500 NMR spectrometers. Infrared spectra were acquired on a Mattson Infinity Gold FTIR spectrometer using CaF_2 solution cells or with KBr pellets. Electrospray ionization mass spectrometry (ESI-MS) and MS-MS measurements were acquired using a Micromass Quattro QHQ quadrupole−hexapole−quadrupole instrument.

Ag[HB(NC)$_3$]. In an adaptation of the procedure from Györi et al.,[18] a solution of 5.880 g (25.17 mmol) of $Me_2S{\cdot}BHBr_2$ in 15 mL of Me_2S was added dropwise to an ice-cooled solution of 10.107 g (75.51 mmol) of AgCN in 40 mL of Me_2S. The slurry was stirred overnight, and the resulting gray solid was collected on a medium-porosity frit. The orange filtrate was diluted with 100 mL of Et_2O to precipitate a white powder, which was collected on the same frit. The combined gray solid was suspended in 300 mL of H_2O. A solution of 3.272 g (50.34 mmol) of KCN in 150 mL of H_2O was added over the course of 30 min. The resulting slurry was sonicated, and the fine white powder of the desired product was then collected on a medium-porosity frit. Yield: 4.89 g (98%). IR (KBr, cm^{-1}): $\nu_{CN} = 2185$, $\nu_{BH} = 2482$. Anal. Calcd for $C_3H_1N_3AgB$ (found): C, 18.22 (23.99); H, 0.51 (1.89); N, 21.25 (18.35). This impure material was used in the next step.

PPN[HB(NC)$_3$]. A solution of 2.979 g (12.42 mmol) of $Na_2S{\cdot}9H_2O$ in 100 mL of H_2O was added dropwise to a solution of 4.891 g (24.81 mmol) of crude Ag[HB(NC)$_3$] in 100 mL of H_2O. The resulting gray-black slurry was stirred for 4 h before filtering off the black Ag_2S. The filtrate was concentrated to 30 mL and treated with a solution of 14.221 g (24.81 mmol) of PPNCl in 3 L of H_2O. The resulting white precipitate was collected by filtration and air-dried. Yield: 9.451 g (61%). ^{1}H NMR (THF): δ 2.56 (q, 1H), 7.64 (m, 30H). ^{11}B NMR (CD_3CN): δ −20.1. ESI-MS: *m/z* 90.4. IR (KBr, cm^{-1}): $\nu_{CN} = 2128$, $\nu_{BH} = 2446$. Anal. Calcd for $C_{39}H_{31}N_4BP_2$ (found): C, 74.54 (73.24); H, 4.97 (4.87); N, 8.92 (8.24).

PPN[HB(CN)$_3$]. A suspension of 5.230 g (1.211 mmol) of the aforementioned, slightly impure PPN[HB(NC)$_3$] in 100 mL of Bu_2O was heated to 120 °C, while open to air to allow the evaporation of H_2O. The flask was then fitted with a water-cooled condenser, and the solution was heated at reflux for 24 h. The cooled slurry was filtered on a medium porosity frit. Yield: 5.121 g (98%). ^{1}H NMR (THF): δ 1.76 (q, 1H), 7.63 (m, 30H). ^{11}B NMR (CD_3CN): δ −40.16. ESI-MS: *m/z* 90.4. IR (KBr, cm^{-1}): $\nu_{CN} = 2209$, $\nu_{BH} = 2393$. Anal. Calcd for $C_{39}H_{31}N_4BP_2$ (found): C, 74.54 (74.28); H, 4.97 (4.91); N, 8.92 (8.85).

