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Inorganic Chemistry

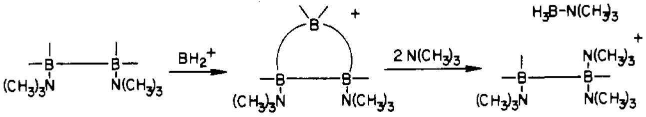
Communications

Isolation and Characterization of Bis(trimethylamine)–Diborane(4)

Sir:

We wish to report that bis(trimethylamine)–diborane(4) has been isolated as a sublimable solid. The trimethylamine adducts of many borane fragments are well-known; however, the amine adduct of the second simplest borane fragment B_2H_4 was not reported previously in the literature. Apparently in the past, the compound was overlooked in the products of certain reactions that should have contained the adduct,[1] or it was not formed by the reactions that were chosen for its synthesis.[2] In general, reports on nitrogen base adducts of diborane(4) have been scarce, and characterizations of the compounds have not been complete.[3] On the other hand, the B_2H_4 adducts of $P(CH_3)_3$,[4,5] $P(C_6H_5)_3$,[6] PF_2X (X = H,[7] $N(CH_3)_2$,[7] F,[8] Cl,[9] and Br[9]), and CO[10] have been isolated and characterized. Recent study in this laboratory on the reaction chemistry of $B_2H_4{\cdot}2P(CH_3)_3$ revealed novel aspects of this compound. These included the formation of a triboron complex cation,[11] the chelation to metal centers through two $B—H\rightarrow M$ bridge bonds,[12] and the framework expansion of borane compounds.[11,13,14] These new developments involving $B_2H_4{\cdot}2P(CH_3)_3$ prompted us to investigate the nature of the trimethylamine analogue of the B_2H_4 adduct and led to the isolation of the once elusive trimethylamine adduct of diborane(4). The behavior of the new adduct toward acids paralleled that of $B_2H_4{\cdot}2P(CH_3)_3$. Yet, certain chemical properties of some of its derivatives appeared to differ from those of the trimethylphosphine analogue. A brief description of one such notable difference is included also in this communication.

Scheme I



Treatment of tetrahydrofuran–triborane(7) with excess trimethylamine in dichloromethane resulted first in the formation of trimethylamine–triborane(7) at −80 °C, and then, when the reaction mixture was warmed to 0 °C, the cleavage of the triborane framework slowly occurred to give $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$. Typically, a 0.5-mmol quantity of $B_3H_7{\cdot}THF$ was dissolved in about 1 mL of CH_2Cl_2 and was allowed to react with 2.0 mmol of $N(CH_3)_3$ at room temperature for 15 min. After removal of the solvent by evaporation, most of the $BH_3{\cdot}N(CH_3)_3$ in the solid residue could be removed by sublimation at 0 °C under vacuum, and then the remaining solid was sublimed at room temperature onto a cold finger (near 0 °C) to obtain a pure sample of $B_2H_4{\cdot}2N(CH_3)_3$. The yield was virtually quantitative. The mass spectrum of the compound (EI, 17 eV) showed the parent ion cluster in the range m/z 142–145, which corresponds to the formula $B_2H_4{\cdot}2N(CH_3)_3$. The NMR shift values were −3.5 ppm for ^{11}B [$BF_3{\cdot}O(C_2H_5)_2$ reference] and 2.45 and 1.67 ppm for the methyl and borane protons, respectively. The ^{11}B-spin-coupled ^1H signal was broad with a doublet feature, which collapsed to a singlet upon irradiation with the ^{11}B resonance frequency.

