Structural Diversity in a Family of Copper(I) Thioether Complexes

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Copper(I) complexes of the tridentate thioether ligands $[PhB(CH_2SCH_3)_3]$ (abbreviated PhTt), $[PhB(CH_2SPh)_3]$ ($PhTt^{Ph}$), $[PhB(CH_2S^tBu)_3]$ ($PhTt^{tBu}$), and $[PhB(CH_2S^pTol)_3]$ ($PhTt^{pTol}$) and bidentate thioether ligands $[Ph_2B(CH_2SCH_3)_2]$ (Ph_2Bt), $[Et_2B(CH_2SCH_3)_2]$ (Et_2Bt), and $[Ph_2B(CH_2SPh)_2]$ (Ph_2Bt^{Ph}) have been prepared and characterized. The solution and solid state structures are highly sensitive to the identity of the borato ligand employed. Ligands possessing the smaller (methylthio)methyl donors, [PhTt] and $[Ph_2Bt]$, yielded tetrameric species, $[(PhTt)Cu]_4$ and $[(Ph_2Bt)Cu]_4$, containing both terminal and bridging thioether ligation. The ligands containing the larger (arylthio)methyl groups, $[PhTt^{Ph}]$ and $[PhTt^{pTol}]$, form monomeric $[PhTt^{Ar}]Cu(NCCH_3)$ in solution and one-dimensional extended structures in the solid state. Each complex type reacted cleanly with acetonitrile, pyridine, or triphenylphosphine generating the corresponding four-coordinate monomer, of which $[PhTt^{Ph}]Cu(PPh_3)$, $[PhTt^{pTol}]Cu(PPh_3)$, and $[Et_2Bt]Cu(PPh_3)_2$ have been structurally characterized.

Introduction

In our continued exploration of the coordination and bioinorganic chemistry of the borato ligand class $PhB(CH_2SR)_3^-$ (abbreviated $[PhTt^R]$),[1−3] we report the preparation, characterization, and reactivity of a family of copper(I) complexes. Significant features of the $[PhTt^R]$ ligands include the anionic charge provided by the borate, the high polarizability of the thioether donors, which contrasts the hard nitrogen donors of the ubiquitous [Tp] ligands, and, most importantly, the synthetic versatility that permits incorporation of a range of boron and sulfur substituents.[4] Indeed, there is now ready preparative access to tridentate, $[PhTt^R]$, and bidentate, $[Ph_2Bt^R]$,[5] derivatives complemented with a range of alkyl and aryl thioether groups. The resulting $[S_3]$ and $[S_2]$ donor sets impart unique electronic and molecular structural properties to the attendant metal complexes. Herein are reported the solution and solid state structures for copper(I) complexes of the following ligands: [PhTt], $[PhTt^{Ph}]$, $[PhTt^{pTol}]$, $[PhTt^{tBu}]$, $[Ph_2Bt]$, $[Et_2Bt]$, and $[Ph_2Bt^{Ph}]$, Chart 1.[6,7] For each ligand a complex of 1:1 empirical stoichiometry was isolated. Solid state structures are highly ligand dependent ranging from monomers, $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$, to cyclic tetramers, $[(PhTt)Cu]_4$ and $[(Ph_2Bt)Cu]_4$, to extended chain structures, $[(PhTt^{Ph})Cu]_\infty$, $[(PhTt^{pTol})Cu]_\infty$, and $[(PhTt^{tBu})Cu]_x$. Nonetheless, each complex serves as a source of monomeric $[PhTt^R]Cu$ or $[Ph_2Bt^R]Cu$ for binding the donors acetonitrile, pyridine, and triphenylphosphine.

Results and Discussion

Ligand Syntheses. The newly reported ligands, $[PhTt^{pTol}]$, $[Ph_2Bt^{Ph}]$, and $[Et_2Bt]$, were prepared following procedures developed in these laboratories for [PhTt], $[PhTt^{tBu}]$, $[PhTt^{Ph}]$, and $[Ph_2Bt]$.[1,2] Briefly, the appropriate methyl sulfide was quantitatively deprotonated by BuLi in the presence of TMEDA. To this solution was added either $PhBCl_2$, for preparation of the tridentate ligands, or Ph_2BBr or $Et_2B(OTs)$, for preparation of the bidentate ligands. Isolation entailed precipitation of the $[Bu_4N]$ salt. In some instances, e.g., $[PhTt^{tBu}]$, greater yields were achieved using cesium or thallium counterions. In general, the yields of the bidentate ligands were significantly higher than those for the corresponding tridentate ligand. Nonetheless, each ligand may be prepared in multigram quantities. All ligands are stable to air and moisture and freely soluble in THF, acetone, acetonitrile, and chlorinated hydrocarbons. Spectroscopic data and elemental analysis are contained in the Experimental Section.

$[(PhTt)Cu]_4$ and $[(PhTt^{Ph})Cu]_\infty$. The syntheses and structures of $[(PhTt)Cu]_4$ and $[(PhTt^{Ph})Cu]_\infty$, reported previously, highlight the structural diversity of this class of copper(I) complexes, Scheme 1.[6,7] In $[(PhTt)Cu]_4$ each copper ion is ligated by four thioethers in a roughly tetrahedral arrangement. Two sulfurs are ligated terminally while the other two are bridging between two adjacent metal ions. The solid state structure persists in noncoordinating solvents. In chlorinated hydrocarbons, the proton NMR spectrum of $[(PhTt)Cu]_4$ clearly supports the solid state structure. The terminal and bridging thioethers are present as distinct sets of resonances. Coordinating solvents or strong donor ligands such as phosphines or thiolates disrupt the tetramer, yielding monomers of the composition [PhTt]Cu(L).[6] $[(PhTt^{Ph})Cu]_\infty$ forms a one-dimensional infinite chain structure in the solid state. Each copper ion is approximately four coordinate. Two sulfur donors are provided by a single borato ligand while the third sulfur donor arises from a second, adjacent borato unit. The copper ion coordination sphere is completed by an η^2-phenyl interaction from the latter ligand; the η^2-phenyl group coordinated through the ipso and one of the ortho carbon atoms. Again, in coordinating solvents or in

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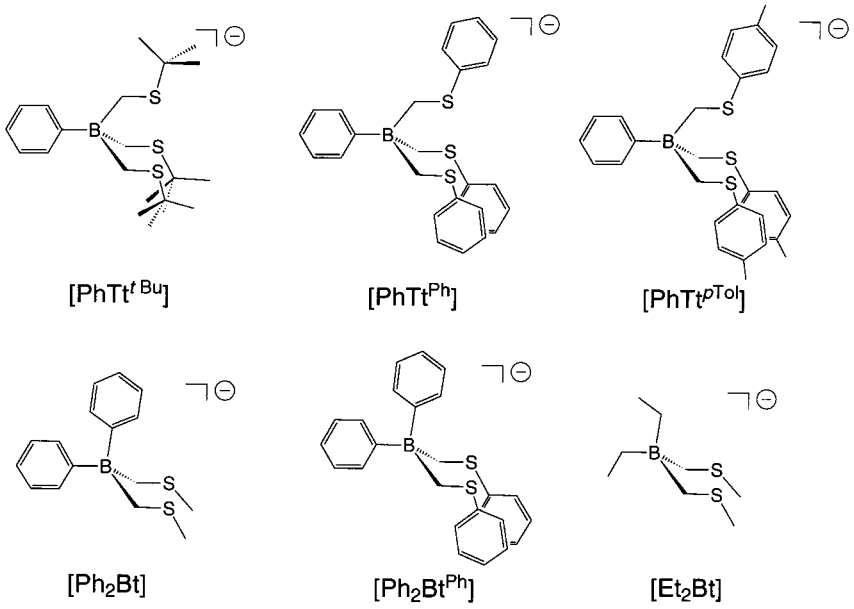
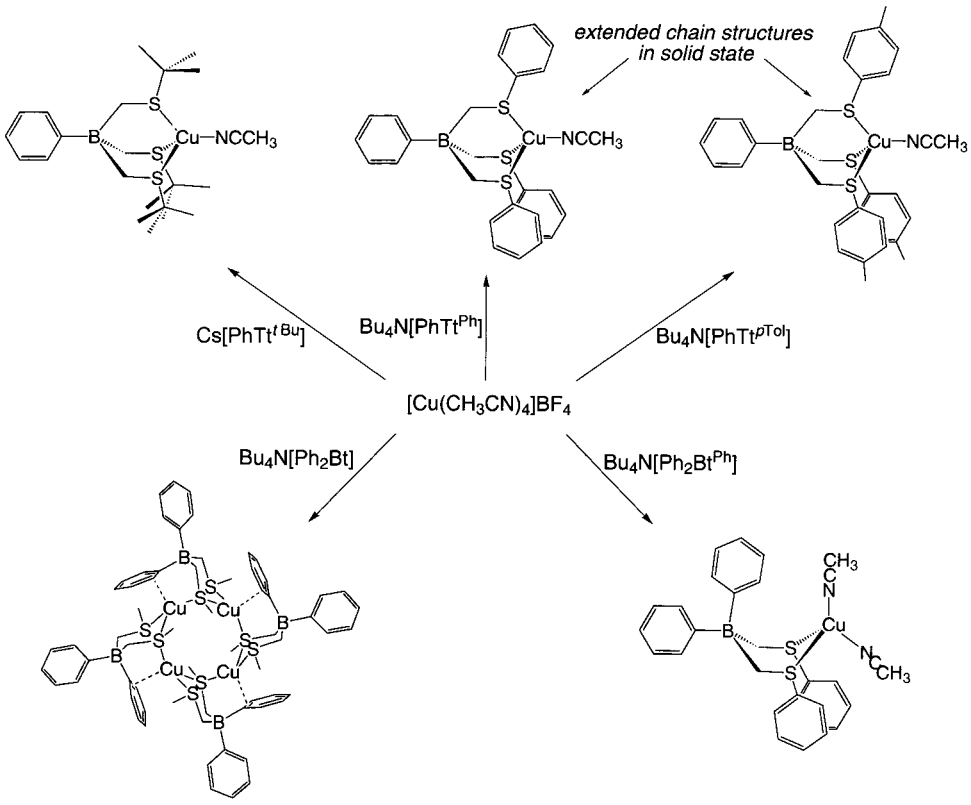
Chart 1