[K(18-crown-6)][PhB(CN)$_3$]. A finely ground sample of 5.21 g (80 mmol) of KCN in a 1-L flask was dried at 100 °C under dynamic vacuum for 20 h. The cooled sample was treated with a solution of 6.1 g (23.1 mmol) of 18-crown-6 in 350 mL of THF. This mixture was refluxed for 20 h, cooled to 0 °C, and then treated with a solution of 2.66 mL (20 mmol) of $PhBCl_2$ in 80 mL of cold (0 °C) THF. The reaction mixture was heated at reflux for 72 h and then allowed to cool. The resulting reaction mixture was filtered through Celite in air. The filtrate was evaporated to dryness, and the resulting crude solid was washed with Et_2O. Approximately 7 g of crude material was extracted into 10 mL of CH_2Cl_2, and this solution was passed through a 15 × 2.5 cm column of acidic alumina (activity 90, 70−230 mesh) followed by a washing with a further 200 mL of CH_2Cl_2. The filtrate was evaporated to dryness, and the residue was recrystallized by extraction into 10 mL of MeCN followed by the addition of 80 mL of Et_2O. Yield: 5.95 g (63%). ^{1}H NMR (CD_3CN): δ 7.49 (m, 2H, C_6H_5), 7.29 (m, 2H, C_6H_5), 7.22 (m, 1H, C_6H_5), 3.55 (s, 24H, OCH_2CH_2O). ^{13}C NMR (CD_3CN): δ 133 (C_6H_5), 129 (C_6H_5), 128 (C_6H_5), 129−131 (q, $J_{B-C} = 65$ Hz, CN), 70.7 (OCH_2CH_2O). ^{11}B NMR ($CDCl_3$): δ −28.5 (s). ESI-MS: *m/z* 166.1. IR (CH_3CN, cm^{-1}): $\nu_{CN} = 2135$. Anal. Calcd for $C_{21}H_{29}N_3BKO_6$ (found): C, 53.74 (53.35); H, 6.23 (6.22); N, 8.95 (8.82).

Et_4N[PhB(CN)$_3$]. A suspension of 1.69 g (10.8 mmol) of Et_4NCN in 60 mL of THF was treated with a solution of 0.48 mL (3.6 mmol) of $PhBCl_2$ in 30 mL of cold (0 °C) THF. The reaction mixture was heated at reflux for 70 h and then allowed to cool. The resulting reaction mixture was filtered through Celite in air. The filtrate was evaporated to dryness, and the resulting crude solid was washed with Et_2O and then extracted with 10 mL of acetone. The acetone extract was concentrated to ∼5 mL and then diluted with 20 mL of H_2O to precipitate a yellow solid. The crude product was dried under a vacuum and crystallized from MeCN−Et_2O. Approximately 450 mg of crude material was extracted into 2 mL of CH_2Cl_2, and this solution was passed through a 15 × 2.5 cm column of acidic alumina (activity 90, 70−230 mesh) followed by a washing with a further 60 mL of CH_2Cl_2. The filtrate was evaporated to dryness, and the residue was recrystallized by extraction into 4 mL of MeCN by the addition of 30 mL of Et_2O. Yield: 0.23 g (22%). ^{1}H NMR (CD_3CN): δ 7.48 (m, 2H, C_6H_5), 7.29 (t, 2H, C_6H_5), 7.22 (t, 1H, C_6H_5), 3.13 (q, 8H, CH_2), 1.18 (m, 12H, CH_3). ^{13}C NMR (CD_3CN): δ 133.4 (C_6H_5), 139.5−141.2 (q, C_6H_5, $J_{BC} = 56$ Hz), 129.0−131.0 (q, CN, $J_{BC} = 66$ Hz), 129.0 (C_6H_5), 127.8 (C_6H_5), 52.9 (CH_2), 7.6 (CH_3). ^{11}B NMR ($CDCl_3$): δ −28.6 (s). ESI-MS: *m/z* 166.1 (M$^-$), 130.5 (M$^+$). IR (KBr, cm^{-1}): $\nu_{CN} = 2203$, 2212. Anal. Calcd for $C_{17}H_{25}N_4B$ (found): C, 68.93 (68.83); H, 8.51 (8.63); N, 18.91 (18.47).