The new bis(trimethylamine) adduct is inert to both trimethylamine and ammonia. However, trimethylphosphine displaces one of the two amine ligands from $B_2H_4{\cdot}2N(CH_3)_3$ readily above 0 °C to give $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$. NMR shifts for $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$: ^{11}B, −2.9 (B_N) and −37.0 ppm (B_P); ^1H, 2.52 (H_{C-N}), 1.14 (H_{C-P}, $^2J \simeq 9$ Hz), 1.75 (H_{B-N}), and 0.03 ppm (H_{B-P}, $^2J \simeq 17$ Hz). The second amine ligand is resistant to this displacement. Thus, only about 15% of the original amount of the adduct was converted into $B_2H_4{\cdot}2PMe_3$ when a solution of $B_2H_4{\cdot}2N(CH_3)_3$ in trimethylphosphine was kept at room temperature for about 3 h. The bis(trimethylamine) adduct of B_2H_4 is reactive toward acids and is cleaved by hydrogen chloride to form $BH_3{\cdot}N(CH_3)_3$ and $BH_2Cl{\cdot}N(CH_3)_3$. When treated with B_2H_6 or B_4H_{10}, it gave a new triboron complex cation, $B_3H_6{\cdot}2N(CH_3)_3{}^+$, the counteranion being $B_2H_7{}^-$ or $B_3H_8{}^-$. See the first step in Scheme I. NMR shift data for the $B_3H_6{\cdot}2N(CH_3)_3{}^+$ cation: ^{11}B, −9.7 (BH_2) and −15.8 ppm (B_N); ^1H, 2.73 (H_C) and 1.93 ppm (H_B). Apparently, migration of the borane hydrogen atoms is rapid relative to the NMR time scale and the 1.93 ppm signal remains a singlet to −90 °C in the ^{11}B-spin-decoupled spectrum. Although the $B_3H_8{}^-$ salt of the triboron cation is stable at room temperature, the $B_2H_7{}^-$ salt decomposes slowly above 0 °C and gives $B_3H_7{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$. The above behavior of $B_2H_4{\cdot}2N(CH_3)_3$ toward acids and the stabilities of the triboron cation salts are similar to those observed for $B_2H_4{\cdot}2P(CH_3)_3$[5] and its triboron cation derivatives.[11] It is noted, however, that the reaction of $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ with N(C-

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$H_3)_3$ proceeded in a manner which was entirely different from that of $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$. The latter compound reacted with $N(CH_3)_3$ and gave the tetraborane(8) adduct $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$.[15] In contrast, the treatment of $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$ (1:2 molar ratio) at −20 °C resulted in the abstraction of a BH_3 unit from the cation; the $B_3H_8{}^-$ anion remained intact. Thus another new diboron complex cation, $B_2H_3{\cdot}3N(CH_3)_3{}^+$, was produced.[16] See the second step in Scheme I. The ^{11}B NMR signals of this diboron cation appeared as broad humps at 12.5 and −3.9 ppm with the half-height widths 300 and 450 Hz, respectively.

Thus, the isolation of $B_2H_4{\cdot}2N(CH_3)_3$ not only has filled the vacancy in the list of representative compounds but also has given an additional insight into the roles of different Lewis base ligands that are responsible for subtle reactivity differences of borane adducts. Further work on the derivative chemistry of $B_2H_4{\cdot}2N(CH_3)_3$ is being pursued, and the details of the results will be reported at a later date.

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Registry No. $B_3H_7{\cdot}THF$, 52842-96-3; $BH_3{\cdot}N(CH_3)_3$, 75-22-9; $B_2H_4{\cdot}2N(CH_3)_3$, 97551-45-6; $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$, 97551-46-7; $B_2H_4{\cdot}2PMe_3$, 67113-98-8; $B_3H_7{\cdot}N(CH_3)_3$, 57808-48-7; $BH_2Cl{\cdot}N(CH_3)_3$, 5353-44-6; $B_2H_7{}^-$, 27380-11-6; $B_3H_8{}^-$, 12429-74-2; B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7; $B_2H_3{\cdot}3N(CH_3)_3{}^+$, 97551-47-8.