Scheme 1



the presence of donor ligands, the monomers, [PhTt^{Ph}]Cu(L), predominate.

[(Ph$_2$Bt)Cu]$_4$. The solid state structure of [(Ph$_2$Bt)Cu]$_4$ displays features present in both [(PhTt)Cu]$_4$ and [(PhTt^{Ph})Cu]$_\infty$, Figure 1A, Table 1. Selected metric parameters are contained in Table 2. The Cu coordination sphere is roughly tetrahedral and contains a mixture of bridging and terminal thioether ligands, as in [(PhTt)Cu]$_4$, and the η^2-phenyl ligation, as observed in [(PhTt^{Ph})Cu]$_\infty$. Here, the absence of a third thioether arm requires the ligation of the phenyl rings to fulfill the tetrahedron of the Cu(I) ions. Furthermore, the small methyl substituents on sulfur permit for bridging thioethers and the formation of a tetrameric structure containing a central Cu_4S_4 ring, similar to [(PhTt)Cu]$_4$. The S−Cu−S bond angles range from 93.13(8)° to 124.03(8)° with an average angle of 110.3°. The smaller angles involve sulfur atoms from the same ligand. Unlike [(PhTt)Cu]$_4$, there is little difference between the average Cu−S$_{bridge}$ distance, 2.301 Å, and the average Cu−S$_{terminal}$ distance, 2.304 Å, in [(Ph$_2$Bt)Cu]$_4$. The average Cu−C$_{ipso}$ and Cu−C$_{ortho}$ distances are 2.633 and 2.420 Å. Slightly different from those distances seen in [(PhTt^{Ph})Cu]$_\infty$ (2.68(1), 2.32(1) Å), these lengths are in accord with η^2-phenyl coordination.[8]

In contrast to [(PhTt)Cu]$_4$, where the Cu_4 unit is planar, the Cu_4 unit of [(Ph$_2$Bt)Cu]$_4$ is distorted toward a "butterfly"

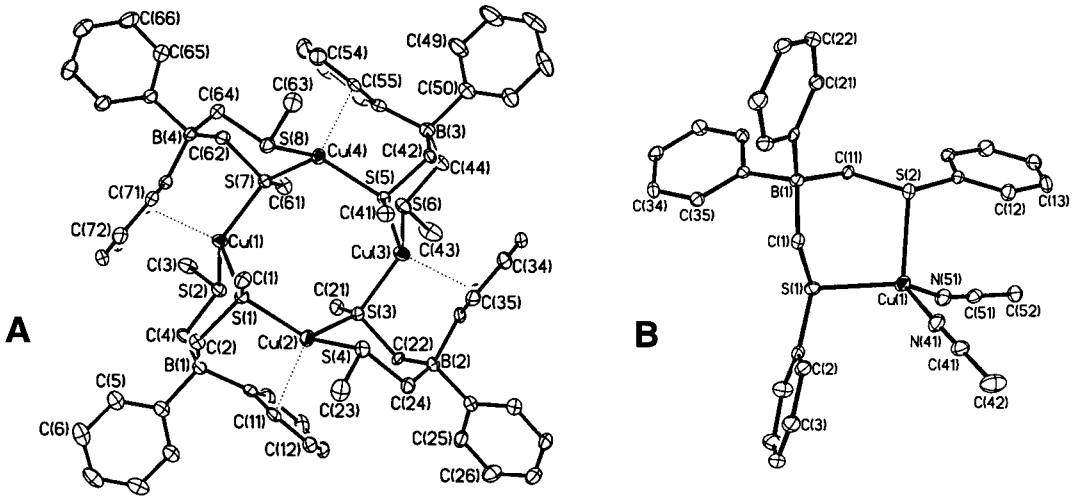


Figure 1. Thermal ellipsoid plots of $[(Ph_2Bt)Cu]_4$ (A) and $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$ (B) at the 30% probability level; hydrogen atoms are not shown.

Table 1. Crystallographic Data for $[(Ph_2Bt)Cu]_4 \cdot Et_2O \cdot CHCl_3$, $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$, $[(PhTt^{Ph})Cu(PPh_3)]$, $[(PhTt^{pTol})Cu(PPh_3)]$, and $[(Et_2Bt)Cu(PPh_3)_2]$

	$[(Ph_2Bt)Cu]_4 \cdot Et_2O \cdot CHCl_3$	$[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$	$[(PhTt^{Ph})Cu(PPh_3)]$	$[(PhTt^{pTol})Cu(PPh_3)]$	$[(Et_2Bt)Cu(PPh_3)_2]$
formula	$C_{69}H_{91}B_4Cl_3Cu_4OS_8$	$C_{30}H_{30}BCuN_2S_2$	$C_{45}H_{31}BCuPS_3$	$C_{48}H_{47}BCuPS_3$	$C_{44}H_{50}BCuP_2S_2$
fw	1596.7	557.0	783.3	825.4	779.3
color habit	pale yellow rod	colorless plate	colorless block	colorless block	colorless rod
cryst size, mm	$0.3 \times 0.3 \times 0.2$	$0.3 \times 0.2 \times 0.1$	$0.4 \times 0.3 \times 0.2$	$0.5 \times 0.4 \times 0.4$	$0.4 \times 0.35 \times 0.2$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_12_12_1$
a, Å	12.1588(2)	11.1694(2)	12.060(6)	26.990(4)	12.9902(2)
b, Å	31.0044(3)	11.8052(2)	19.69(2)	13.864(3)	14.8748(3)
c, Å	19.9278(3)	21.8502(2)	16.98(2)	24.05(1)	21.4937(4)
β, deg	94.023(1)	101.548(1)	94.4(1)	109.54(3)	90
V, Å^3	7493.8(2)	2822.8(1)	4019(6)	8482(5)	4153.2(1)
Z	4	4	4	8	4
T, K	203(2)	173(2)	293(2)	250(2)	198(2)
λ, Å (Mo Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calc), g cm^{-3}	1.415	1.311	1.294	1.293	1.246
μ(Mo Kα), cm^{-1}	14.90	9.43	7.70	7.33	7.33
$R(F)$, $Rw(F)$[a]	6.07, 12.84	5.31, 8.66	5.32, 12.85	4.61, 11.32	4.96, 9.96

[a] Quantity minimized $= R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum|F_o - F_c|/(F_o) \times 100\%$.

arrangement of metal ions. As a consequence of this conformation, the Cu−Cu distances, 3.947, 3.948, 3.950, and 3.932 Å, are shorter (on average, 0.27 Å shorter) than in $[(PhTt)Cu]_4$. The deviations of the copper atoms from the least squares plane are as follows: Cu1, −0.522 Å; Cu2, 0.524 Å; Cu3, −0.524 Å; Cu4, 0.521 Å.

