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Phenyltris((*tert*-butylthio)methyl)borate: A Second Generation S_3^- Ligand That Enforces Tetrahedral Coordination

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In our continued development of a ligand class designed to provide a face-capping, S_3^- donor set to metal ions,[1] we report the synthesis of Tl[PhTt^{t-Bu}],[2] **1**, and two representative metal derivatives, [PhTt^{t-Bu}]MCl, M = Co (**2**), Ni (**3**) as well as preliminary reactivity studies of **3**. This ligand was designed to expand the coordination chemistry of the parent derivative, PhTt$^-$, which, due to the small alkyl substituents on sulfur, is dominated by formation of 2:1 complexes, $[PhTt]_2M$.[1b] The resulting complexes display a limited range of reactivity given the lack of accessible metal ion coordination sites. To elaborate the scope of reactivity of attendant complexes we have prepared second generation ligands possessing the larger substituents phenyl, *para*-tolyl and *tert*-butyl on sulfur. The aryl derivatives have proven potent to this end in the preparation of Cu(I) complexes of reduced nuclearity.[3] Cu(I) reacts with the parent ligand, PhTt$^-$, to yield a homoleptic tetramer, $[(PhTt)Cu]_4$, containing terminal and bridging (methylthio)methyl groups.[1c] Replacement of methyl with phenyl as in PhTt^{Ph-} precludes tetramer formation by preventing formation of bridging thioethers.[3] Consequently, [(PhTt^{Ph})Cu·CH_3CN] is monomeric in solution while forming an infinite, one-dimensional, extended structure in the solid-state. The present report demonstrates PhTt^{t-Bu-} is sufficiently large so as to prevent 2:1 complex formation with Co(II) or Ni(II). The resulting four-coordinate complexes possess approximate C_{3v} symmetry.

Tl[PhTt^{t-Bu}], **1**, was prepared from the *in situ* reaction of excess $LiCH_2S^tBu$ with $PhBCl_2$ in hexanes under nitrogen followed by precipitation with $TlNO_3$ from aqueous solution. Spectroscopic and analytical data[4,5] support the empirical formula for **1** that has been confirmed by single-crystal X-ray diffraction analysis.[6] In the solid state **1** forms a one-dimensional, extended structure, Figure 1. Each thallium ion is coordinated to three sulfur donors (Tl−S$_{av}$, 3.107 Å) and a phenyl ring in an η^6-mode that may be described roughly as a three-legged piano stool coordination environment. The Tl−C distances range from 3.272(8) to 3.446(8) Å. Two sulfur donors are provided by a single borate while the third sulfur donor and the phenyl substituent arise from a second borate. This coordination motif repeats in one dimension through the crystal lattice. A similar solid-state structure occurs in [(PhTt^{Ph})Cu·CH_3CN].[3] Two sulfurs coordinate to a single Cu(I) ion while the third sulfur and the η^2-phenyl substituent on boron coordinate to a neighboring Cu(I). **1** displays 3-fold equivalence of the thioether groups in its proton NMR spectrum consistent with a monomeric species in solution.

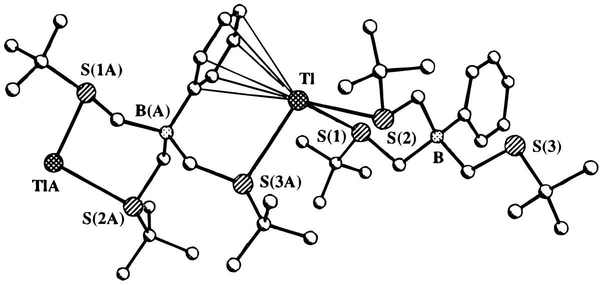

Figure 1. Representation of two repeat units of **1** in the crystal lattice depicting the one-dimensional, extended structure. Selected bond distances (Å) and bond angles (deg): Tl−S(1), 3.081(4); Tl−S(2), 3.149(3); Tl(A)−S(3), 3.092(4); S(1)−Tl−S(2), 78.06(9).

Addition of 1 equiv of **1** in methylene chloride to an acetone solution of $CoCl_2 \cdot 6H_2O$ resulted in an immediate color change to a blue-green solution with concomitant precipitation of TlCl. Recrystallization from methylene chloride at 0 °C produced **2** as blue rods in 67% yield. The analogous Ni(II) derivative, **3**, prepared similarly, was isolated as red blocks in 76% yield. Analytical and combustion data[4,7] are consistent with the indicated formulas that have been corroborated by X-ray diffraction analysis.[6] Solution magnetic moment values of 4.5 μ_B for **2** and 2.5 μ_B for **3** are in accord with $S = {}^3/_2$ and $S = 1$ ground states, respectively.[6] The molecular structure of **3** is depicted in Figure 2 (**2** and **3** are isomorphous) with selected metric parameters for **2** and **3** contained in the figure caption. The molecular geometry is distorted tetrahedral, with the borate ligand providing a 3-fold

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(1) (a) Ge, P.; Riordan, C. G.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8406−8407. (b) Ohrenberg, C.; Ge, P.; Schebler, P.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 749−754. (c) Ohrenberg, C.; Saleem, M. M.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1996**, 1081−1082. (d) Ge, P.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 5408−5409. (e) Schebler, P.; Riordan, C. G.; Liable-Sands, L.; Rheingold, A. L. *Inorg. Chim. Acta* **1998**, *270*, 543−549.

