ELSEVIER

Coordination Chemistry Reviews
174 (1998) 301–311

COORDINATION CHEMISTRY REVIEWS

Synthesis, solid-state structure and reactivity of $[PhTt^{Ph}]Cu$[1]

Carl Ohrenberg [a], Charles G. Riordan [a,*2], Louise Liable-Sands [b],
Arnold L. Rheingold [b]

[a] *Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA*
[b] *Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA*

Received 1 October 1997; accepted 23 January 1998

Contents

Abstract

$[Bu_4N]PhTt^{Ph}(PhTt^{Ph-}$ = phenyltris((phenylthio)methyl)borate) reacts with $[Cu(CH_3CN)_4]BF_4$, to yield $[(PhTt^{Ph})Cu\cdot CH_3CN]$, **1**. In acetonitrile solution, **1** is monomeric. X-ray analysis shows that **1** forms an infinite, one-dimensional solid-state extended structure. Each copper ion is coordinated by three sulfur donors, two from one ligand and the third from a second ligand. The approximate tetrahedral coordination sphere is completed by an

---

* Corresponding author. Tel: +1-302-831-1073; Fax: +1-302-831-6335; e-mail: riordan@udel.edu

[1] Dedicated to Professor Daryle H. Busch for his innovative work at the forefront of coordination chemistry and for the mentoring and continued friendship he provides.

[2] Current address: Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA.

PII S0010-8545(98)00083-6

η^2-phenyl from the phenyl ring attached to boron on the ligand providing a single thioether donor. Although **1** is stable to O_2, and H_2O, it reacts with PPh_3, pyridine, or benzonitrile to yield the corresponding monomer, $(PhTt^{Ph})Cu(L)$ ($L = PPh_3$, **2**; py, **3**; PhCN, **4**).

Keywords: Sulfur ligands; Copper complexes

1. Introduction

The guiding tenet in the work of Daryle Busch over the past 40 years is that ligand design is at the heart of coordination chemistry. In pioneering the fields of macrocycle and lacunar ligand development, Busch's molecular design principles permitted access to a diverse array of coordination complexes with specific and unique structure–function properties. Illustrative of these accomplishments was the development of the first totally synthetic iron(II) dioxygen carriers based on lacunar cyclidene ligands [1]. Today, Busch is applying these principles to prepare exotic materials based on orderly molecular entanglements [2].

In our ligand design efforts, we have followed many of the principles developed by Busch. The present case focuses on acyclic chelates containing sulfur donors. In our continued development of the poly((methylthio)methyl)borates [3–8] and derivatives, we sought to increase the steric requirements at sulfur through replacement of the methyl substituents. In the present case, our aim was to use this approach to reduce the nuclearity of Cu(I) complexes. Cu(I) reacts with the parent ligand, $PhTt^{-}$[3], to yield a homoleptic tetramer, $[(PhTt)Cu]_4$, containing terminal and bridging (methylthio)methyl groups [4]. Inspection of the molecular structure revealed close contacts between the methyl carbons of bridging arms at 3.97 Å. It was anticipated that replacement of methyl with larger substituents at sulfur would result in unfavorably close contacts between the bridging groups and, consequently, disruption of the tetrameric core. Molecular modeling studies were in agreement with this assertion[4]. For example, replacement of methyl with phenyl, as in the ligand $PhTt^{Ph-}$, would preclude tetramer formation. In fact, this ligand seemed sufficiently large to prevent the formation of bridging thioethers entirely. Therefore, the resulting complex should be of lower nuclearity—either a monomer with a coordinated solvent molecule, $(PhTt^{Ph})Cu(NCCH_3)$, or a polynuclear species, $[(PhTt^{Ph})Cu]_x$, with copper ions coordinated to terminal thioethers only. These alternative structures were expected to permit access to a greater diversity of reactivity than inherent in $[(PhTt)Cu]_4$. Finally, it was clear the phenyl for methyl modification of the ligand would significantly alter the electronic donor properties of the ligand—aryl thioethers being poorer σ-donors than methyl thioethers. Herein, we describe the preparation

---

[3] Abbreviations: $PhTt^{-}$, phenyltris((methylthio)methyl)borate; $PhTt^{Ph-}$, phenyltris(Cphdnylthio)-methyl)borate; Ph_2Bt^{-}, diphenylbis((methylthio)methyl)borate.