The solution structure of $[(Ph_2Bt)Cu]_4$ is highly solvent dependent. Proton NMR spectra of $[(Ph_2Bt)Cu]_4$ in CD_3CN and $CDCl_3$ are shown in Figure 2. The spectrum in CD_3CN displays two peaks in the aliphatic region and a single set of aromatic resonances which is consistent with the formation of a C_2 symmetric monomer with two molecules of CD_3CN coordinated to the copper ion. However, the spectrum in $CDCl_3$ is considerably more complex and is consistent with the persistence of the tetrameric solid state structure in solution. In the aromatic region of the latter spectrum, two distinct sets of phenyl resonances are present, arising from bonded and nonbonded phenyl rings. The η^2-coordination to the copper ion alters the electronics of the bonded phenyl ring such that the ortho protons are shifted considerably upfield, δ 6.72, while the meta and para protons are shifted downfield, appearing as part of a multiplet at δ 7.60. The binding of olefins to copper(I) is known to result in upfield shifts of the ^{1}H NMR signals for protons attached to the carbons involved in the interaction.[9] Notably, the ortho protons of the η^2-bound phenyl ring appear as a doublet, inconsistent with the solid state structure. This result implies that on the NMR time scale the ligated phenyl ring is rapidly moving between two "static" structures in which the metal is coordinated to the two different $C_{ipso}-C_{ortho}$ bonds. The diastereotopic methylene protons result from the rigidity of the six-membered chelate ring. The singlets at δ 2.24 and 2.10 correspond to protons of the distinct bridging and terminal thioether methyl groups, respectively, assigned by comparison to the proton NMR spectrum of $[(PhTt)Cu]_4$.[6]

$[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$ and $[(Ph_2Bt^{Ph})Cu]_x$. As with $[PhTt^{Ph}]$, the reaction of Cu(I) with $[Ph_2Bt^{Ph}]$ was expected to result in the formation of an extended linear structure in the solid state, $[(Ph_2Bt^{Ph})Cu]_\infty$. Alternatively, the reaction could lead to a monomer with ligation of two solvent molecules completing the coordination sphere. Both products were formed depending upon the reaction conditions. In acetonitrile, the monomer, $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$, was formed, Scheme 1. This is the first example in this series of complexes in which acetonitrile remains

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(Ph_2Bt)Cu]_4 \cdot Et_2O \cdot CHCl_3$, $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$, $[(PhTt^{Ph})Cu(PPh_3)]$, $[(PhTt^{pTol})Cu(PPh_3)]$, and $[(Et_2Bt)Cu(PPh_3)_2]$

	$[(Ph_2Bt)Cu]_4$		
Cu1−S2	2.306(2)	Cu4−S8	2.307(2)
Cu1−S7	2.316(2)	Cu4−C55	2.374(7)
Cu1−S1	2.324(2)	S2−Cu1−S7	111.36(8)
Cu1−C75	2.365(7)	S2−Cu1−S1	93.13(8)
Cu1−C76	2.528(8)	S7−Cu1−S1	122.01(7)
Cu2−S1	2.296(2)	S1−Cu2−S4	114.84(8)
Cu2−S4	2.301(2)	S1−Cu2−S3	124.03(8)
Cu2−S3	2.303(2)	S4−Cu2−S3	94.57(7)
Cu2−C11	2.433(7)	S3−Cu3−S6	114.13(8)
Cu3−S3	2.286(2)	S3−Cu3−S5	122.51(7)
Cu3−S6	2.300(2)	S6−Cu3−S5	94.26(8)
Cu3−S5	2.304(2)	S7−Cu4−S5	122.29(8)
Cu3−C31	2.511(8)	S7−Cu4−S8	95.51(7)
Cu4−S7	2.292(2)	S5−Cu4−S8	114.89(8)
Cu4−S5	2.292(2)		
	$[Ph_2Bt^{Ph}]Cu(CH_3CN)_2$		
Cu1−N51	1.970(4)	N51−Cu1−S1	122.3(1)
Cu1−N41	1.987(4)	N41−Cu1−S1	112.9(1)
Cu1−S1	2.311(1)	N51−Cu1−S2	106.8(1)
Cu1−S2	2.394(1)	N41−Cu1−S2	108.4(1)
N41−C41	1.135(5)	S1−Cu1−S2	97.00(4)
N51−C51	1.130(5)	C41−N41−Cu1	175.4(4)
N51−Cu1−N41	108.0(1)	C51−N51−Cu1	159.3(4)
	$[PhTt^{Ph}]Cu(PPh_3)$		
Cu−P	2.201(2)	P−Cu−S1	126.07(8)
Cu−S3	2.329(2)	S3−Cu−S1	96.81(9)
Cu−S1	2.331(2)	P−Cu−S2	119.61(7)
Cu−S2	2.354(3)	S3−Cu−S2	93.81(8)
P−Cu−S3	119.92(8)	S1−Cu−S2	93.11(8)
	$[PhTt^{pTol}]Cu(PPh_3)$		
Cu−P	2.195(1)	P−Cu−S1	121.41(4)
Cu−S3	2.309(2)	S3−Cu−S1	93.89(4)
Cu−S1	2.339(1)	P−Cu−S2	116.19(4)
Cu−S2	2.355(1)	S3−Cu−S2	94.12(5)
P−Cu−S3	127.35(5)	S1−Cu−S2	96.84(4)
	$[Et_2Bt]Cu(PPh_3)_2$		
Cu−P1	2.294(1)	P1−Cu−S1	116.21(5)
Cu−P2	2.318(1)	P2−Cu−S1	110.17(5)
Cu−S1	2.351(1)	P1−Cu−S2	117.19(4)
Cu−S2	2.371(1)	P2−Cu−S2	102.63(4)
P1−Cu−P2	113.50(5)	S1−Cu−S2	95.04(4)

coordinated. The coordinated acetonitrile ligands give rise to two weak ν_{CN} vibrations at 2302 and 2277 cm^{-1}.[10]

The molecular structure of $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$, determined by X-ray diffraction, is contained in Figure 1B with selected bond distances and angles in Table 2. The coordination geometry about copper is roughly tetrahedral. The Cu−S bond lengths are 2.394(1) and 2.311(1) Å. The S−Cu−S bond angle of 97.00(4)° is similar to the borato bite angle observed for other ligands of this class.[5] In $[(PhTt^{Ph})Cu]_\infty$ the angle is 98.42(7)°, and in $[(Ph_2Bt)Cu]_4$ the angles range from 93.13(8)° to 95.51(7)°.[7]

The reaction of $[Cu(CH_3CN)_4][BF_4]$ with $[Ph_2Bt^{Ph}]$ in acetone yielded a complex with the empirical formula $[(Ph_2Bt^{Ph})Cu]$. By analogy to the crystallographically characterized $[(PhTt^{Ph})Cu \cdot CH_3CN]_\infty$, a structure is proposed in which the copper coordination sphere contains two terminal thioether sulfurs and two η^2-ligation to phenyl borato substituents, Figure 3. The proton NMR spectrum of $[(Ph_2Bt^{Ph})Cu]_\infty$ in CD_3CN is identical to the spectrum of $[(Ph_2Bt^{Ph})Cu(CD_3CN)_2]$ in the same solvent. Additionally, the FT-IR spectra of $[(Ph_2Bt^{Ph})Cu]_\infty$ and $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$ are essentially superimposable, with the exception of the two ν_{CN} stretches present for $[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$.

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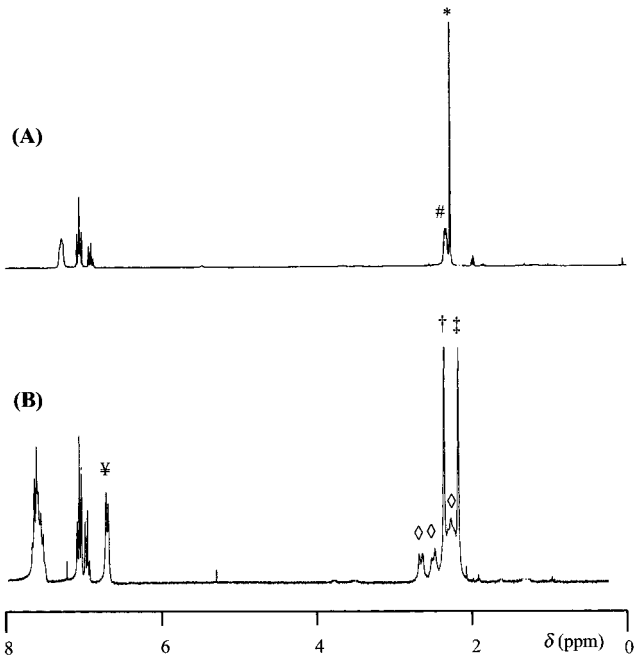

Figure 2. (A) ^1H NMR spectrum of $[(Ph_2Bt)Cu(CD_3CN)_2]$ in CD_3CN, indicating the formation of a monomer in solution with single BCH_2 (#) and SCH_3 (*) resonances. (B) ^1H NMR spectrum of $[(Ph_2Bt)Cu]_4$ in $CDCl_3$ showing diastereotopic methylene protons (◊), a shift in the η^2-bound ortho protons (¥), and both terminal (‡) and bridging (†) thioether methyl substituents.

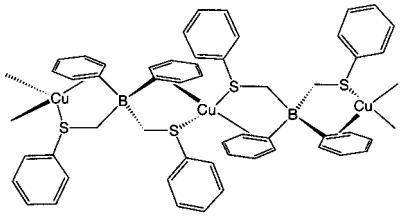

Figure 3. Proposed solid state structure of $[(Ph_2Bt^{Ph})Cu]_x$.