[K(18-crown-6)][octB(CN)$_3$]. A 500 mL flask was charged with 3.65 g (56 mmol) of finely powdered KCN and heated at 100 °C under a vacuum for 18 h. After cooling to ambient temperature, the flask was charged further with 4.1 g (15.5 mmol) of 18-crown-6 and 250 mL of THF. The mixture was stirred at reflux for 10 h and then cooled to 0 °C. A solution of 2.8 g (14.4 mmol) of $octBCl_2$ in 70 mL of THF (0 °C) was added, and the reaction mixture was brought to reflux. After 72 h, the cooled reaction mixture was filtered through Celite in air. Evaporation of the filtrate gave an oily residue, which was extracted with 100 mL of Et_2O, the evaporation of which gave a light yellow oil, which was washed with hexane several times. A solution of the crude oil in 5 mL of CH_2Cl_2 was passed through a 15 cm column of alumina, eluting with 1:6 hexane−CH_2Cl_2. Evaporation of the eluate gave a white solid, which was recrystallized from Et_2O−hexane. Yield: 3.3 g (44%). ^{1}H NMR (500 MHz, CD_3CN): δ 3.56 (s, 24H, OCH_2CH_2O),

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Table 1. Crystallographic Data for $Et_4N[MesGa(CN)_3]$, $2[PhB(CN)_3]_2Cu(NCMe)]\cdot MeCN$, $Cu[PhB(CN)_3]_2[K(C_{12}H_{24}O_6)](CH_3CN)$, $[octB(CN)_3Cu(NCMe)]\cdot MeCN$, and $[PhB(CN)_3Cu(PCy_3)_2$

parameter	$Et_4N[mesGa(CN)_3]$	$2[PhB(CN)_3]_2Cu(NCMe)]\cdot MeCN$	$Cu[PhB(CN)_3]_2[K(C_{12}H_{24}O_6)]\cdot MeCN$
chemical formula	$C_{20}H_{31}GaN_4$	$C_{24}H_{19}B_2Cu_2N_9$	$C_{37}H_{19}B_2CuKN_7O_6$
T (K)	193(2)	193(2)	193(2)
cryst. size (mm^3)	0.48 × 0.46 × 0.01	0.27 × 0.18 × 0.10	0.08 × 0.10 × 0.60
space group	*Pbca*	*Pm*	*pbca*
a (Å)	10.442(2)	8.464(5)	13.387(2)
b (Å)	15.998(4)	7.613(5)	15.805(3)
c (Å)	25.863(6)	13.176(8)	35.961(6)
α (deg)	90	90	90
β (deg)	90	90.482(9)	90
γ (deg)	90	90	90
V ($Å^3$)	4320.5(16)	849(9)	7609(2)
Z	8	1	8
D_{calcd} ($mg\ m^{-3}$)	1.221	1.139	1.292
μ (Mo Kα, mm^{-1})	1.283	1.277	0.732
reflns measured/ independent	45 788/3967	8816/3328	60 872/6975
data/restraints/params	3967/0/234	3328/57/111	6975/0/443
GOF	1.021	0.919	1.021
R_{int}	0.0511	0.1809	0.0783
R_1 [$I > 2\sigma$] (all data)[a]	0.0285 (0.0488)	0.0948 (0.2367)	0.0398 (0.0734)
wR_2 [$I > 2\sigma$] (all data)[b]	0.0779 (0.0850)	0.2165 (0.2699)	0.0837 (0.0934)
max. peak/hole ($e^-/Å^3$)	0.381/−0.225	1.437/−0.529	0.378/−0.207
descriptor	$[octB(CN)_3Cu(NCMe)]\cdot MeCN$	$[PhB(CN)_3Cu(PCy_3)_2]$	

parameter	$Et_4N[mesGa(CN)_3]$	$2[PhB(CN)_3]_2Cu(NCMe)]\cdot MeCN$
chemical formula	$C_{15}H_{23}BCuN_5$	$C_{45}H_{71}BCuN_3P_2$
T (K)	193(2)	293(2)
cryst. size (mm^3)	0.48 × 0.46 × 0.01	0.60 × 0.10 × 0.03
space group	*C*2/*m*	*P2*(1)/*n*
a (Å)	12.874(4)	14.591(9)
b (Å)	7.821(3)	14.190(8)
c (Å)	21.225(7)	21.788(12)
α (deg)	90	90
β (deg)	106.493(5)	98.372(11)
γ (deg)	90	90
V ($Å^3$)	2049.3(12)	4463(4)
Z	4	4
D_{calcd} ($mg\ m^{-3}$)	1.127	1.176
μ (Mo Kα, mm^{-1})	1.068	0.594
reflns measured/ independent	8122/2020	35 624/8201
data/restraints/params	2020/178/215	8201/398/637
GOF	0.969	0.954
R_{int}	0.0939	0.1149
R_1 [$I > 2\sigma$] (all data)[a]	0.0492 (0.0860)	0.0529 (0.1217)
wR_2 [$I > 2\sigma$] (all data)[b]	0.0996 (0.1095)	0.0988 (0.1186)
max peak/hole ($e^-/Å^3$)	0.525/−0.258	0.366/−0.336