(2) Abbreviations: PhTt^{t-Bu-}, phenyltris((*t*-butylthio)methyl)borate; PhTt^{Ph-}, phenyltris((phenylthio)methyl)borate; PhTt$^-$, phenyltris((methylthio)methyl)borate; Ph_2Bt^-, diphenylbis((methylthio)methyl)borate.

(3) Ohrenberg, C.; Riordan, C. G.; Liable-Sands, L.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, in press.

(4) Complete data contained in Supporting Information.

(5) ^{1}H NMR ($CDCl_3$): δ 7.57 ((o-C_6H_5)B, br, 2 H), 7.39 ((m-C_6H_5)B, t, 2 H), 7.19 ((p-C_6H_5)B, t, 1 H), 2.38 (BCH_2, q, ^2J = 3.9 Hz, 6 H), 1.30 ($(CH_3)_3$, s, 27 H). Anal. Calcd for $C_{21}H_{38}BS_3Tl$: C, 41.9; H, 6.36. Found: C, 41.7; H, 6.32.

(6) X-ray structure determinations: **1** (MW = 601.87) is monoclinic, $P2_1/n$, $a = 9.9542(2)$ Å, $b = 18.5590(1)$ Å, $c = 14.8306(3)$ Å, $\beta = 98.9957(7)°$, $V = 2706.1(1)$ Å^3, $Z = 4$, $T = 218(2)$ K, μ(Mo Kα) = 62.03 cm^{-1}, D_{calc} = 1.477 g/cm^3, $R(F)$ = 7.39% for 3604 observed independent reflections ($4 \le 2\theta \le 56°$). **2** (MW = 491.88) is monoclinic, $P2_1/n$, $a = 9.6413(2)$ Å, $b = 21.0835(7)$ Å, $c = 14.8306(3)$ Å, $\beta = 98.478(2)°$, $V = 2558.7(1)$ Å^3, $Z = 4$, $T = 213(2)$ K, μ(Mo Kα) = 10.25 cm^{-1}, D_{calc} = 1.277 g/cm^3, $R(F)$ = 4.77% for 2481 observed independent reflections ($4 \le 2\theta \le 56°$). **3** (MW = 491.66) is monoclinic, $P2_1/n$, $a = 9.597(8)$ Å, $b = 20.984(7)$ Å, $c = 12.779(2)$ Å, $\beta = 98.51(3)°$, $V = 2545(2)$ Å^3, $Z = 4$, $T = 238(2)$ K, μ(Mo Kα) = 11.18 cm^{-1}, D_{calc} = 1.283 g/cm^3, $R(F)$ = 4.12% for 3698 observed independent reflections ($4 \le 2\theta \le 56°$). Empirical absorption corrections were applied for **1** using the program *DIFABS*. All non-hydrogen atoms (except one disordered atom, C(8) in **1**) were refined anisotropically. Hydrogen atoms were treated as idealized contributions. **2** and **3** are isomorphous. *DIFABS* is described by N. Walker and D. Stuart in *Acta Crystallogr.* **1983**, *A39*, 158−166.

(7) Data for **2**: ^{1}H NMR ($CDCl_3$): δ 17.5 (br), 10.9 (br), 7.9 (br), 6.1 (br). UV−vis (CH_2Cl_2), λ_{max} (ϵ, M^{-1} cm^{-1}): 245 (4300), 298 (2800), 360 (sh, 1300), 664 (880), 695 (740), 932 (130). Anal. Calcd for $C_{21}H_{38}BClCoS_3$: C, 51.3; H, 7.79. Found: C, 49.2; H, 7.82 For **3**: ^{1}H NMR ($CDCl_3$): δ 19.1 (br), 7.7 (br), 7.1 (br). UV−vis (CH_2Cl_2), λ_{max} (ϵ, M^{-1} cm^{-1}): 282 (4600), 298 (2900), 388 (3900), 425 (3300), 534 (280), 836 (220). Anal. Calcd for $C_{21}H_{38}BClNiS_3$: C, 51.3; H, 7.79. Found: C, 49.7; H, 7.71.