$[(PhTt^{tBu})Cu]_n$. Similar to $[(Ph_2Bt)Cu]_4$, $[(PhTt^{tBu})Cu]$ is monomeric in coordinating solvents and oligomeric in noncoordinating solvents. The ^1H NMR spectrum of $[(PhTt^{tBu})Cu(CD_3CN)]$ in acetonitrile displays two aliphatic resonances corresponding to the *tert*-butyl and methylene protons consistent with a C_3 symmetric monomer. The ^1H spectrum of the same material in $CDCl_3$ is consistent with a significantly lower symmetry structure. Multiple resonances are present for the methylene and aromatic protons. There are four distinct, equal intensity signals for the *tert*-butyl substituents. Given the low symmetry and the good solubility of the material, a low nuclearity oligomeric structure is likely. Unfortunately, repeated attempts to elucidate the nuclearity of this material by X-ray structural analysis, ESI-MS analysis, and solution molecular weight determination by osmometry proved unsuccessful.

Monomeric Pyridine Adducts. Each of the homoleptic complexes, $[(PhTt)Cu]_4$, $[(PhTt^{Ph})Cu]_\infty$, $[(PhTt^{pTol})Cu]_\infty$, $[(PhTt^{tBu})Cu]_n$, $[(Ph_2Bt)Cu]_4$, and $[(Ph_2Bt^{Ph})Cu]_\infty$, reacts reversibly with pyridine to form the appropriate four-coordinate monomer, as determined by ^1H NMR spectroscopy.[6,7] For example, dissolution of $[(PhTt^{tBu})Cu]_n$ in d_5-pyridine resulted in a high-symmetry spectrum exhibiting single methylene and *tert*-butyl signals in accord with C_3 symmetric ligation of the borato ligand. The spectrum is very similar to that recorded in CD_3CN and

Table 3. ^{1}H NMR Chemical Shifts of Borato Ligand Methylene Protons in the PPh_3 Complexes and the Corresponding Free Ligands

PPh_3 complex	δ SCH_2, ppm[a]	free ligand (L)	δ SCH_2, ppm[a]
[(PhTt)Cu(PPh_3)]	2.23	[Bu_4N][PhTt]	1.97
[(PhTt^{Ph})Cu(PPh_3)]	2.78	[Bu_4N][PhTt^{Ph}]	2.40
[(PhTt^{pTol})Cu(PPh_3)]	2.83	[Bu_4N][PhTt^{pTol}]	2.34
[(PhTt^{tBu})Cu(PPh_3)]	2.18	Cs[PhTt^{tBu}]	1.81[b]
[(Ph_2Bt)Cu(PPh_3)$_2$]	2.37	[Bu_4N][Ph_2Bt]	2.23
[(Ph_2Bt^{Ph})Cu(PPh_3)$_2$]	2.73	[Bu_4N][Ph_2Bt^{Ph}]	2.58
[(Et_2Bt)Cu(PPh_3)$_2$]	1.83	[Bu_4N][Et_2Bt]	1.55

[a] $CDCl_3$. [b] As the Cs(I) salt in $(CD_3)_2SO$; δ 2.38 as the Tl(I) salt in $CDCl_3$.

Table 4. ^{31}P{^{1}H} NMR Spectral Data for PPh_3 Complexes and Selected [Tp$^{RR'}$Cu(PPh_3)$_n$] Complexes

	δ, ppm[a]	fwhm, Hz		δ, ppm[b]
[(PhTt)Cu(PPh_3)]	7.39	595	[TpCu(PPh_3)][15]	−6.12[c]
[(PhTt^{Ph})Cu(PPh_3)]	6.16	340	[Tp^{Me}Cu(PPh_3)][d]15	−4.92
[(PhTt^{pTol})Cu(PPh_3)]	6.28	284	[Tp*Cu(PPh_3)][d]15	−4.99
[(PhTt^{tBu})Cu(PPh_3)]	5.49	567	[Tp^{*Cl}Cu(PPh_3)][d]15	−5.00
[(Ph_2Bt)Cu(PPh_3)$_2$]	0.89	181	[pzTpCu(PPh_3)$_2$][11]	0.41
[(Ph_2Bt^{Ph})Cu(PPh_3)$_2$]	0.07	255	[BpCu(PPh_3)$_2$][11]	−1.92
[(Et_2Bt)Cu(PPh_3)$_2$]	−3.20	124		

[a] $CDCl_3$, referenced vs 85% H_3PO_4 as external standard. [b] $CDCl_3$, δ in ppm from TMS, calibrated against internal deuterium solvent peak. [c] Measured at −40 °C. [d] Tp^{Me} = hydridotris(3-methylpyrazolyl)borate, Tp* = hydridotris(3,5-dimethylpyrazolyl)borate, Tp^{*Cl} = hydridotris(4-chloro-3,5-dimethylpyrazolyl)borate.

assigned as [(PhTt^{tBu})Cu(CD_3CN)]. Therefore, the structure of the species in pyridine is monomeric [(PhTt^{tBu})Cu(py)]. Further support for this assignment comes from spectral and structural characterization of the PPh_3 adducts, described below. Pyridine is competitive with acetonitrile binding as evidenced by NMR spectral titrations of [(PhTt^{Ph})Cu(CD_3CN)] in CD_3CN. At 25 °C, K_{eq} for pyridine binding is 300 M^{-1}. The tetramer, [(PhTt)Cu]$_4$, binds pyridine much less avidly, even in noncoordinating solvents. At 25 °C, K_{eq} for pyridine in $CDCl_3$ is 1×10^{-2} M^{-1}. The dramatic 10^5 difference in K_{eq} for pyridine binding to [(PhTt^{Ph})Cu(CD_3CN)] versus [(PhTt)Cu]$_4$ is likely a consequence of the nature of the initial Cu(I) complexes in solution. [(PhTt)Cu]$_4$ is tetrameric in $CDCl_3$, and the disassembly of this structure is required in order for the formation of the pyridine complex to occur, while the latter is already a monomer in CD_3CN and only requires the displacement of a solvent molecule for the formation of the pyridine adduct.

Phosphine Complexes. (a) Synthesis. Two routes were employed in the synthesis of [(PhTt^R)Cu(PPh_3)] and [(Ph_2Bt^R)Cu(PPh_3)$_2$] derivatives. In the first approach, the complexes were prepared by reacting PPh_3 with the appropriate [(PhTt^R)Cu] or [(Ph_2Bt^R)Cu] precursor in either acetonitrile or THF. The second method entailed reaction of the appropriate ligand with equimolar [Cu(CH_3CN)$_4$][BF_4] and an excess of PPh_3. The latter reactions were conducted in THF. The PPh_3 complexes have excellent solubility in chlorinated hydrocarbons and good solubility in aromatic hydrocarbons. In addition, they are stable to air and moisture both in the solid state and in solution for several days.

(b) NMR Spectroscopy. The ^{1}H and ^{31}P NMR spectra of the PPh_3 complexes have been obtained, and the chemical shift data are reported in Tables 3 and 4. In all cases, the ^{1}H NMR spectra support monomeric structures. Specifically, there is a single methylene resonance indicative of symmetric borato ligation. Similar results are seen for the other [PhTt^R]Cu(L) derivatives, and this distinction in the ^{1}H NMR spectrum is diagnostic for the formation of a monomeric complex.[6]

Furthermore, examination of the ^{1}H NMR spectra of the Cu(I)−PPh_3 complexes allows for assessment of the effects of binding on the chemical shift of the thioether protons. This is not possible in the case of the [(PhTt^R)Cu]$_x$ complexes where their oligomeric nature gives rise to complex spectra. One easily observable trend is that the thioether methylene protons shift downfield upon binding to copper.

The ^{31}P chemical shift data and full width at half peak maximum for each of the PPh_3 complexes is listed in Table 4 along with the chemical shifts for some related poly(pyrazolyl)borate Cu(I) complexes, including two bis(phosphine) complexes, [pzTpCu(PPh_3)$_2$] and [BpCu(PPh_3)$_2$] (pzTp = tetrakis(pyrazolyl)borate, Bp = dihydridobis(pyrazolyl)borate).[11] In all cases the ^{31}P{^{1}H} NMR spectra of the PPh_3 complexes exhibit a single broad resonance at room temperature. Addition of 1 equiv of PPh_3 to a solution of [(PhTt)Cu(PPh_3)] in $CDCl_3$ causes the ^{31}P resonance to move upfield toward free PPh_3, shifting from δ 7.39 to 0.39. The observation of a single broad peak in the presence of excess PPh_3 is consistent with fast exchange between bound and free PPh_3. This phenomenon has been documented for related [Tp] complexes.[12] In all cases, the ^{31}P resonances occur upfield of free PPh_3 (−6.0 ppm).[13] The chemical shift differences between [(Ph_2Bt^R)Cu(PPh_3)$_2$] and free PPh_3 are considerably smaller than the differences between [(PhTt^R)Cu(PPh_3)] and free PPh_3 due to a greater shielding of the phosphorus atom. This observation is likely a result of a weaker interaction between the phosphorus and copper caused by steric crowding around the metal atom, preventing closer access to the Cu(I) ion. This is supported by the longer Cu−P bond lengths in [(Et_2Bt)Cu(PPh_3)$_2$] and is suggested to occur in [Tp*Cu(PCy_3)] (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate) where there are steric interactions between the bulky cyclohexyl groups and the methyl substituents of the borato ligand preventing the phosphine from coming closer to the copper ion.[14] It is interesting to note that in the poly(pyrazolyl)borate complexes the ^{31}P chemical shifts of the *bis* triphenylphosphine complexes are displaced upfield relative to the *mono* triphenylphosphine derivatives.