[4] Molecular mechanics calculations were performed at the MM2 level using CAChe software (Oxford Molecular Group, Inc.).

of the phenyl substituted ligand, $PhTt^{Ph-}$, and the synthesis, solution and solid-state structures of its copper(I) complex, $[(PhTt^{Ph})Cu \cdot CH_3CN]$.

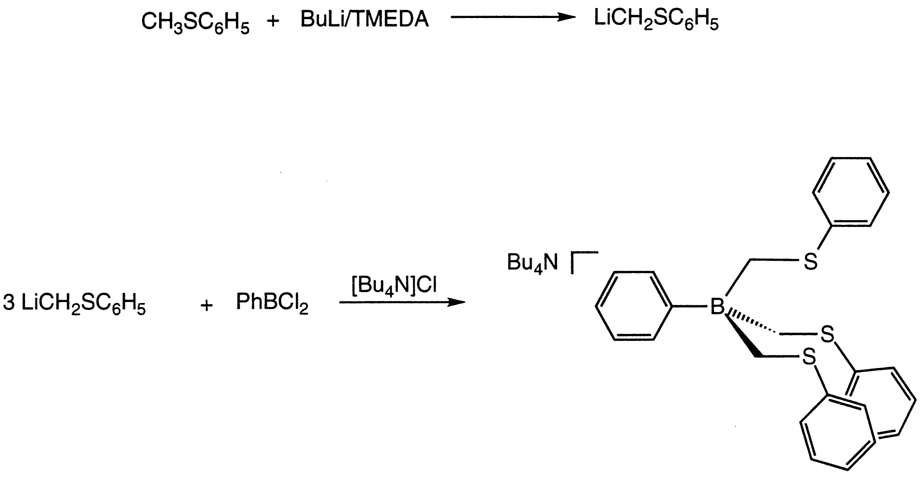
2. Results and discussion

2.1. Ligand synthesis

$PhTt^{Ph-}$ may be prepared in moderate yields, isolated as the corresponding Bu_4N^+ salts as outlined in Scheme 1. $C_6H_5SCH_3$ was quantitatively deprotonated by BuLi in the presence of TMEDA [9]. Three equivalents of the resulting carbanion, $LiCH_2SC_6H$, reacted with $C_6H_5BCl_2$ to yield the desired product. The Bu_4N^+ salt was isolated as a white solid from ethyl acetate upon addition of H_2O. The reaction proceeds more rapidly than, and in yields comparable with, the corresponding methyl sulfide, $LiCH_2SCH_3$ [5]. $[Bu_4N]PhTt^{Ph}$ is soluble in chlorinated hydrocarbons, tetrahydrofuran, acetone and acetonitrile. Spectroscopic data are contained in Section 4.

2.2. Synthesis and solution structure of $[(PhTt^{Ph})Cu \cdot CH_3CN]$

Reaction of $[Bu_4N]PhTt^{Ph}$ with $[Cu(CH_3CN)_4]BF_4$ in acetonitrile resulted in formation of a homogeneous solution from which a white powder was isolated (Section 4). The product was identified as $[(PhTt^{Ph})Cu \cdot CH_3CN]$, **1**, based on its ^1H NMR spectrum and X-ray diffraction analysis (vide infra). Combustion analysis of a dried, powder sample of **1** is consistent with the empirical formula $[(PhTt^{Ph})Cu]$. **1** is soluble, slightly, in acetonitrile and benzonitrile. The ^1H NMR spectrum in d_3-acetonitrile contained a single methylene resonance at $\delta 2.3$ and six



Scheme 1. Ligand synthesis.