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Articles

Contribution from the Faculty of Chemistry,
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Synthetic, Spectroscopic, X-ray Structural, and Quantum-Chemical Studies of Cyanothiomolybdates with Mo_2S, Mo_2S_2, Mo_3S_4, and Mo_4S_4 Cores: A Remarkable Class of Species Existing with Different Electron Populations and Having the Same Central Units as the Ferredoxins

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Spectroscopic (IR, Raman, resonance Raman, electronic absorption, photoelectron (XPS)) properties of the cyanothiomolybdates $[Mo_4S_4(CN)_{12}]^{8-}$ (**1**), $[Mo_3S_4(CN)_9]^{5-}$ (**2**), $[Mo_2S_2(CN)_8]^{6-}$ (**3**), $[Mo_2S_2(CN)_8]^{4-}$ (**4**), and $[Mo_2S(CN)_{12}]^{6-}$ (**5**) (which might have been of importance for the evolution of Mo enzymes and for the prebiotic evolution in general) have been investigated and discussed on the basis of EH–SCCC–MO calculations. The complexes (with central units comparable to those of the ferredoxins) exist with different electron populations. The preparations of $K_5[Mo_3S_4(CN)_9]{\cdot}2H_2O$ (**2a**) (obtained by extrusion from MoS_3), $[(C_6H_5)_4P]_4[Mo_2S_2(CN)_8]{\cdot}2H_2O$ (**4a**), and the related compound $K_6[Mo_2S_2(NO)_2(CN)_6]{\cdot}4H_2O$ (**6a**) are reported as well as the X-ray structures of $K_5[Mo_3S_4(CN)_9]{\cdot}3KCN{\cdot}4H_2O$ (**2b**) and $[(C_6H_5)_4P]_4[Mo_2S_2(CN)_8]{\cdot}nH_2O$ (**4b**) and the indexed powder diffraction data of $K_8[Mo_4S_4(CN)_{12}]{\cdot}4H_2O$ (**1a**). Salts of **1** and **2** can be directly prepared by reaction of MoS_3 with CN^- in aqueous solution. **2b** crystallizes in the monoclinic space group *Cm* ($Z = 2$): $a = 15.661$ (3) Å, $b = 18.807$ (3) Å, $c = 6.552$ (1) Å, and $\beta = 116.39$ (1)°. On the basis of 1985 unique data ($F_o > 3.92\sigma(F_o)$, θ–2θ scan) the structure was refined to $R = 3.1\%$. The central $\{Mo_3S_4\}$ unit of the anion **2** (idealized symmetry C_{3v}) can be described as an incomplete distorted cube (d_{av}(Mo–Mo) = 2.773 Å, d_{av}(Mo–(μ-S)) = 2.322 Å, d_{av}(Mo–(μ_3-S)) = 2.361 Å) with pseudooctahedral coordination of the Mo atoms (three bridging S atoms and three cyano ligands; d_{av}(Mo–C) = 2.210 Å, d_{av}(C–N) = 1.136 Å). **4b** crystallizes in the orthorhombic space group *Pnna* ($Z = 4$): $a = 29.871$ (21) Å, $b = 24.278$ (26) Å, and $c = 13.405$ (11) Å. On the basis of 1868 unique data ($F_o > 3.92\sigma(F_o)$, ω scan) the structure could only be refined to $R = 15.7\%$ (due to the poor quality of crystals). The anion **4** (idealized symmetry D_{2h}) contains planar $Mo(S_{br})_2Mo$ units (d(Mo–Mo) = 2.758 (7) Å, d_{av}(Mo–S) = 2.296 Å) with pseudooctahedral coordination of the Mo atoms (two bridging S atoms and four cyano ligands; d_{av}(Mo–C) = 2.12 Å, d_{av}(C–N) = 1.18 Å). For the highly symmetrical **1** a detailed vibrational analysis including an approximate normal-coordinate analysis has been performed.

Introduction

Cyanothiomolybdates seem to have been of importance for the evolution of Mo enzymes and for the prebiotic evolution in general.[2-5] We were able to show that species with different electron populations having the same (or roughly the same) central units as the ferredoxins (2 Fe, 3 Fe, 4 Fe type) can be prepared, and some of these even under possible prebiotic conditions (e.g., by reaction of aqueous CN^- with MoS_x phases). A very remarkable one is the tetranuclear species $[Mo_4S_4(CN)_{12}]^{8-}$ (**1**)[6] with an Mo_4S_4 cube and with T_d symmetry. The other complexes under

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