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Communications to the Editor

Organometallic Cobalt(II) and Nickel(II) Complexes Supported by Thioether Ligation: Unexpected Nickel Alkylation by the Borato Ligand Phenyltris((*tert*-butylthio)methyl)borate

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The organometallic chemistry of cobalt and nickel is well developed and of great utility in a wide diversity of stoichiometric and catalytic transformations.[1] However, few complexes have been prepared and structurally authenticated in which the organometalloid fragment is supported by thioether donors.[2] This is surprising given the importance of this ligand combination in biological[3] and industrial[4] catalysis. For example, the $NiFe_4S_4$ enzyme acetyl CoA synthase (ACS) catalyzes the reversible formation of acetyl-CoA from methyl, CO, and CoA groups via a series of organometalloid intermediates.[5] The general scarcity of such ligand combinations prompted us to utilize the borato ligands, [PhTt^{R}], in this pursuit. Our recently reported [PhTt$^{t\mathrm{Bu}}$] ligand[6] seemed to provide an ideal framework, permitting access to synthetic precursors of the type [PhTt$^{t\mathrm{Bu}}$]MCl in which three thioether substituents coordinate in a facial array.[7] Preparative manipulations using the chloride derivatives were designed to yield the target T_d [PhTt$^{t\mathrm{Bu}}$]M(R) complexes. The decision to prepare T_d organometallic derivatives is additionally motivated by the scarcity of these divalent late metal species and, therefore, the potential to elucidate their novel molecular and electronic structures and patterns of reactivity.[8] Specifically, T_d nickel alkyls are without precedent. Furthermore, the target complexes are expected to be paramagnetic and of low ($<$18) electron count—uncommon properties in organometallic chemistry.

Reaction of [PhTt$^{t\mathrm{Bu}}$]CoCl[4] with freshly prepared $(CH_3)_2Mg$ or CH_3Li in THF resulted in a rapid color change from blue to forest green, Scheme 1. Recrystallization of [PhTt$^{t\mathrm{Bu}}$]Co(CH_3) from concentrated pentanes produced green crystals in 85% yield.

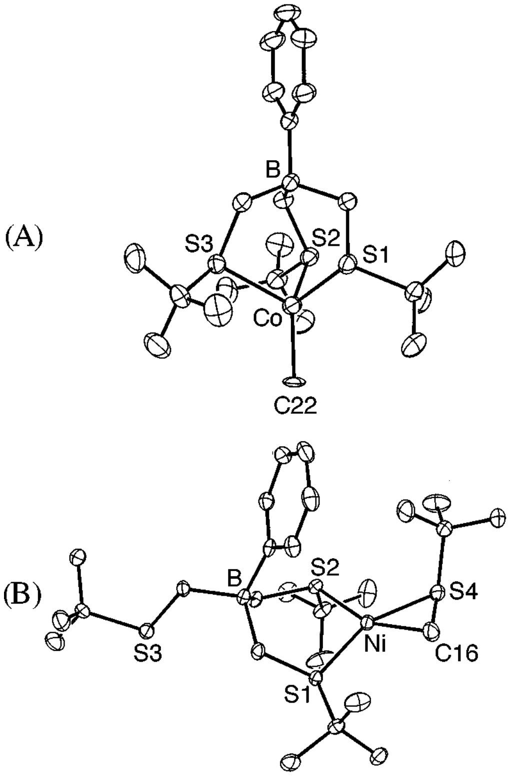

Figure 1. Thermal ellipsoid plots of [PhTt$^{t\mathrm{Bu}}$]Co(CH_3) (A) and [κ^2-PhTt$^{t\mathrm{Bu}}$]Ni(η^2-CH_2SBu^t) (B) at the 30% probability level with hydrogen atoms not shown. Selected bond distances (Å) for [PhTt$^{t\mathrm{Bu}}$]Co(CH_3): Co−C, 2.052(3); Co−S1, 2.341(1); Co−S2, 2.341(2); Co−S3, 2.352(2). Selected bond distances (Å) and bond angles (deg) for [κ^2-PhTt$^{t\mathrm{Bu}}$]Ni(η^2-CH_2SBu^t): Ni−C, 1.939(5); Ni−S1, 2.180(2); Ni−S2, 2.256(2); Ni−S4, 2.172(2); S1−Ni−S2, 96.22(4); S2−Ni−S4, 106.92(5); S4−Ni−C16, 49.8(2).