overlapping aromatic resonances consistent with three magnetically equivalent phenylthio substituents and a unique phenyl substituent on boron. The most reasonable assignment of the solution structure is a monomer in which the ligand is tridentate and a solvent molecule is providing the fourth donor to copper. Structures of this type are common in the coordination chemistry of copper(I) [10]. Attempts to determine the solution molecular mass of **1** by osmometry were unsuccessful owing to its very low solubility in nitrile solvents. This structure differs significantly from that of $[(PhTt)Cu]_4$, reported recently, which is tetrameric in solution and the solid state [4]. In the tetramer, each borate ligand is oriented such that one sulfur is in a μ_2 position and the remaining two sulfurs are terminally ligated to adjacent copper ions. The terminal and bridging groups are distinguishable in the ^1H NMR spectrum. Each copper ion resides in a tetrahedral coordination environment of two terminal and two bridging thioethers.

2.3. *Solid-state structure of* $[(PhTt^{Ph})Cu \cdot CH_3CN]$

Dissolution of **1** in acetonitrile followed by slow evaporation yielded colorless, blade crystals suitable for X-ray analysis (Table 1). The solid-state structure of **1** is presented in Fig. 1 and selected metric parameters are summarized in Table 2. **1** forms a one-dimensional, extended structure in the solid state. Each copper ion is approximately four coordinate. Two sulfur donors are provided by a single borate, while the third sulfur donor arises from a second borate. The copper ion coordination sphere is completed by an η^2-phenyl of the second borate. The η^2-phenyl is coordinated through the *ipso* and one of the *ortho* carbon atoms. The crystal lattice contains one uncoordinated acetonitrile per copper. This coordination motif repeats

Table 1
Crystallographic data for **1**

Formula	$C_{29}H_{29}BCuNS_3$
Formula weight	562.06
Space group	$P2_12_12_1$
a (Å)	10.1162(2)
b (Å)	14.1356(2)
c (Å)	19.1680(3)
V (Å^3)	2741.00(8)
Z	4
Cryst. dimens. (mm)	0.02 × 0.10 × 0.45
Cryst. color, habit	Colorless, thin blade
$D_{(calc)}$ (g cm^{-3})	1.362
μ(MoKα) (cm^{-1})	10.44
Temp. (K)	218(2)
Diffractometer	Siemens P4/CCD
Radiation	MoKα ($\lambda = 0.71073$ Å)
$R(F)$ (%)[a]	5.47
$R(wF^2)$ (%)[a]	13.58

[a] $R(F) = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |F_o - F_c|$; $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)2]/\Sigma[(wF_o^2)^2]^{1/2}$.

