orange crystalline precipitates were soon formed. Analytical data (Table III) for the materials isolated suggest the formulation $[Fe(L)]_2O{\cdot}C_3H_6O$, where L = 5-NO_2SALDPT or 5-NO_2SALMeDPT. This type of oxidation is frequently encountered in iron(II) chemistry. For example, another iron(II) Schiff base complex, Fe(SALEN), reacts with oxygen to give the μ-oxo complex $[Fe(SALEN)]_2O$.[16] This compound has been well characterized and exhibits a metal–oxygen asymmetric stretching vibration at 825 cm^{-1} in the infrared spectrum. The room-temperature magnetic moment is 1.86 μ_B, consistent with the oxidation to low-spin iron(III).[17]

The μ-oxo complexes with pentadentate ligands give similar results. $[Fe(5\text{-}NO_2SALDPT)]_2{\cdot}C_3H_6O$ has a room-temperature magnetic moment of 1.89 μ_B while that of $[Fe(5\text{-}NO_2SALMeDPT]_2O{\cdot}C_3H_6O$ is 1.91 μ_B. Comparison of the infrared spectra of these compounds to that of the iron(II) complex reveals a new peak which has been assigned to the Fe–O stretching mode. This peak occurs at 810 cm^{-1} in the spectrum of $[Fe(5\text{-}NO_2SALDPT)]_2O$ and at 815 cm^{-1} in the spectrum of the methyl derivative. In both spectra there is a new band, just below 1700 cm^{-1}, which is the carbonyl stretching of the solvated acetone. The electronic spectra of these compounds are also different from that of the precursor (see Figure 2b). $[Fe(5\text{-}NO_2SALDPT)]_2O$ has a band at 4300 Å and $[Fe(5\text{-}NO_2SALMeDPT)]_2O$ has a band at 4000 Å plus a slight shoulder at 5000 Å. These spectra are very similar to that of $[Fe(SALEN)]_2O$ which also exhibits a single band in this area.

Solution spectra of Fe(SALDPT) and other derivatives show similar changes when exposed to oxygen. However, an interesting feature of these spectra is that there is an apparent difference in the reactivity of Fe(SALDPT) as compared to the methyl, ethyl, and propyl derivatives. For example, a chloroform solution of Fe(SALDPT) prepared in air gives only the iron(III) spectrum. A solution of Fe(SALMeDPT) prepared in a similar manner gives the same spectrum as the obtained in the solid state. This spectrum changes over a period of several minutes as the sample reacts with oxygen. The initial spectra of Fe(SALEtDPT) and Fe(SALPrDPT) are also the same as observed for the solid state and change with time, but more slowly than that of the methyl derivative. If oxygen is bubbled through the solution, the spectra immediately change. The reaction is irreversible even after purging with nitrogen.

In order to understand the significance of all this, one needs to compare the corresponding cobalt complexes. It has also been found that the reaction of oxygen is slower for Co(SALMeDPT) than for Co(SALDPT).[8] From the x-ray structure[18] of $[Co(SALDPT)]_2O_2{\cdot}C_6H_5CH_3$ it was determined that the position of attack is cis to the central nitrogen donor. Placing a methyl group on this nitrogen somewhat blocks this cis coordinate site, thus decreasing reactivity. It was also suggested[8] that the methyl group prevents dimerization and therefore μ-peroxo complexes are not formed with this type of derivative. However, the formation of a μ-oxo complex with Fe(5-NO_2SALMeDPT) suggests either that a rearrangement is taking place so that dimerization is more sterically favored or that an additional mode of attack is operating for the iron compounds.

In summary, iron(II) complexes with pentadentate Schiff base ligands are similar to other metal chelates of this type. These ferrous compounds, however, do not provide good models for biological oxygen carriers since reaction with oxygen in solutions leads to irreversibly oxidized ferric complexes. Of interest are the relative stability of these complexes with amine substituents and the inertness of all the pentadentate complexes toward oxidation in the solid state.