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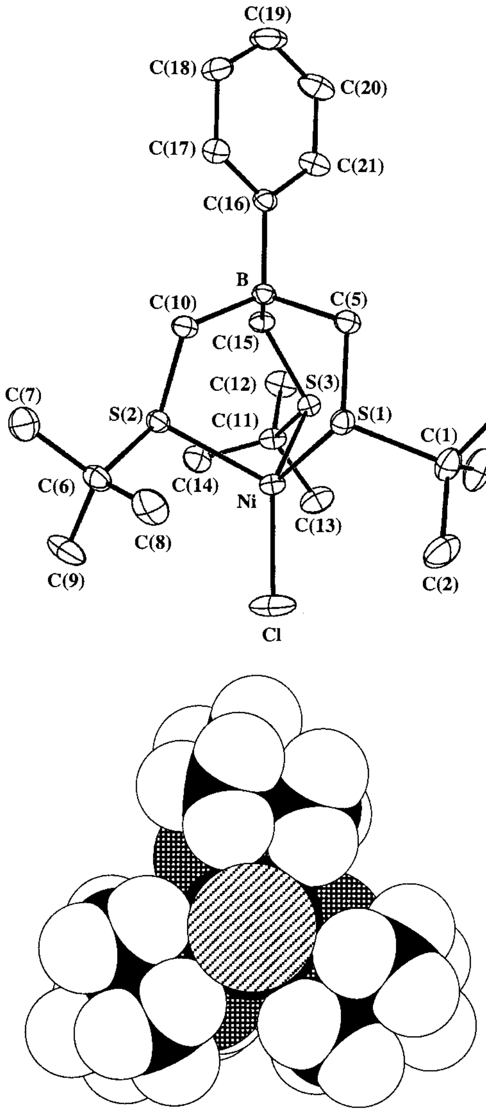

Figure 2. (A) Thermal ellipsoid plot of **3** at 30% probability level with hydrogen atoms not shown for clarity. Selected bond distances (Å) and bond angles (deg) for **2**: Co−S(1), 2.321(1); Co−S(2), 2.320(1); Co−S(3), 2.326(1); Co−Cl, 2.189(1); S(1)−Co-S(2), 99.09(5); S(2)−Co-S(3), 100.53(5); S(1)−Co-S(3), 98.35(5); Cl−Co−S(1), 120.35(6); Cl−Co−S(2), 117.56(5); Cl−Co−S(3), 117.11(5); for **3**: Ni−S(1), 2.276(2); Ni−S(2), 2.282(1); Ni−S(3), 2.279(1); Ni−Cl, 2.152(1); S(1)−Ni−S(2), 94.04(4); S(2)−Ni−S(3), 95.80(4); S(1)−Ni−S(3), 94.75(6); Cl−Ni−S(1), 125.46(5); Cl−Ni−S(2), 120.17(5); Cl−Ni−S(3), 119.57(5). (B) Space-filling view along the 3-fold axis.

axis (containing the M-Cl vector) that is not crystallographically imposed. The M−S distances are within the range of other four-coordinate Co(II) and Ni(II) complexes containing thioether donors.[8] The pyramidalization at each sulfur requires that the three *tert*-butyl substituents are canted in the same direction. The proximity of the *tert*-butyl groups to the metal ion combined with the requisite small C−S−C (*tert*-butyl) bond angles (average 108°) result in a tight pocket at the metal ion. The experimentally determined cone angle for PhTt$^{t-\mathrm{Bu}-}$ of 276° is larger than that of PhTt$^{\mathrm{Ph}-}$ (264°) and comparable to that of Tp$^{t-\mathrm{Bu}-}$ (268°).[9] As evidenced by the space-filling perspective contained in Figure 2, formation of L_2M complexes appears to be precluded. Furthermore, the *tert*-butyl substituents render these first transition series metal ions sufficiently inaccessible so as to limit coordination numbers to four. In contrast, the phenyl-substituted ligand, $B(CH_2SC_6H_5)_4^-$, forms a six-coordinate complex with the second transition series Mo ion, *fac*-$[B(CH_2SC_6H_5)_4]Mo(CO)_3^-$.[10] While the phenyl groups are of adequate dimensions to prevent bischelate formation, they can be arranged on a larger metal to accommodate three additional ligands. Current experiments are designed to establish the feasibility of higher coordination number complexes derived from PhTt$^{\mathrm{Ph}-}$ coordinated to first transition series ions, e.g. [PhTt$^{\mathrm{Ph}}$]NiL(X).