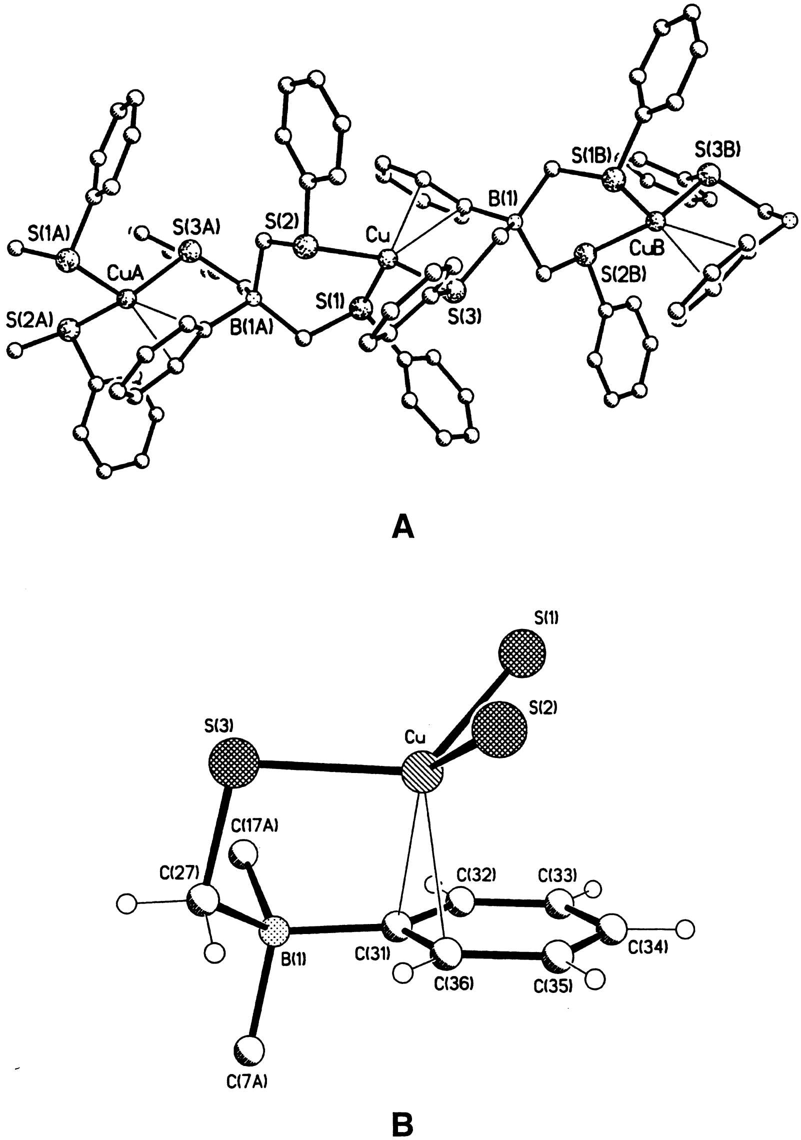


Fig. 1. (a) Solid-state structure of **1** with labeling scheme displaying three repeat units of the one-dimensional chain. Hydrogen atoms and solvent (CH_3CN) have been omitted for clarity. (b) View of the copper coordination sphere in **1**.

in one dimension through the crystal lattice. The Cu–S bond lengths of 2.297(2), 2.301(2) and 2.330(2) Å are essentially the same as the Cu–S distances in $[(PhTt)Cu]_4$, which average to 2.305 Å and are shorter than in $(PhTt)Cu(PPh_3)$, Cu–S_{ave} 2.337 Å [4]. The S–Cu–S bond angles are 98.42(7), 115.04(8) and

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Cu–S(1)	2.301(2)
Cu–S(2)	2.330(2)
Cu–S(3)	2.297(2)
Cu–C(31)	2.678(9)
Cu–C(36)	2.321(7)
S(1)–C(6)	1.789(8)
S(1)–C(7)	1.824(8)
S(2)–C(16)	1.774(8)
S(2)–C(17)	1.824(8)
S(3)–C(26)	1.780(8)
S(3)–C(27)	1.791(7)
S(1)–Cu–S(2)	98.42(7)
S(1)–Cu–S(3)	118.92(9)
S(2)–Cu–S(3)	115.04(8)
S(1)–Cu–C(31)	102.7(2)
S(2)–Cu–C(31)	141.5(3)
S(3)–Cu–C(31)	81.9(2)
S(1)–Cu–C(36)	116.0(2)
S(2)–Cu–C(36)	110.1(2)
S(3)–Cu–C(36)	99.0(2)
C(6)–S(1)–C(7)	105.1(4)
C(6)–S(1)–Cu	106.8(3)
C(7)–S(1)–Cu	99.7(3)
C(16)–S(2)–C(17)	106.8(4)
C(16)–S(2)–Cu	105.6(2)
C(17)–S(2)–Cu	102.2(3)
C(26)–S(3)–C(27)	105.4(4)
C(26)–S(3)–Cu	108.6(3)
C(27)–S(3)–Cu	102.6(3)
B(1)–C(7)–S(1)	111.7(5)
B(1)–C(17)–S(2)	110.9(5)
B(1)–C(27)–S(3)	111.4(5)