Spectroscopic data[9] are consistent with the indicated formula confirmed by X-ray diffraction analysis.[10] Paramagnetic [PhTt$^{t\mathrm{Bu}}$]-Co(CH_3) displays well-resolved, contact-shifted proton NMR resonances for the *tert*-butyl and phenyl protons. The Co−CH_3 resonance could not be detected and was presumed broadened into the baseline. The solution magnetic moment of 5.1 μ_B is in accord with the $S = {}^3/_2$ ground state.[11] The molecular structure of [PhTt$^{t\mathrm{Bu}}$]Co(CH_3) is depicted in Figure 1. Expectedly, [PhTt$^{t\mathrm{Bu}}$]-Co(CH_3) is isomorphous with the starting chloride complex. The methyl group resides on the molecular pseudo 3-fold axis, ∠B−Co−C, 178.9°. The average Co−S bond length of 2.345 Å is slightly longer than that for [PhTt$^{t\mathrm{Bu}}$]CoCl. The Co−C bond distance is 2.052(3) Å, in the range found for other T_d Co(II) alkyls reported recently.[8a,c]

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(2) (a) Stavropoulos, P.; Carrié, M.; Muetterties, M. C.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 8485−8492. (b) Sellmann, D.; Schillinger, H.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1992**, *198*, 351−357.

(3) Ragsdale, S. W.; Riordan, C. G. *J. Biol. Inorg. Chem.* **1996**, *1*, 489−493.

(4) Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysts in Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1996.

(5) Ragsdale, S. W.; Riordan, C. G. *J. Biol. Inorg. Chem.* **1996**, *1*, 489−493.

(6) Abbreviations: [PhTt$^{t\mathrm{Bu}}$], phenyltris((*tert*-butylthio)methyl)borate; [Tp$^{t\text{-}\mathrm{Bu}}$], hydrotris(3-*tert*-butylpyrazolyl)borate; [PhTp$^{t\mathrm{Bu}}$], phenyltris(3-*tert*-butylpyrazolyl)borate.

(7) Schebler, P.; Riordan, C. G.; Guzei, I.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 4754−4755.

(8) Recently, examples of late metal alkyls based on bulky [Tp^{R}] ligands have appeared. (a) Jewson, J. D.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1999**, *18*, 300−305. (b) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561−10562. (c) Shirasawa, N.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Chem. Commun.* **1999**, 417−418.

(9) [PhTt$^{t\mathrm{Bu}}$]Co(CH_3): ^{1}H NMR (C_6D_6) δ 18.9 (br, C_6H_5), 10.8 (br, C_6H_5), 9.8 (br, C_6H_5), 3.2 (br, $C(CH_3)_3$); UV−vis (CH_2Cl_2), λ_{max} (ϵ, M^{-1} cm^{-1}) 632 (570), 658 (690), 707 (710), 930 (90).

(10) X-ray data: [PhTt$^{t\mathrm{Bu}}$]Co(CH_3), $C_{22}H_{41}BCoS_3$, FW = 471.47, monoclinic, $P2_1/n$, green block, $a = 9.7856(2)$ Å, $b = 21.6045(4)$ Å, $c = 12.6512(2)$ Å, $\beta = 99.1316(5)°$, $V = 2640.73(8)$ Å^3, $Z = 4$, $Z' = 1$, $T = 295(2)$ K, GOF = 1.757, $R(F) = 4.99\%$ for 4125 observed independent reflections ($4° \le 2\theta \le 50°$).

(11) The experimental value exceeds the predicted spin-only moment due to spin−orbit coupling which is significant for T_d Co(II). See: Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992; p 486.

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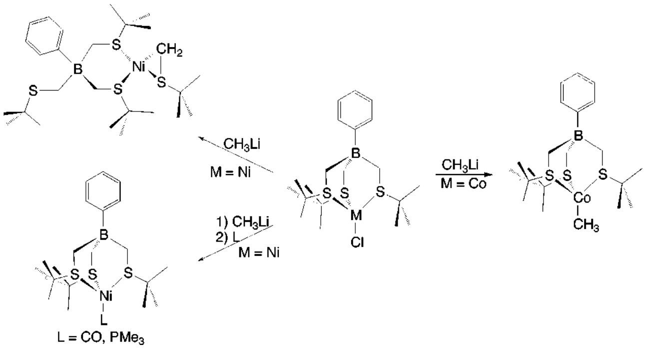
Scheme 1