The cyclic voltammogram of **2** is characterized by an irreversible reduction at −1511 mV (vs Fc/Fc$^+$, CH_2Cl_2, 100 mV/s). The reduction potential of **3** is −1302 mV (irreversible) in CH_2Cl_2. For comparison, electrochemical reduction of square planar [Ph$_2$-Bt]Ni occurs at $E° = -1051$ mV (quasi-reversible).[1d] Preliminary reactivity studies confirm that **3** is a useful synthon for the preparation of a range of tetrahedral derivatives. **3** reacts cleanly with NO yielding deep blue [PhTt$^{t-\mathrm{Bu}}$]Ni(NO), **4**.[11] Also, **3** reacts with CO reversibly to yield a species tentatively assigned as the Ni(II) dicarbonyl, [(κ^2-PhTt$^{t-\mathrm{Bu}}$)Ni(CO)$_2$]Cl, **5**.[11] Molecular models are consistent with the requirement that one of the thioether substituents need be displaced to permit coordination of two additional ligands. Ni(II) carbonyls are rare complexes[12] that may provide precedent for Ni−CO intermediates in CO dehydrogenase/acetyl CoA synthase and for the CO-inhibited form of [NiFe] H$_2$ase. Alternatively, **3** provides entry into mono-valent nickel derivatives. Sodium-amalgam reduction of **3** in THF results in formation of an air-sensitive, brown compound that gives rise to a rhombic EPR signal, *g* values, 2.40, 2.18, 2.12.[1d,11] We formulate the compound as [PhTt$^{t-\mathrm{Bu}}$]Ni(THF), **6**. Current experiments are exploring the scope of reactivity of **2** and **3** as well as more completely characterizing **5** and **6**.

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Supporting Information Available: Experimental details and spectroscopic data for **1**−**6** and tables giving structure determination summary, atomic coordinates, bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **1**, **2** and **3** are available (23 pages). Ordering information is given on any current masthead page.

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(8) For representative examples of Co(II) thioether complexes, see: (a) Kajitani, M.; Hatano, H.; Fujita, T.; Okumachi, T.; Nagao, H.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *430*, C64−C67. (b) Sheldrick, W. S.; Hauck, E.; Korn, S. *J. Organomet. Chem.* **1994**, *467*, 283−292. (c) Takayama, C.; Sakamoto, N.; Harada, T.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Organometallics* **1996**, *15*, 5077−5079. A search of the Cambridge Crystallographic Database found no tetrahedral Ni(II) thioether complexes. For representative examples of Ni(II) thioether derivatives in square planar geometries, see: (a) Davis, P. H.; White, L. K.; Belford, R. L. *Inorg. Chem.* **1975**, *14*, 1753−1757. (b) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364−4366. (c) Yamamura, T.; Arai, H.; Nakamura, N.; Miyamae H. *Chem. Lett.* **1990**, 2121−2124. (d) Desper, J. M.; Vyvyan, J. R.; Mayer, M. J.; Ochrymowycz, L. A.; Gellman, S. H. *Inorg. Chem.* **1993**, *32*, 381−382. (e) Sellmann, D.; Haussinger, D.; Knoch, F.; Moll, M. *J. Am. Chem. Soc.* **1996**, *118*, 5368−5374.

(9) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Liable-Sands, L.; Rheingold, A. L. Unpublished result.

(10) Ge, P.; Riordan, C. G.; Rheingold, A. L. Unpublished result.

(11) Data for **4**. UV−vis (CH_2Cl_2), λ_{max} (ϵ, $M^{-1}cm^{-1}$): 235 (5100), 283 (2600), 299 (sh, 2100), 370 (180), 595 (250). IR (CH_2Cl_2): $\nu_{NO} = 1785$ cm^{-1}; X-ray data (collected and solved by L. M. Liable-Sands): (MW = 606.43), monoclinic, $P2_1/n$, $a = 9.67940(3)$ Å, $b = 21.0838(3)$ Å, $c = 12.6350\ (2)$ Å, $\beta = 99.3217(8)°$, $V = 2544.49(6)$ Å^3, $Z = 4$, $T = 198(2)$ K, μ(Mo Kα) = 62.03 cm^{-1}, $D_{calc} = 1.269$ g/cm^3, $R(F) = 3.39\%$ for 4495 observed independent reflections ($4 \le 2\theta \le 57°$). Data for **5**. IR (CH_2Cl_2): $\nu_{CO} = 2040$, 1994 cm^{-1}. Data for **6**. UV−vis (THF), λ_{max} (ϵ, M^{-1} cm^{-1}): 222 (9900), 267 (3200), 274 (3200), 307 (2400), 470 (210). EPR (X-band, THF, 77 K) *g* values: 2.40, 2.18, 2.12.

(12) (a) Macgregor, S. A.; Lu, Z.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **1994**, *33*, 3616−3618. (b) Nguyen, D. H.; Hsu, H.-F.; Millar, M.; Koch, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 8963−8964. (c) Liaw, W.-F.; Horng, Y.-C.; Ou, D.-S.; Ching, C.-Y.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **1997**, *119*, 9299−9300.