118.92(9)°. The smaller angle results from the natural bite of the chelate ligand—the two sulfurs in this angle are from the same borate. For example, in (PhTt)Cu(PPh$_3$) the S–Cu–S bond angles are 96.36, 98.37 and 91.34°. S–M–S bond angles close to 90° are also found in octahedral [PhTt]$_2$M (M = Fe, Co, Ni) [5]. The Cu–C(36) and Cu–C(31) distances of 2.321(7) and 2.678(9) Å, respectively, are shorter than the sum of their covalent radii. The large difference in the Cu–C bond distances, 0.36 Å, is the result of a non-symmetric η^2-coordination arising from geometrical demands of the chelate. More compelling metric evidence for the η^2-phenyl is the displacement of the copper from the S$_3$ plane towards the phenyl ring by 0.30 Å [Fig. 1(b)]. Were the proximity of the PhB to copper a consequence of constraints imposed by the crystal lattice, the ligand itself or both, rather than an electronic bonding interaction, the copper would be expected to lie in a trigonal plane containing the three sulfur donors. Precedent for Cu(I)–olefin complexes include coordination of ethylene [11], cyclohexene [12], styrene [13] and

η^2-cyclopentadiene [14]. However, examples of aromatic rings coordinated to Cu(I) are much less common. Most closely related to **1** is the structure of $[(en)Cu(CO)]BPh_4$ reported by Floriani [15]. In this molecular complex, the copper coordination sphere includes an $\eta^2-PhBPh_3^-$. The *ortho* and *meta* carbons from one of the phenyl rings are in bonding distance, 2.706(4) and 2.919(5) Å. The longer distances in Floriani's complex may result from the two π-acids, CO and η^2-Ph competing for electron density at the metal. In **1**, the η^2-Ph does not compete with another π-acid. Additionally, in $[(Ph_2Bt)Cu]_4$ each Cu(I) ion is coordinated by three sulfurs and an η^2-phenyl (Ohrenberg et al., unpublished results).

2.4. Reactivity of $[(PhTt^{Ph})Cu \cdot CH_3CN]$ with donor ligands

1 reacts with pyridine, benzonitrile or PPh_3 to yield the corresponding monomer $(PhTt^{Ph})Cu(L)$, Scheme 2. Dissolution of **1** in CH_3CN followed by addition of the donor ligand results in a significant increase in solubility consistent with formation of discrete monomers. Proton NMR spectra confirm the C_3 coordination of $PhTt^{Ph-}$. Formation of **3** and **4** are reversible processes. Similar reversible binding of pyridine has been observed for $[(PhTt)Cu]_4$. **2** is formed irreversibly upon addition of PPh_3. Alternatively, **2** is produced directly, in high yield, upon mixing equal molar proportions of $[Cu(CH_3CN)_4]BF_4$, $[Bu_4N]PhTt^{Ph}$ and PPh_3 in THF. **2** is highly soluble in THF, benzene and chlorinated hydrocarbons.