(c) Molecular Structures of PPh_3 Adducts. The structures of [(PhTt^{Ph})Cu(PPh_3)],[7] [(PhTt^{pTol})Cu(PPh_3)], and [(Et_2Bt)Cu(PPh_3)$_2$] have been determined by X-ray crystallography, Table 1. The thermal ellipsoid plots of [(PhTt^{pTol})Cu(PPh_3)] and [(Et_2Bt)Cu(PPh_3)$_2$] are contained in Figure 4. Table 2 lists pertinent structural parameters for the three molecules. In each complex, the Cu(I) ion is in a roughly tetrahedral environment. The tetrahedral coordination sphere is completed by PPh_3 ligation, the number of which is dictated by the denticity of the borate ligand. All of the S−Cu−S bond angles are smaller than that for a perfect tetrahedron, ranging from 91.34(4)° to 98.37(4)°. As seen before in the [(PhTt^R)Cu(PPh_3)] and [(Ph_2Bt^R)Cu(PPh_3)$_2$] complexes, this is a consequence of the inherent bite of the ligand. This results in correspondingly wide P−Cu−S angles, with an average of 118.5°. The Cu−S distances in the [(PhTt^R)Cu(PPh_3)] complexes are in the same range as those seen for the [(PhTt^R)Cu]$_n$ complexes. The Cu−P bond distances lie within the range reported for other known Cu(I) phosphine

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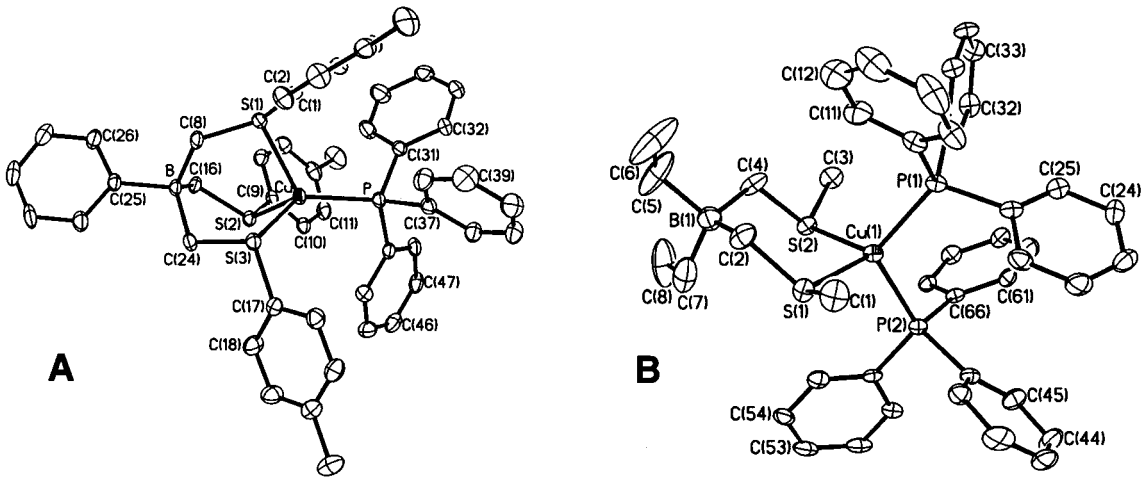

Figure 4. Thermal ellipsoid plots of $[PhTt^{pTol}]Cu(PPh_3)$ (A) and $[Et_2Bt]Cu(PPh_3)_2$ (B) at the 30% probability level; hydrogen atoms are not shown.

complexes, 2.15−2.30 Å, and are less than the sum of the covalent radii.[15] The Cu−S distances, 2.351(1) and 2.371(1) Å, and the Cu−P distances, 2.294(1) and 2.318(1) Å, in $[(Et_2Bt)Cu(PPh_3)_2]$ are longer on average than the metrics of $[(PhTt^{Ph})Cu(PPh_3)]$ and $[(PhTt^{pTol})Cu(PPh_3)]$. Similarly, longer Cu−P bonds are seen in the complex $[(k^2\text{-pzTp})Cu(PPh_3)_2]$, 2.273(1) and 2.359(1) Å,[11] compared to $[TpCu(PPh_3)]$. This could arise from the steric crowding of the PPh_3 ligands.

Summary

Reaction of a series of poly(thioether)borate ligands with $[Cu(CH_3CN)_4][BF_4]$ led to a set of structurally diverse 1:1 complexes. These results show that the structural chemistry of Cu(I) thioether complexes of this type can be rationally controlled by the proper substitution at the thioether sulfur and the central boron atom, as well as by judicious choice of the number of chelate arms incorporated in the ligand. Ligands possessing the smaller (methylthio)methyl donors, [PhTt] and $[Ph_2Bt]$, yield tetrameric species, $[(PhTt)Cu]_4$ and $[(Ph_2Bt)Cu]_4$, containing both terminal and bridging thioether ligation. However, ligands possessing the larger (arylthio)methyl groups, $[PhTt^{Ph}]$ and $[PhTt^{pTol}]$, form copper(I) one-dimensional extended structures in the solid state. Clearly, in cases where there are an insufficient number of thioether donors to satisfy a T_d coordination environment, η^2 ligation via the phenyl substituent on boron permits for completion of the coordination sphere. The η^2-phenyl interaction represents a significant driving force for these structures. Although three-coordinate Cu(I) structures are well precedented, in the present studies this structure type was not observed.

Experimental Section

General Procedures. Unless otherwise stated, all reagents were obtained from commercial sources and used without further purification. When dry solvents were required, they were distilled under N_2 and dried as indicated. Hexanes, Et_2O, THF, toluene, benzene, and pentane were freshly distilled over Na/benzophenone. Acetonitrile, CH_2Cl_2, pyridine, and TMEDA were distilled over CaH_2, the latter two under reduced pressure. HPLC grade acetone (≤0.05% H_2O) and benzonitrile (≤0.005% H_2O) were purchased from Acros Organics, Fisher Scientific. HPLC grade acetonitrile (≤0.001% H_2O) was purchased from Burdick and Jackson, Inc. $[Cu(CH_3CN)_4][BF_4]$,[10] $Et_2B(OTs)$,[16] Ph_2BBr,[17] and Bu^tSCH_3[18] were prepared according to procedures previously outlined in the literature. $[Bu_4N]PhTt^{Ph}$ was prepared as described previously.[7] All ligands and metal complexes were dried under vacuum at refluxing acetone temperatures unless otherwise stated. Elemental analyses were performed by Desert Analytics, Inc., Tuscon, AZ. Electronic spectra were recorded with SLM-Aminco 3000 or Hewlett-Packard 8453 diode array spectrophotometers. NMR spectra were recorded on a 400 MHz Brüker spectrometer equipped with a Sun workstation, a Brüker AM-250, or a Brüker AC-250 spectrometer. Samples were referenced to the solvent signal. Cyclic voltammetry was performed on a BAS 50W system. All experiments were performed in an Ar-filled glovebox in a cell consisting of a glassy carbon or platinum disk working electrode ($r = 1$ mm), Pt wire counter electrode, and Ag/AgCl reference electrode. Solutions contained 0.1 M electrolyte ($[Bu_4N][PF_6]$, dried prior to use) and 10 mM sample. Potentials were referenced to internal Fc/Fc^+ (+410 mV vs Ag/AgCl).

CAUTION! The sulfides employed in the following syntheses are flammable liquids and possess a hazardous stench. The deprotonation reactions should be vented through aqueous NaOCl.

$[Bu_4N]Ph_2Bt$, Tetrabutylammonium Diphenylbis((methylthio)-methyl)borate.[5] Methyl sulfide (3.5 mL, 48 mmol) and TMEDA (0.1 mL, 0.65 mmol) were charged into a round-bottom flask. To the mixture was added *n*-BuLi (10.0 mL 2.5 M in hexanes) dropwise with vigorous stirring. The viscous yellow solution was stirred for 1 h at room temperature (RT) before heating to 45 °C for an additional hour to remove excess methyl sulfide. THF (20 mL) was added and the solution cooled to −78 °C followed by dropwise addition of a benzene solution (20 mL) of Ph_2BBr (3.1 g, 12.5 mmol). The reaction mixture was warmed to RT and stirred for 12 h. H_2O (30 mL) was added to quench, and the organic volatiles were removed under vacuum. The remaining aqueous solution was filtered through Celite. To the filtrate was added $[Bu_4N]Br$ (4.0 g, 12.5 mmol), resulting in precipitation was a white solid, which was collected by filtration and washed with H_2O (2 × 25 mL). Yield: 5.3 g (80%). $[Bu_4N]Ph_2Bt$ is soluble in acetone, THF, acetonitrile and chlorinated hydrocarbons. Mp: 117−118 °C. ^1H NMR ($CDCl_3$): δ 7.46 (br, *m*-C_6H_5, 4 H), 7.04 (d, *o*-C_6H_5, 4 H), 6.86 (t, *p*-C_6H_5, 2 H), 2.80 (t, NCH_2, 8 H), 2.27 (br, BCH_2, 4 H), 2.04 (s, SCH_3, 6H), 1.35 (m, NCH_2CH_2, 8 H), 1.06 (m, $N(CH_2)_2CH_2$, 8 H), 0.99 (t, $N(CH_2)_3CH_3$, 12 H). Anal. Calcd for $C_{32}H_{56}BNS_2$: C, 72.6; H, 10.7; N, 2.64. Found: C, 72.3; H, 10.34; N, 2.84.