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

1.28 (m, 12H, Me(C*H*$_2$)$_7$B), 0.87 (t, 3H, C*H*$_3$(CH$_2$)$_7$B), 0.42 (t, 2H, Me(C*H*$_2$)$_7$B). ^{13}C NMR (CD_3CN): δ 130.1−131.5 (q, BCN), 70.9 (OCH_2CH_2O), 33.5, 32.6, 30.3, 30.1, 28.5, 27.2, 23.3, 14.4 (octyl). ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −30.2 (s). ESI-MS: *m*/*z* 202.2 (M^-), 303.4 (M^+). IR (CH_3CN, cm^{-1}): $\nu_{CN} = 2132$. Anal. Calcd for $C_{23}H_{41}N_3BKO_6$ (found): C, 54.65 (54.55); H, 8.18 (8.26); N, 8.31 (8.11).

$Et_4N[PhB(NC)_3]$. To a solution of 9.1 g (67.8 mmol) of AgCN in 35 mL of Me_2S was slowly added a solution of 3.58 g (22.6 mmol) of $PhBCl_2$ in 10 mL of Me_2S at 0 °C. After stirring the mixture at room-temperature overnight, the solids were filtered off. The yellow filtrate was added dropwise to 25 mL of diglyme at 80 °C over the course of 2 h and using a fast N_2 stream to remove the Me_2S. The pale powder was collected by filtration and washed with Et_2O. A suspension of the solid in 10 mL of H_2O was added to a solution of 3.52 g of KCN (54 mmol) in 5 mL of H_2O. After 15 min, the product was collected by filtration, washed with 5 mL of H_2O, and dried under a vacuum at 100 °C to give 5.85 g of colorless $AgPhB(NC)_3$. To a suspension of the entire portion of $AgPhB(NC)_3$ in 20 mL of H_2O was added 2.57 g (21.4 mmol) of $Na_2S\cdot 9H_2O$ in 20 mL of H_2O. After stirring overnight, the suspension was filtered to remove black Ag_2S. To this filtrate was added a solution of 3.6 g (17.12 mmol) of Et_4NBr in 10 mL of H_2O. The resulting white solid was collected by filtration, washed with H_2O, and crystallized with acetone/H_2O to give colorless crystals. Yield: 2.2 g (33%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, 2H, C$_6$*H*$_5$), 7.30 (t, 2H, C$_6$*H*$_5$), 7.26 (t, 1H, C$_6$*H*$_5$), 3.07 (q, 8H, MeC*H*$_2$N), 1.23 (m, 12H, C*H*$_3$CH$_2$N). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 165.6 (CN), 142.0 (broad, BC_6H_5), 130.4 (C_6H_5), 127.2 (C_6H_5), 51.8 (CH_2), 6.8 (CH_3). ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −13.4 (s). ESI-MS: *m*/*z* 166.5 (M^-), 130.5 (M^+). IR (KBr, cm^{-1}): $\nu_{CN} = 2145$, 2126. Anal. Calcd for $C_{17}H_{25}N_4B$ (found): C, 68.93 (68.53); H, 8.51 (8.55); N, 18.91 (18.44).