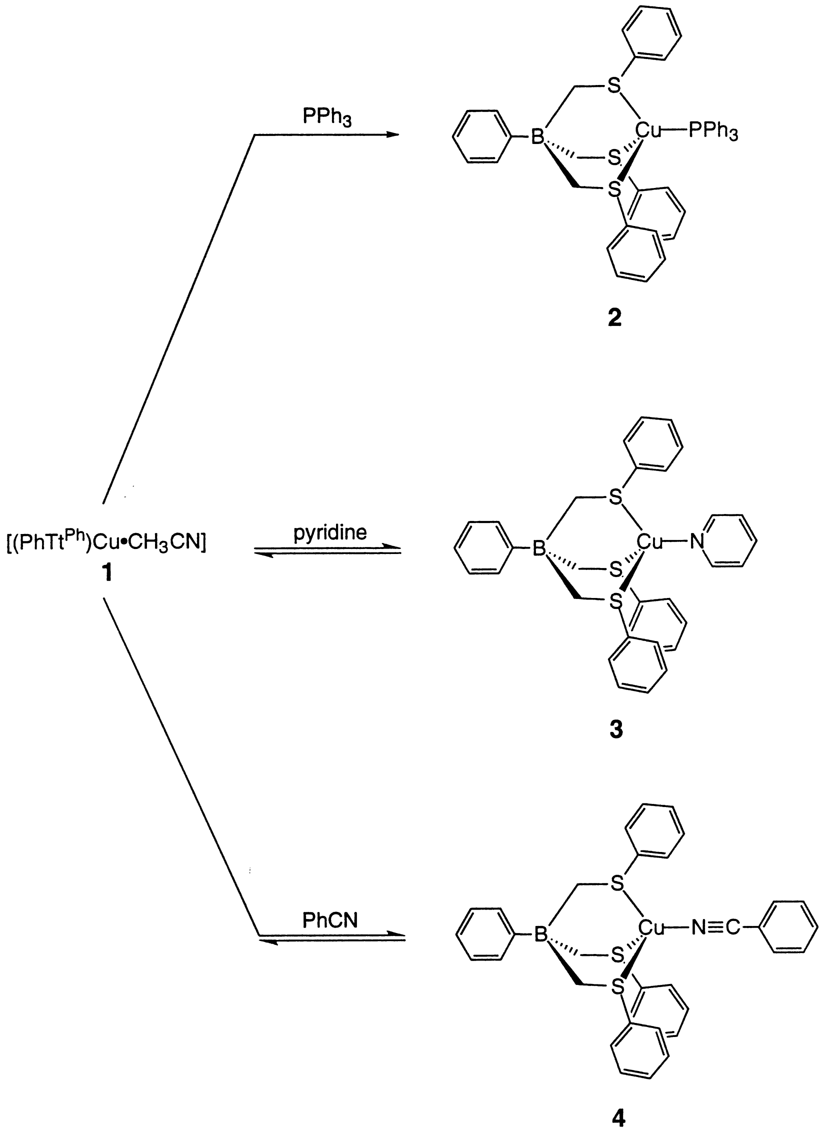
3. Summary

We have prepared a derivative of the parent ligand, $PhTt^-$, containing phenyl substituents on sulfur, $PhTt^{Ph-}$. This substitution results in demonstrative changes in the ligand's coordination chemistry as evidenced by reactions with copper(I). The former ligand yielded a homoleptic tetramer with copper(I). The structure consists of bridging and terminal thioether donors. The nuclearity persists in solution as well as the solid state. In contrast, $PhTt^{Ph-}$ reacted with copper(I) to yield a homoleptic complex that is monomeric in solution. However, in the solid state, $[(PhTt^{Ph})Cu]$ forms an infinite, one-dimensional solid-state extended structure. The structure is highlighted by the coordination of the PhB to copper in an η^2-fashion. The different nuclearity of the latter complex is a result of the inability of the larger PhS donor to bridge two copper ions in a manner present in $[(PhTt)Cu]_4$. These results suggest that the structural chemistry available to this ligand set can be controlled by judicious choice of substituents at both sulfur and boron. Future studies are aimed at preparing ligands of the form $BuTt^{Ph-}$ to elaborate this point.

4. Experimental section

4.1. Materials and methods

All reagents were distilled under N_2 and dried as indicated. THF, Et_2O, hexanes and pentane were freshly distilled over Na/benzophenone. Acetonitrile was



Scheme 2. Substitution reactions.

distilled over CaH_2. TMEDA was distilled under reduced pressure. $PhBCl_2$, BuLi, acetone, ethyl acetate, $[Bu_4N]Cl$, and PPh_3 were used as received. $[Cu(CH_3CN)_4][BF_4]$ was prepared by a modified literature procedure replacing HPF_6 with HBF_4 [16]. Elemental analyses were performed by Desert Analytics, Inc. NMR spectra were recorded on a 400 MHz Brüker spectrometer equipped with a Sun workstation.