In contrast to the transformation outlined above for Co, attempts to prepare an unprecedented T_d Ni$-$CH$_3$ species by reaction of [PhTt^{tBu}]NiCl[7] with (CH$_3$)$_2$Mg or CH$_3$Li resulted in production of an orange-red, diamagnetic complex in moderate (40%) yield, Scheme 1. [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t) has been characterized fully[12] and its molecular structure, determined by X-ray diffraction,[13] is contained in Figure 1. The borato ligand is coordinated in the bidentate mode with the chelate ring in the twist boat conformation. The Ni$-$S bond distance for the thioether trans to the alkyl group is 2.256(2) Å compared with the other, mutually trans thioethers at Ni$-$S = 2.180(2) and 2.172(2) Å. The solid-state structure shows a slight twist from square planar, 14°, a consequence of close contact between the phenyl substituent of the borato ligand and the *tert*-butyl of the alkyl. Surprisingly, [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t) does not react with CO. Commonly, nickel alkyls react readily with CO to afford the corresponding acyl derivatives.[14,15]

In an effort to elucidate the mechanism of formation of [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t), [PhTt^{tBu}]NiCl was reacted with [PhTt^{tBu}]Tl. This reaction led to isolation of the metallacyclic complex in greater than 85% yield, suggesting the reaction of [PhTt^{tBu}]NiCl and CH$_3$Li results in liberation of free borato ligand that subsequently alkylates [PhTt^{tBu}]NiCl.[16] Generation of the borato ligand could occur either via formation of an unstable T_d [PhTt^{tBu}]Ni(CH$_3$) which undergoes ligand loss as a decomposition pathway or via CH$_3$Li reduction of [PhTt^{tBu}]NiCl yielding a Ni(I) species that could also be unstable with respect to borato ligand loss. To discriminate between the two proposed decomposition routes, the reaction of [PhTt^{tBu}]NiCl with CH$_3$Li was carried out in the presence of a suitable donor ligand to trap potential intermediates (Scheme 1). Addition of P(CH$_3$)$_3$ or CO intercepted Ni(I) complexes of the form [PhTt^{tBu}]Ni(L) in high yield as stable, isolable species. Each has been characterized by X-ray diffraction.[17] In [PhTt^{tBu}]Ni(CO) the CO is located on the molecular pseudo-3-fold axis. The average Ni$-$S bond distance is 2.24 Å and Ni$-$C is 1.754(7) Å with the Ni$-$C$-$O angle at 171.0(8)°. [PhTt^{tBu}]Ni(L) complexes display sharp, contact-shifted ^{1}H NMR resonances at room temperature.[18] The IR spectrum of [PhTt^{tBu}]Ni(CO) contains ν_{CO} at 1999 cm^{-1} that shifts appropriately, to 1951 cm^{-1}, for the ^{13}CO derivative. The value reproduces that observed in the carbonylated form of ACS, 1999 cm^{-1}.[19] Additionally, Na/Hg reduction of [PhTt^{tBu}]NiCl yielded [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t) in the absence of trap and [PhTt^{tBu}]Ni(CO) under CO trapping conditions. Taken together, the observations point to the reductive mechanism as the most likely route to the species observed without requiring intermediacy of [PhTt^{tBu}]Ni(CH$_3$).

In summary, the sterically demanding borato ligand, [PhTt^{tBu}], provides a sulfur-only donor environment capable of stabilizing T_d organocobalt(II) functional groups. Attempts to prepare the corresponding T_d organonickel complex resulted in clean formation of a novel metallacycle generated by borato ligand alkylation as confirmed by control experiments. Efforts to trap a methylnickel intermediate led to isolation of neutral Ni(I) complexes, [PhTt^{tBu}]Ni(L), L = CO, P(CH$_3$)$_3$. Experiments continue to attempt interception of [PhTt^{tBu}]Ni(CH$_3$).

Acknowledgment. This work was supported by the National Science Foundation (CHE-997628 and an NYI award to C.G.R.). We thank Brian Rhatigan for solving the X-ray structures of [PhTt^{tBu}]Ni(PMe$_3$) and [PhTt^{tBu}]Ni(CO).