$[PhB(CN)_3Cu(PCy_3)_2]$. A solution of 218 mg (0.833 mmol) of PCy_3 in 10 mL of MeCN was added dropwise to a solution of 155 mg (0.417 mmol) of $[Cu(NCMe)_4]PF_6$ in 5 mL of MeCN. After 1 h, this solution was treated with a solution of 196 mg (0.417 mmol) of [K(18-crown-6)][$PhB(CN)_3$] in 10 mL of MeCN, resulting in the immediate formation of a white precipitate. The solid was collected by filtration and washed with 20 mL of MeCN. Yield: 256 mg (82%). ^{1}H NMR (500 MHz, THF): δ 1.34 (m, 31H), 1.83 (m, 31H), 7.16 (m, 1H), 7.22 (m, 2H), 7.53 (m, 2H). ^{31}P NMR (125.7 MHz, THF): δ 16.2, 14.7. IR (KBr, cm^{-1}): $\nu_{CN} = 2173$, 2129. Anal. Calcd for $C_{45}H_{71}N_3BCuP_2$ (found): C, 68.38 (67.56); H, 9.05 (9.14); N, 5.32 (5.49). Crystals were obtained by layering a solution of 30 mg of [PhB(CN)$_3$Cu(PCy$_3$)$_2$] in 3 mL of THF with 8 mL of hexanes.

[PhB(CN)$_3$Cu(NCMe)]. A solution of 80 mg (0.214 mmol) of [Cu(NCMe)$_4$]PF$_6$ in 10 mL of MeCN was added dropwise to a solution of 100 mg (0.214 mmol) of [K(18-crown-6)][PhB(CN)$_3$] in 10 mL of MeCN. The resulting colorless precipitate was collected by filtration and washed with MeCN. Yield: 49 mg (85%). IR (KBr, cm^{-1}): $\nu_{CN} = 2173$. Anal. Calcd for $C_{11}H_8N_4BCu$ (found): C, 48.83 (47.69); H, 2.98 (2.50); N, 20.70 (18.34). Crystals were obtained by refluxing 30 mg of [PhB(CN)$_3$Cu(NCMe)] in 10 mL of MeCN followed by slowly cooling this solution to room temperature.

[K(18-crown-6)]Cu[PhB(CN)$_3$]$_2$. A solution of 141 mg (0.3 mmol) of [K(18-crown-6)][PhB(CN)$_3$] in 10 mL of MeCN was added dropwise to a solution of 56 mg (0.15 mmol) of [Cu(NCMe)$_4$]PF$_6$ in 10 mL of MeCN. After stirring for 4 h, the reaction solution was concentrated to ~5 mL, and this solution was layered with 10 mL of Et$_2$O. Colorless needlelike crystals formed over the course of 72 h. Yield: 86 mg (82%). ^{1}H NMR (500 MHz, CD$_3$CN): δ 3.56 (s, 24H), 7.23 (m, 2H), 7.30 (m, 4H), 7.47 (m, 4H). IR (KBr, cm^{-1}): $\nu_{CN} = 2164$. Anal. Calcd for $C_{30}H_{34}N_6B_2CuKO_6$ (found): C, 51.56 (51.68); H, 4.90 (4.90); N, 12.02 (12.95). Single crystals were obtained upon addition of Et$_2$O to the MeCN solution.

[octB(CN)$_3$Cu(NCMe)]. A solution of 192 mg (0.515 mmol) of [Cu(NCMe)$_4$]PF$_6$ in 15 mL of MeCN was added dropwise to a solution of 260 mg (0.515 mmol) of [K(18-crown-6)][octB(CN)$_3$] in 15 mL of MeCN, resulting in the immediate precipitation of a white solid, which was filtered and washed with MeCN. Yield: 121 mg (77%). IR (KBr, cm^{-1}): $\nu_{CN} = 2167$. Anal. Calcd for $C_{13}H_{20}N_4BCu$ (found): C, 50.91 (50.15); H, 6.57 (6.46); N, 18.26 (17.42). Crystals were obtained by extracting 30 mg of [octB(CN)$_3$Cu(NCMe)] with 10 mL of MeCN followed by slowly cooling the extract to room temperature.