$[Bu_4N]Ph_2Bt^{Ph}$, Tetrabutylammonium Diphenylbis((phenylthio)-methyl)borate. $[Bu_4N]Ph_2Bt^{Ph}$ was prepared according to the procedure above for $[Bu_4N]Ph_2Bt$ using thioanisole in place of methyl sulfide. Thioanisole (3.1 g, 25 mmol) and TMEDA (0.1 mL, 0.65 mmol) were charged into a round-bottom flask. To the mixture was added *n*-BuLi (10.0 mL 2.5 M in hexanes) dropwise with vigorous stirring. The viscous yellow solution was stirred for 2 h at RT. THF (20 mL) was

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added and the solution cooled to −78 °C followed by dropwise addition of a benzene solution (20 mL) of Ph_2BBr (3.1 g, 12.5 mmol). The reaction mixture was warmed to RT and stirred for 24 h. H_2O (30 mL) was added to quench, and the organic volatiles were removed under vacuum. The remaining aqueous solution was filtered through Celite. To the filtrate was added $[Bu_4N]Br$ (4.0 g, 12.5 mmol), resulting in precipitation was a white solid, which was collected by filtration and washed with H_2O (2 × 25 mL). Yield: 3.5 g (50%). $[Bu_4N]Ph_2Bt^{Ph}$ is soluble in acetone, THF, acetonitrile, and chlorinated hydrocarbons. Mp: 152−153 °C. ^{1}H NMR ($CDCl_3$): δ 7.49 (d, C_6H_5, 4 H), 7.28 (d, C_6H_5, 4 H), 7.11 (m, C_6H_5, 8 H), 6.91 (m, C_6H_5, 4 H), 2.59 (br, BCH_2, 4 H), 2.40 (br, NCH_2, 8 H), 1.14 (m, NCH_2CH_2, 8 H), 1.06 (m, $N(CH_2)_2CH_2$, 8 H), 0.90 (t, $N(CH_2)_3CH_3$, 12 H).

$[Bu_4N]PhTt^{pTol}$, Tetrabutylammonium Phenyltris((*p*-tolylthio)-methyl)borate. $[Bu_4N]PhTt^{pTol}$ was prepared according to the procedure for $[Bu_4N]PhTt^{Ph}$ replacing thioanisole with methyl *p*-tolyl sulfide.[7] The following reagent quantities were employed in the reaction: methyl *p*-tolyl sulfide (9.3 mL, 69 mmol), TMEDA (13.0 mL, 86 mmol), BuLi (27.6 mL, 2.5 M in hexanes), and $PhBCl_2$ (3.0 mL, 23 mmol). Isolation was carried out as follows. The reaction was quenched with 30 mL of H_2O, and 100 mL of THF was added before filtering through Celite. The filtrate was concentrated by rotary evaporation, and $[Bu_4N]Cl$ (6.3 g, 23 mmol), in a minimum of acetone, was added. The product was precipitated from this solution with ethyl acetate and collected by filtration. The crude product was washed with H_2O (3 × 20 mL) and recrystallized from acetone/H_2O to produce a fine white powder. Yield: 6.7 g (39%). $[Bu_4N]PhTt^{pTol}$ is soluble in acetone, THF, acetonitrile, and chlorinated hydrocarbons. Mp: 175 °C. ^{1}H NMR ($CDCl_3$): δ 7.59 (d, (o-C_6H_5)B, 2 H), 7.14 (d, (o- $C_6H_4(CH_3)$)S, 6 H), 7.09 (t, (m-C_6H_5)B, 2 H), 6.92 (m, (p-C_6H_5)B and (m-$C_6H_4(CH_3)$)S, 7 H), 2.51 (m, NCH_2, 8 H), 2.34 (br, BCH_2, 6 H), 2.21 (s, ($C_6H_4(CH_3)$)S, 9H), 1.16 (m, NCH_2CH_2, 8 H), 1.06 (m, $N(CH_2)_2CH_2$, 8 H), 0.86 (t, $N(CH_2)_3CH_3$, 12 H). Anal. Calcd. for $C_{46}H_{68}BNS_3$: C, 74.5; H, 9.24; N, 1.88. Found: C, 74.6; H, 9.34; N, 1.82.

Cs[PhTt^{tBu}], Cesium Phenyltris((*tert*-butylthio)methyl)borate. The synthetic procedure for $Cs[PhTt^{tBu}]$ was analogous to that reported for $Tl[PhTt^{tBu}]$.[2] Isolation was achieved by extracting the reaction mixture with H_2O (4 × 50 mL), filtering the combined aqueous portions through Celite, and adding aqueous CsCl. The resulting white powder was collected by filtration and washed with Et_2O. $Cs[PhTt^{tBu}]$ is soluble in acetone, acetonitrile, and THF but is insoluble in chlorinated hydrocarbons. Mp: 206 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.53 (br, (o-C_6H_5)B, 2 H), 6.96 (t, (m-C_6H_5)B, 2 H), 6.80 (t, (p-C_6H_5)B, 1 H), 1.81 (br, BCH_2, 6 H), 1.18 (s, $C(CH_3)_3$, 18 H).

$[Bu_4N]Et_2Bt$, Tetrabutylammonium Diethylbis((methylthio)methyl)borate. $[Bu_4N]Et_2Bt$ was prepared according to the procedure reported for $[Bu_4N]PhTt$[1] replacing $PhBCl_2$ with $Et_2B(OTs)$. In a typical reaction the following reagent quantities were used: methyl sulfide (8.1 mL, 110 mmol), TMEDA (9.1 mL, 60 mmol), BuLi (22 mL, 2.5 M in hexanes), $Et_2B(OTs)$ (25 mL, 1.1 M in toluene), and $[Bu_4N]Br$ (4.6 g, 14 mmol). The reaction required 72 h of stirring after the addition of the $Et_2B(OTs)$. Yield: 2.7 g (23%). $[Bu_4N]Et_2Bt$ has good solubility in acetone, acetonitrile, aromatic and chlorinated hydrocarbons, THF, and alcohols. Mp: 58−66 °C. ^{1}H NMR ($CDCl_3$): δ 3.15 (m, NCH_2, 8 H), 1.96 (s, SCH_3, 6 H), 1.55 (m, BCH_2, and NCH_2CH_2, 12 H), 1.40 (h, $N(CH_2)_2CH_2$, 8 H), 0.95 (t, CH_3, 12 H), 0.72 (t, BCH_2CH_3, 6 H), 0.07 (q, BCH_2CH_3, 4 H). Anal. Calcd for $C_{24}H_{56}BNS_2$: C, 66.5; H, 13.0; N, 3.23. Found: C, 66.2; H, 13.1; N, 3.48. Alternatively, the product was isolated as the $[Ph_4P]$ salt by the addition $[Ph_4P]Br$ (6.0 g, 15 mmol). The solubility properties of $[Ph_4P]Et_2Bt$ are similar to those of the $[Bu_4N]Et_2Bt$.

$[(Ph_2Bt)Cu]_4$. $[(Ph_2Bt)Cu]_4$ was prepared from $[Cu(CH_3CN)_4][BF_4]$ (0.91 g, 2.89 mmol) and $[Bu_4N]Ph_2Bt$ (1.53 g, 2.89 mmol) using the procedure for $[(PhTt)Cu]_4$.[6] Reaction time was 10 min. $[(Ph_2Bt)Cu]_4$ was dried under vacuum at RT. Yield: 0.60 g (60%). $[(Ph_2Bt)Cu]_4$ is soluble in THF and chlorinated hydrocarbons and reacts with acetonitrile and pyridine. Mp: 68 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.60 (m, η^2-(p-C_6H_5)B, (o-C_6H_5)B and η^2-(m-C_6H_5)B, 5 H), 7.09 (t, (m-C_6H_5)B, 2 H), 6.97 (t, (p-C_6H_5)B, 1 H), 6.72 (d, η^2-(o-C_6H_5)B, 2 H), 2.62 (d, SCH_2, 1 H), 2.42 (d, SCH_2, 1 H), 2.24 (s, S_bCH_3, 3 H), 2.20 (m, SCH_2, 2 H), 2.10 (s, S_tCH_3, 3 H). ^{1}H NMR (CD_3CN): δ 7.28 (br, (o-C_6H_5)B, 4 H), 7.05 (t, (m-C_6H_5)B, 4 H), 6.90 (t, (p-C_6H_5)B, 2 H), 2.32 (m, BCH_2, 4 H) 2.26 (s, SCH_3, 6 H). Anal. Calcd for $C_{64}H_{80}B_4Cu_4S_8$: C, 54.8; H, 5.75. Found: C, 53.9; H, 5.79.