4.2. [Bu_4N]$PhTt^{Ph}$

$C_6H_5SCH_3$ (3.5 ml, 30 mmol) and TMEDA (5.7 ml, 37.5 mmol) were added to a 200 ml flask under a N_2 atmosphere that was vented through an aqueous solution of NaOCl. BuLi (12 ml, 2.5 M in hexanes) was added dropwise via syringe over 5 min. As the BuLi was added the mixture turned yellow and viscous. Freshly distilled hexanes (50 ml) were added to the mixture following the BuLi to facilitate stirring. After 1 h at 25 °C, the solution was cooled to −78 °C and $C_6H_5BCl_2$ (1.3 ml, 10 mmol) was added via syringe. The mixture was allowed to warm to 25 °C and stirred for 24 h. The reaction was terminated by addition of 15 ml H_2O. Some of the insoluble material was brought into solution with 30 ml THF and the mixture was filtered through Celite and transferred to a separatory funnel. The organics were removed and the aqueous portion was extracted with THF (2 × 15 ml). The extracts were combined, concentrated by rotary evaporation, and a 10 ml solution of acetone containing [Bu_4N]Cl (3.2 g, 11.5 mmol) was added. The resulting solution was again concentrated by rotary evaporation, 25 ml of ethyl acetate added, and the product precipitated by addition of H_2O. The floculent white product was isolated by filtration, washed with Et_2O (3 × 20 ml) and dried under vacuum. Yield: 3.1 g (44%). [Bu_4N]$PhTt^{Ph}$ is soluble in chlorinated hydrocarbons, tetrahydrofuran, acetone, and acetonitrile and can be recrystallized from acetone–Et_2O. mp, 13 °C. ^1H NMR (($(CD_3)_2CO$): δ 7.60 ((o-C_6H_5)B, *d*, 2H), 7.25 ((o-C_6H_5)S, *d*, 6H), 7.15 ((m-C_6H_5)S, *t*, 6H), 7.04 ((m-C_6H_5)B, *t*, 2H), 6.89 ((p-C_6H_5)B and (p-C_6H_5)S, *m*, 4H), 3.25 (NCH_2, *q*, 8H), 2.40 (BCH_2, *s*, 6H) 1.70 (NCH_2CH_2, *p*, 8H), 1.38 ($N(CH_2)_2CH_2$, *h*, 8H), 0.98 ($N(CH_2)_3CH_3$, *t*, 12H). Anal. calcd. for $C_{43}H_{62}BNS_3$: C, 73.78; H, 8.93; N, 2.00. Found: C, 73.14; H, 8.99; N, 2.11.

4.3. [$(PhTt^{Ph})Cu \cdot CH_3CN$]$_x$

[$Cu(CH_3CN)_4$][BF_4] (140 mg, 0.45 mmol) in 30 ml acetonitrile was added to [Bu_4N]$PhTt^{Ph}$ (300 mg, 0.43 mmol) in 50 ml acetonitrile and was allowed to stir overnight before removing the solvent under vacuum. The resulting colorless oil was triturated with 30 ml Et_2O to produce a fine white solid that was collected by vacuum filtration, washed with acetone (3 × 20 ml) and dried under vacuum. Yield: 185 mg (83%). mp (dec.) 101 °C. ^1H NMR (CD_3CN): δ 7.42 ((o-C_6H_5)B, *d*, 2H), 7.28 ((o-C_6H_5)S and (m-C_6H_5)S, *m*, 12H), 7.12 ((m-C_6H_5)B and (p-C_6H_5)S, *m*, 5H), 7.00 ((p-C_6H_5)B, *t*, 1H), 2.30 (BCH_2, *s*, 6H). Anal. calcd. for $C_{27}H_{26}BCuS_3$: C, 62.24; H, 5.03. Found: C, 61.97; H, 5.20.