Et$_4$N[BuGa(CN)$_3$]. A 500 mL flask was charged with a solution of 6.41 g of Et$_4$NCN (41 mmol) in 200 mL of THF followed by a solution of 2.685 g (13.6 mmol) of BuGaCl$_2$ in 30 mL of THF. The reaction mixture was heated to reflux. After 4.5 days, the reaction mixture was allowed to cool to room temperature and was filtered under nitrogen. The filtrate was evaporated under a vacuum, and the oily residue was washed with two 30 mL portions of Et$_2$O and dried under a vacuum. Yield: 4 g (88%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 2.40 (q, $J = 7$ Hz, 8H, MeCH_2N), 1.74 [m, 2H, Me(CH_2)$_3$Ga], 1.47 [m, 2H, $J = 7.5$ Hz, CH$_3$(CH_2)$_3$Ga], 0.92 [t, 3H, $J = 7.5$ Hz, CH_3(CH$_2$)$_3$Ga], 0.73 [t, 2H, $J = 8$ Hz, CH_3(CH$_2$)$_3$Ga], 0.68 (m, 12H, CH_3CH$_2$N). ^{13}C NMR (125.6 MHz, d^8-THF): δ 131.8 (CN), 53.01 (Et$_4$N), 29.4, 27.7, 14.2 (Bu), 9.7 [Me(CH$_2$)$_2$CH$_2$-Ga], 7.7 (Et$_4$N). ESI-MS: m/z 204.2 (M$^-$). IR (THF, cm^{-1}): $\nu_{CN} = 2169$. Anal. Calcd for $C_{15}H_{29}N_4Ga$ (found): C, 53.76 (53.14); H, 8.72 (8.67); N, 16.72 (16.59).

Et$_4$N[mesGa(CN)$_3$]. A 500 mL flask was charged with 4.69 g (30 mmol) of Et$_4$NCN in 250 mL of THF followed by a solution of 2.60 g (10 mmol) of mesityl GaCl$_2$ in 50 mL of THF. The reaction mixture was heated to reflux. After 9 days, the reaction mixture was allowed to cool to room temperature and was then filtered under nitrogen. The filtrate was concentrated to ~80 mL under a vacuum, and the resulting solid was filtered off. The volume of filtrate was further concentrated to 20 mL before being diluted with 100 mL of Et$_2$O, which precipitated a colorless solid, which was collected by filtration. Yield: 3.05 g (77%). ^{1}H NMR (500 MHz, d^8-THF): δ 6.72 (s, 2H, C$_6H_2$), 3.29 (q, $J = 7$ Hz, 8H, MeCH_2N), 2.47 (s, 6H, ArCH_3), 2.19 (s, 3H, ArCH_3), 1.28 (m, 12H, CH_3CH$_2$N). ^{13}C NMR (125.6 MHz, d^8-THF): δ 145.8, 138.2, 135.5 (CN), 133.0, 128.2, 53.01 (Et$_4$N), 21.2 (CH$_3$ of ArCH_3), 7.6 (Et$_4$N). ESI-MS: m/z 266.4 (M$^-$). IR (THF, cm^{-1}): $\nu_{CN} = 2170$. Anal. Calcd for $C_{20}H_{31}N_4Ga$ (found): C, 60.48 (59.46); H, 7.87 (7.82); N, 14.11 (13.31).

Crystallography. Crystals were mounted on thin glass fibers using Paratone-N oil (Exxon) before being transferred to a Siemens Platform/CCD automated diffractometer for data collection. Data processing was performed with SAINT PLUS, version 6.22. Structures were solved using direct methods and refined using full-matrix least squares on F^2 using the Bruker program SHELXTL, version 6.10. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.5× those of the attached carbon atoms. The data were corrected for absorption on the basis of Ψ scans. Details for each crystal are given in Table 1.

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Supporting Information Available: Crystallographic files (CIF) for Et$_4$N[mesGa(CN)$_3$], [PhB(CN)$_3$Cu(NCMe)], [octB(CN)$_3$Cu(NCMe)], [PhB(CN)$_3$Cu(PCy$_3$)$_2$], and [K(18-crown-6)]{Cu[PhB(CN)$_3$]$_2$} (see also CCDC 253992−253995 and 264411). This material is available free of charge via the Internet at http://pubs.acs.org.

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