Supporting Information Available: Synthetic details and spectroscopic analyses of new compounds and tables of crystal data, structure solution and refinement, atomic coordinates, and bond lengths and bond angles for [PhTt^{tBu}]Co(CH$_3$), [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t), [PhTt^{tBu}]Ni(P(CH$_3$)$_3$), and [PhTt^{tBu}]Ni(CO) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t): ^{1}H NMR (C$_6$D$_6$) δ 7.91 (d, *o*-C$_6$*H*$_5$, 2 H), 7.41 (t, *m*-C$_6$*H*$_5$, 2 H), 7.20 (t, *p*-C$_6$*H*$_5$, 1 H), 2.40 (d, BC*H*$_2$, 3 H), 2.28 (d, BC*H*$_2$, 3 H), 1.47 (d, NiC*H*$_2$, 1 H), 1.28 (s, (C*H*$_3$)$_3$ 27 H), 1.04 (d, NiC*H*$_2$, 1 H), 0.75 (s, (C*H*$_3$)$_3$ 9 H). UV–vis (CH$_2$Cl$_2$), $\lambda_{\max}$ (ϵ, M^{-1} cm^{-1}) 465 (210).

[13] X-ray data: [κ^2-PhTt^{tBu}]Ni(η^2-CH$_2$SBu^t), C$_{26}$H$_{49}$BNiS$_4$, FW = 559.41, monoclinic, $P2_1/n$, orange block, a = 13.6906(2) Å, b = 16.4889(2) Å, c = 14.6641(2) Å, β = 110.574(1)°, V = 3099.17(6) Å^3, Z = 4, Z' = 1, T = 173(2) K, GOF = 1.889, *R(F)* = 6.27% for 4989 observed independent reflections (4° ≤ 2θ ≤ 50°).

[14] Matsunaga, P.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1748–1749.

[15] Kubiak, C. P. In *Comprehensive Organometallic Chemistry*; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1994; Vol. 9, Section 1.2.

[16] Reaction of the bidentate ligand [Ph$_2$Bt^{tBu}]Tl with NiCl$_2$ in a 2:1 stoichiometry yielded the analogous metallacycle, [Ph$_2$Bt^{tBu}]Ni(η^2-CH$_2$SBu^t); the structure was confirmed by X-ray diffraction analysis. P. Ge unpublished results.

[17] [PhTt^{tBu}]Ni(CO): ^{1}H NMR (C$_6$D$_6$) δ 116 (br, BC*H*$_2$), 14 (br, C$_6$*H*$_5$), 10 (br, C$_6$*H*$_5$), 9 (br, C$_6$*H*$_5$), −1 (br, (C*H*$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) δ 250 (br, *C*O); IR (KBr) ν_{CO} 1999 cm^{-1}; X-ray data for C$_{22}$H$_{38}$BNiOS$_3$, FW = 484.22, monoclinic, $P2_1/n$, yellow plate, a = 9.595(1) Å, b = 20.868(3) Å, c = 12.471(2) Å, β = 99.498(3)°, V = 2462.8(6) Å^3, Z = 4, Z' = 1, T = 173(2) K, GOF = 1.438, *R(F)* = 8.01% for 4136 observed independent reflections (4° ≤ 2θ ≤ 50°). [PhTt^{tBu}]Ni(P(CH$_3$)$_3$): ^{1}H NMR (C$_6$D$_6$) δ 86 (br, BC*H*$_2$), 22 (br, P(C*H*$_3$)$_3$), 18 (br, C$_6$*H*$_5$), 11 (br, C$_6$*H*$_5$), 10 (br, C$_6$*H*$_5$), −6 (br, (C*H*$_3$)$_3$); ^{31}P NMR (C$_6$D$_6$) δ 264; X-ray data for C$_{24}$H$_{47}$BNiPS$_3$, FW = 532.29, orthorhombic, $P2_12_12_1$, yellow block, a = 11.7026(6) Å, b = 14.2156(8) Å, c = 17.703(1) Å, V = 2945.1(3) Å^3, Z = 4, Z' = 1, T = 173(2) K, GOF = 0.854, *R(F)* = 4.06% for 6468 observed independent reflections (4° ≤ 2θ ≤ 56°).

[18] Consistent with the informative ^{1}H NMR spectra, [PhTt^{tBu}]Ni(L) do not exhibit EPR signals at 77 K.

[19] Kumar, M.; Ragsdale, S. W. *J. Am. Chem. Soc.* **1992**, *114*, 8713–8715.