4.4. ($PhTt^{Ph}$)$Cu(PPh_3)$

A slurry of [$Cu(CH_3CN)_4$][BF_4] (115 mg, 0.37 mmol) in 20 ml THF was added to PPh_3 (100 mg, 0.38 mmol) and [Bu_4N]$PhTt^{Ph}$ (250 mg, 0.36 mmol) in 20 ml THF under an Ar atmosphere, upon which the [$Cu(CH_3CN)_4$][BF_4] was brought into solution immediately. The reaction was allowed to stir overnight before the solvent was removed by rotary evaporation. The resulting white solid was extracted with dry Et_2O (100 ml) and filtered. The solvent was removed from the filtrate by rotary evaporation and the resulting product was washed with pentane (3 × 25 ml) and dried under vacuum. Yield: 165 mg (60%). MP 86 °C. ^1H NMR ($(CD_3)_2CO$): δ 7.45 ((o-C_6H_5)B and (p-C_6H_5)P, *t*, 5H), 7.29 ((m-C_6H_5S)S, *t*, 6H), 7.15 ((m-C_6H_5)B, (o-C_6H_5)S, (p-C_6H_5)S and (m-C_6H_5)P, *m*, 16H), 6.98 ((o-C_6H_5)P and (p-C_6H_5)B, *t*, 7H), 2.30 (BCH_2, *s*, 6H). Anal. calcd. for $C_{45}H_{41}BCuS_3P$: C, 69.00; H, 5.28. Found: C, 69.04; H, 5.54.

4.5. Crystallographic structural determination

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected and mounted on the tip of a glass capillary with paratone oil and placed immediately in a stream of nitrogen. The data were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector.

The systematic absences in the diffraction data are consistent for the orthorhombic space group, $P2_12_12_1$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The absolute configuration of the structure was determined [Flack parameter = 0.06(3)]. There is a molecule of acetonitrile in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement coefficients and hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (Version 5.03) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Structure determination summary, atomic coordinates, bond lengths, bond angles and structure factor tables for **1** (16 pages) is available from the authors.

Acknowledgements

We thank the Petroleum Research Fund administered by the ACS for partial support of this research (30627-AC3). C.G.R. thanks National Science Foundation for a National Young Investigator Award (CHE-9457714). The University of Delaware acknowledges the National Science Foundation for their support of the purchase of the CCD-based diffractometer (CHE-9628768).

References

[1] D.H. Busch, N.W. Alcock, Chem. Rev. 94 (1994) 585–623.
[2] D.H. Busch, in: L. Fabbrizzi (Ed.), Transition Metal Ions in Supramolecular Chemistry, Kluwer, Dordrecht, 1994, pp. 55–79.
[3] P. Ge, C.G. Riordan, B.S. Haggerty, A.L. Rheingold, J. Am. Chem. Soc. 116 (1994) 8406–8407.
[4] C. Ohrenberg, M.M. Saleem, C.G. Riordan, G.P.A. Yap, A.L.J. Rheingold, Chem. Soc. Chem. Commun. (1996) 1081–1082.
[5] C. Ohrenberg, P. Ge, P. Schebler, C.G. Riordan, G.P.A. Yap, A.L. Rheingold, Inorg. Chem. 35 (1996) 749–754.

[6] P. Ge, C.G. Riordan, G.P.A. Yap, A.L. Rheingold, Inorg. Chem. 35 (1996) 5408–5409.
[7] A.L. Sargent, E.P. Titus, C.G. Riordan, A.L. Rheingold, P. Ge, Inorg. Chem. 35 (1996) 7095–7101.
[8] P. Schebler, C.G. Riordan, L. Liable-Sands, A.L. Rheingold, Inorg. Chim. Acta 270 (1998) 543–549.
[9] D.J. Peterson, J. Org. Chem. 32 (1967) 1717–1720.
[10] B.P. Murphy, Coord. Chem. Rev. 124 (1993) 63–105.
[11] J.S. Thompson, J.F. Whitney, Inorg. Chem. 23 (1984) 2813–2819.
[12] J.S. Thompson, J.F. Whitney, J. Am. Chem. Soc. 105 (1983) 5488.
[13] H. Masuda, K. Machida, M. Munakata, S. Kitagawa, H.J. Shimono, Chem. Soc. Dalton Trans. (1988) 1907.
[14] P. Jutzi, W. Wieland, B. Neumann, H. Stammler, J. Organomet. Chem. 501 (1995) 369.
[15] M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, Inorg. Chem. 19 (1980) 1191–1197.
[16] G.J. Kubas, in: D. Shriver (Ed.), Inorganic Synthesis, Vol. 19, Wiley-Interscience, New York, 1979, pp. 90–92.