$[(PhTt^{pTol})Cu]_\infty$. $[Cu(CH_3CN)_4][BF_4]$ (125 mg, 0.40 mmol) in 20 mL of acetonitrile was added to $[Bu_4N]PhTt^{pTol}$ (290 mg, 0.39 mmol) in 20 mL of acetonitrile under a N_2 atmosphere, yielding a cloudy white solution within 1 h. The reaction was stirred for 6 h. The fine white powder was collected under N_2 by filtration, washed with acetonitrile (2 × 15 mL) and Et_2O (2 × 15 mL), and dried under vacuum at 65 °C. Yield: 162 mg (74%). $[(PhTt^{pTol})Cu]_\infty$ is soluble in benzonitrile and pyridine. Mp: 135−138 °C dec. ^{1}H NMR (pyridine-d_5): see $[(PhTt^{pTol})Cu(py)]$ below. Anal. Calcd for $C_{30}H_{32}BS_3Cu$: C, 64.0; H, 5.73. Found: C, 64.0; H, 5.82.

$[(PhTt^{tBu})Cu]_n$. $[Cu(CH_3CN)_4][BF_4]$ (223 mg, 0.71 mmol) in 20 mL of acetone was added to $Cs[PhTt^{tBu}]$ (372 mg, 0.70 mmol) in 20 mL of acetone with gentle stirring under a N_2 atmosphere. A fine white powder formed immediately upon mixing, and the reaction was terminated after 30 min. The powder was collected via vacuum filtration and washed with H_2O (4 × 15 mL) and pentane (3 × 15 mL). Yield: 220 mg (68%). $[(PhTt^{tBu})Cu]_n$ is soluble in acetonitrile (as $[(PhTt^{tBu})Cu(CH_3CN)]$), THF, and chlorinated hydrocarbons. Solid samples of $[(PhTt^{tBu})Cu]_n$ are stable to air and water, but solutions turn blue over several hours when exposed to O_2. Mp: 104−106 °C dec. ^{1}H NMR (CD_3CN): δ 7.31 (br, (o-C_6H_5)B, 2 H), 7.08 (t, (m-C_6H_5)B, 2 H), 6.93 (t, (p-C_6H_5)B, 1 H), 1.93 (BCH_2, br, 6 H), 1.31 (s, $C(CH_3)_3$ 27 H). Anal. Calcd for $[(PhTt^{tBu})Cu]_n$ $C_{21}H_{38}BCuS_3$: C, 54.7; H, 8.31. Found: C, 54.1; H, 7.99.

$[(Ph_2Bt^{Ph})Cu(CH_3CN)_2]$. $[Cu(CH_3CN)_4][BF_4]$ (300 mg, 0.46 mmol) in 10 mL of acetonitrile was added to $[Bu_4N]Ph_2Bt^{Ph}$ (290 mg, 0.39 mmol) in 20 mL of acetonitrile under a N_2 atmosphere, yielding a homogeneous pale yellow solution. The solution was stirred for 2 h and then concentrated in vacuo to produce white crystalline material. Yield: 175 mg (80%). ^{1}H NMR ($(CD_3)_2SO$): δ 7.17 (m, C_6H_5, 14 H), 7.04 (d, C_6H_5, 4 H), 6.91 (t, C_6H_5, 2 H) 2.50 (br, BCH_2, coincident with residual dmso) 2.06 (s, $NCCH_3$, 6 H). ^{1}H NMR (CD_3CN): δ 7.30 (m, C_6H_5, 12 H), 7.17 (d, C_6H_5, 2 H) 7.08 (t, C_6H_5, 4 H), 6.94 (t, C_6H_5, 2H), 2.60 (b, BCH_2, 4 H). Anal. Calcd for $C_{30}H_{30}BCuN_2S_2$: C, 64.7; H, 5.43; N, 5.03. Found: C, 64.5; H, 5.38; N, 4.77

$[(PhTt^{Ph})Cu(PPh_3)]$.[7] The synthesis and isolation of $[(PhTt^{Ph})Cu(PPh_3)]$ were performed using the procedure reported for $[(PhTt)Cu(PPh_3)]$.[6] PPh_3 (200 mg, 0.76 mmol) in 20 mL of acetonitrile was added to $[(PhTt^{Ph})Cu]_\infty$ (300 mg, 0.58 mmol) in 50 mL of acetonitrile. Yield: 375 mg (83%). Mp: 86 °C. ^{1}H NMR ($(CD_3)_2CO$): δ 7.45 (t, (o-C_6H_5)B and (p-C_6H_5)P, 5 H), 7.29 (t, (m-C_6H_5)S, 6 H), 7.15 (m, (m-C_6H_5)B, (o-C_6H_5)S, (p-C_6H_5)S and (m-C_6H_5)P, 16 H), 6.98 (t, (o-C_6H_5)P and (p-C_6H_5)B, 7 H), 2.78 (s, BCH_2, 6 H). ^{1}H NMR (C_6H_6): δ 7.83 (d, (o-C_6H_5)B, 2 H), 7.49 (t, (m-C_6H_5)B, 2 H), 7.31 (t, (p-C_6H_5)B, 1 H), 7.15 ((o-C_6H_5)S, coincident with C_6D_6), 7.01 (t, (m-C_6H_5)S, 6 H), 6.93 (t, (p-C_6H_5)S, 3 H), 6.85 (m, (C_6H_5)P, 15 H), 3.17 (br, SCH_2, 6 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 6.2. Anal. Calcd for $C_{45}H_{41}BCuPS_3$: C, 69.0; H, 5.28. Found: C, 69.0; H, 5.54.

$[(PhTt^{pTol})Cu(PPh_3)]$. A slurry of $[Cu(CH_3CN)_4][BF_4]$ (210 mg, 0.67 mmol) in 20 mL of THF was added to PPh_3 (260 mg, 0.99 mmol) and $[Bu_4N]PhTt^{pTol}$ (500 mg, 0.67 mmol) in 20 mL of THF under a N_2 atmosphere. Upon addition, the Cu(I) salt was immediately brought into solution. The reaction was stirred overnight before the solvent was removed by rotary evaporation. The resulting white solid was extracted with 100 mL of dry Et_2O and filtered. The solvent was removed under vacuum, and the resulting product was collected and washed with pentane (3 × 25 mL). Yield: 530 mg (96%). Mp: 135−138 °C dec. ^{1}H NMR (C_6H_6): δ 7.79 (d, (o-C_6H_5)B, 2 H), 7.43 (t, (m-C_6H_5)B, 2 H), 7.40 (t, (p-C_6H_5)B, 1 H), 7.09 (C_6H_5, m, 21 H, coincident with C_6H_6), 6.95−6.78 (m, C_6H_5, 10 H), 6.63 (d, C_6H_5, 6 H), 3.17 (br, SCH_2, 6 H) 1.93 (s, CH_3, 9 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 6.3. Anal. Calcd for $C_{48}H_{47}BCuPS_3$: C, 69.8; H, 5.74. Found: C, 69.9; H, 5.85.

$[(PhTt^{tBu})Cu(PPh_3)]$. $[(PhTt^{tBu})Cu]_n$ (100 mg, 0.27 mmol) in 20 mL of acetonitrile was combined with PPh_3 (108 mg, 0.41 mmol) in 5 mL of acetonitrile and stirred overnight. The resulting white precipitate was collected by filtration and washed with pentane (4 × 15 mL). Yield: 85 mg (54%). Mp: 148 °C dec. ^{1}H NMR (C_6H_6): δ 7.99 (br, (o-C_6H_5)B, 2 H), 7.56 (m, (m-C_6H_5)B and $(C_6H_5)_3P$, 8 H), 7.30 (t, (p-

C_6H_5)B, 1 H), 7.03 (m, $(C_6H_5)_3$P, 9 H), 2.68 (br, BCH_2, 6 H), 1.17 (s, C(CH_3)$_3$, 28 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.49. Anal. Calcd for $C_{39}H_{53}BCuPS_3$: C, 64.8; H, 7.38. Found: C, 65.1; H, 7.19.

[(Ph$_2$Bt)Cu(PPh$_3$)$_2$]. The synthesis and isolation of [(Ph$_2$Bt)Cu(PPh$_3$)$_2$] were performed using the procedure reported for [(PhTt)Cu(PPh$_3$)].[6] [(Ph$_2$Bt)Cu]$_4$ (254 mg, 0.18 mmol) and PPh$_3$ (370 mg, 1.41 mmol) were combined in THF. Yield, 400 mg (65%). Mp: 142 °C dec. ^{1}H NMR (C_6H_6): δ 7.95 (d, (*o*-C_6H_5)B, 4 H), 7.49 (t, (*m*-C_6H_5)B, 4 H), 7.29 (t, (*p*-C_6H_5)B, 2 H), 7.22 (t, $(C_6H_5)_3$P, 11 H), 6.93 (m, $(C_6H_5)_3$P, 18 H), 2.80 (b, BCH_2, 4 H), 1.72 (s, SCH_3, 6 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.9. Anal. Calcd for $C_{52}H_{50}BCuP_2S_2$: C, 71.4; H, 5.76. Found: C, 71.4; H, 5.70.

[(Ph$_2$Bt^{Ph})Cu(PPh$_3$)$_2$]. [Bu$_4$N]Ph$_2$Bt^{Ph} (310 mg, 0.47 mmol), [Cu(CH$_3$CN)$_4$][BF$_4$] (155 mg, 0.49 mmol), and PPh$_3$ (250 mg, 0.95 mmol) were combined as above for [(PhTt^{pTol})Cu(PPh$_3$)]. The reaction was stirred for 1 h, resulting in the precipitation of the product as a white solid. The solid was collected by filtration. Yield: 270 mg (58%). [(Ph$_2$Bt^{Ph})Cu(PPh$_3$)$_2$] is soluble in aromatic and chlorinated hydrocarbons. Mp: 157 °C. ^{1}H NMR (C_6H_6): δ 7.99 (d, *o*-C_6H_5, 4 H), 7.43 (t, (*m*-C_6H_5), 4 H), 7.27 (t, (*p*-C_6H_5), 2 H), 6.99 (m, (*p*-C_6H_5) and $(C_6H_5)_3$P, 19 H), 6.87 (t, $(C_6H_5)_3$P, 15 H), 6.75 (t, (*m*-C_6H_5), 4 H), 6.57 (d, (*o*-C_6H_5), 4H), 3.20 (br, SCH_2, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −0.1. Anal. Calcd for $C_{26}H_{54}BCuP_2S_2$: C, 74.5; H, 5.45. Found: C, 74.4; H, 5.51.

[(Et$_2$Bt)Cu(PPh$_3$)$_2$]. The synthesis and isolation of [(Et$_2$Bt)Cu(PPh$_3$)$_2$] were combined as above for [(PhTt^{pTol})Cu(PPh$_3$)] employing [Cu(CH$_3$CN)$_4$][BF$_4$] (169 mg, 0.54 mmol), PPh$_3$ (282 mg, 1.08 mmol), and [Bu$_4$N]Et$_2$Bt (225 mg, 0.52 mmol). Yield: 300 mg (74%). Mp: 126 °C dec. ^{1}H NMR (C_6H_6): δ 7.35 (m, $(C_6H_5)_3$P, 12 H), 6.97 (m, $(C_6H_5)_3$P, 18 H), 2.36 (br, BCH_2, 4 H), 1.74 (s, SCH_3, 6 H), 1.62 (t, CH_3, 6 H), 1.10 (m, BCH_2, 4 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −3.2. Anal. Calcd for $C_{44}H_{50}BCuP_2S_2$: C, 67.8; H, 6.47. Found: C, 68.0; H, 6.62.

In Situ Preparation of Monomeric Copper Pyridine Complexes. The pyridine complexes [PhTt^R]Cu(py) and [Ph$_2$Bt^R]Cu(py)$_2$ were formed by dissolution of 10 mg of the appropriate parent complex in pyridine-d_5 and detected in situ by ^{1}H NMR spectroscopy. **[(PhTt^{Ph})Cu(py)]:** δ 8.20 (d, (*o*-C_6H_5)B, 2 H), 7.49 (m, (*m*-C_6H_5)B and (*o*-C_6H_5)S, 8H), 7.18 (m, (*p*-C_6H_5)B and (*m*-C_6H_5)S, ∼7 H, coincident with py), 7.00 (t, (*p*-C_6H_5)S, 3 H), 3.06 (br, SCH_2, 6 H). **[(PhTt^{pTol})Cu(py)]:** δ 8.21 (d, (*o*-C_6H_5)B, 2 H), 7.49, 7.44 (t, (*m*-C_6H_5)B, and (d, (*o*-$C_6H_4(CH_3)$)S, 8H), 7.25 (t, (*p*-C_6H_5)B, 1 H), 7.02 (d, (*m*-C_6H_4-(CH_3))S, 6 H), 3.05 (br, BCH_2, 6 H), 2.12 (s, (C_6H_4(CH_3))S, 9 H). **[(Ph$_2$Bt)Cu(py)$_2$]:** δ 7.91 (d, (*o*-C_6H_5)B, 4 H), 7.37 (t, (*m*-C_6H_5)B, 4 H), 7.20 (m, (*p*-C_6H_5)B, coincident with py), 2.78 (br, BCH_2, 4 H), 2.08 (s, SCH_3, 6 H). **[(Ph$_2$Bt^{Ph})Cu(py)$_2$]:** δ 8.11 (d, (*o*-C_6H_5)B, 4 H), 7.48 (d and t (*m*-C_6H_5)B and (*o*-C_6H_5)S, 8H), 7.18 (m, (*p*-C_6H_5)B and (m, *m*-C_6H_5)S, 8 H), 7.00 (t, (*p*-C_6H_5)S, 3 H), 3.23 (br, SCH_2, 4 H). **[(PhTt^{tBu})Cu(py)]:** δ 8.10 (d, (*o*-C_6H_5)B, 2H), 7.45 (t, (*m*-C_6H_5)B, 2 H), 7.20 ((*p*-C_6H_5)B, coincident with py), 2.50 (br, BCH_2, 6 H), 1.22 (s, C(CH_3)$_3$, 28 H).

Equilibrium Constant Determination for Pyridine Binding to [(PhTt)Cu]$_4$ and [(PhTt^{Ph})Cu(NCCH$_3$)]. Copper complex (10 mg) was dissolved in 0.7 mL of CD_3CN (for [(PhTt^{Ph})Cu]$_\infty$) or $CDCl_3$ (for [(PhTt)Cu]$_4$) along with 9 mg of ferrocene as an internal standard. To this solution were added neat aliquots of pyridine (1.5 μL per addition). Equilibrium ratios were calculated by integration of the SCH_2 resonances for the individual complexes.

Crystallographic Structure Determinations. Suitable crystals for X-ray analysis were obtained by slow diffusion of Et_2O into concentrated chloroform solutions of [(Ph$_2$Bt)Cu]$_4$, slow evaporation of concentrated acetonitrile solutions of [(Ph$_2$Bt^{Ph})Cu(CH$_3$CN)$_2$], slow diffusion of pentanes into concentrated toluene solutions of [(PhTt^{Ph})Cu(PPh$_3$)] and [(PhTt^{pTol})Cu(PPh$_3$)], and slow diffusion of pentanes into concentrated benzene solutions of [(Et$_2$Bt)Cu(PPh$_3$)$_2$]. Suitable crystals were chosen and mounted on glass fibers with epoxy cement. Crystal data, collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space groups for [(Ph$_2$Bt)Cu]$_4$, [(Ph$_2$Bt^{Ph})Cu(CH$_3$CN)$_2$], [(PhTt^{Ph})Cu(PPh$_3$)], and [(Et$_2$Bt)Cu(PPh$_3$)$_2$]. The systematic absences in the diffraction data are consistent for the *C*-centered monoclinic space groups, *Cc* and *C*2/*c* for [(PhTt^{pTol})Cu(PPh$_3$)]. The *E*-statistics suggested the centrosymmetric space group for [(PhTt^{pTol})Cu(PPh$_3$)], and solution in the corresponding space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix, least-squares procedures. There is one molecule each of chloroform and diethyl ether in the asymmetric unit of [(Ph$_2$Bt)Cu]$_4$. Two of the carbon atoms of the diethyl ether molecule of [(Ph$_2$Bt)Cu]$_4$ are disordered over two positions, 80/20 and 55/45, respectively. The carbon atoms of the diethyl ether molecule of [(Ph$_2$Bt)Cu]$_4$ were refined isotropically. All other non-hydrogen atoms on the diethyl ether molecule of [(Ph$_2$Bt)Cu]$_4$ were ignored, and all other hydrogen atoms were treated as idealized contributions. The sulfur atoms S(1), S(2), and S(3) of [(PhTt^{Ph})Cu(PPh$_3$)] and one of the methyl carbon atoms, C(6), of [(Et$_2$Bt)Cu(PPh$_3$)$_2$] are disordered over two positions, 90/10 and 65/35, respectively. The hydrogen atoms on the methylene carbon atom in [(Et$_2$Bt)Cu(PPh$_3$)$_2$] bound to the disordered methyl carbon atoms, C(6), were ignored in the refinement because of the disorder, and all other hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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