Registry No. Fe(SALDPT), 65802-41-7; Fe(3-CH_3OSALDPT), 65802-42-8; Fe(5-NO_2SALDPT), 65802-40-6; Fe(SALMeDPT), 65802-39-3; Fe(3-CH_3OSALMeDPT), 65802-38-2; Fe(5-NO_2SALMeDPT), 65802-37-1; Fe(SALEtDPT), 65802-36-0; Fe(SALPrDPT), 65802-35-9; $[Fe(5\text{-}NO_2SALDPT)]_2O$, 65802-34-8; $[Fe(5\text{-}NO_2SALMeDPT)]_2O$, 65802-33-7; SAL, 90-02-8; DPT, 56-18-8; 3-CH_3OSAL, 148-53-8; 5-NO_2SAL, 97-51-8; MeDPT, 105-83-9; EtDPT, 2372-77-2.

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Contribution from Union Carbide Corporation, Corporate Research Laboratory,
Tarrytown, New York 10591

A One-Step Synthesis of $B_{11}H_{14}^-$ Ion from $NaBH_4$

GARY B. DUNKS* and KATHY PALMER ORDONEZ

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A facile synthesis of tetradecahydroundecaborate(1−) ion, $B_{11}H_{14}^-$, is described from $BF_3{\cdot}O(C_2H_5)_2$ and salts of $B_3H_8^-$ ion or from $B_3H_8^-$ ion prepared in situ from $BF_3{\cdot}O(C_2H_5)_2$ and $NaBH_4$.

Introduction

The synthesis of tetradecahydroundecaborate(1−) ion, $B_{11}H_{14}^-$, was first accomplished by the reaction of metal borohydrides with decaborane(14).[1,2] Later it was shown that

$$MBH_4 + B_{10}H_{14} \xrightarrow[R_2O]{90\,^\circ C} MB_{11}H_{14} + 2H_2 \qquad (1)$$

$B_{11}H_{14}^-$ ion could be prepared directly from sodium borohydride and diborane(6) or pentaborane(9) in high-pressure equipment,[3] and in low yield from diborane(6) in the presence of dimethyl sulfide.[3] These methods suffer from the necessity of utilizing as starting materials hazardous and expensive boron hydrides.

We report here the facile synthesis of $B_{11}H_{14}^-$ ion from

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$BF_3{\cdot}O(C_2H_5)_2$ and purified salts of $B_3H_8^-$ ion or preferably from $B_3H_8^-$ ion prepared in situ from $BF_3{\cdot}O(C_2H_5)_2$ and sodium borohydride.

Results and Discussion

In the course of studying the ^{11}B NMR spectra of aliquots from the reaction of $NaBH_4$ and $BF_3{\cdot}O(C_2H_5)_2$ to produce $B_3H_8^-$ ion,[4,5] we found that with the addition of $BF_3{\cdot}O(C_2H_5)_2$ beyond the stoichiometric amount necessary to satisfy eq 2,

$$5BH_4^- + 4BF_3{\cdot}O(C_2H_5)_2 \rightarrow 2B_3H_8^- + 3BF_4^- + 2H_2 + 4O(C_2H_5)_2 \qquad (2)$$

the concentration of $B_3H_8^-$ ion in the reaction mixture decreased and a simultaneous appearance of $B_{11}H_{14}^-$ ion occurred. When approximately 160% of the $BF_3{\cdot}O(C_2H_5)_2$ required by eq 2 had been added, the concentration of $B_3H_8^-$ ion had reached zero, and with the exception of $B_{11}H_{14}^-$ ion only traces of other boron containing species were present (Table I).

The overall process is represented by the proposed stoichiometry of eq 3.

$$17BH_4^- + 20BF_3{\cdot}O(C_2H_5)_2 \rightarrow 2B_{11}H_{14}^- + 15BF_4^- + 20O(C_2H_5)_2 + 20H_2 \qquad (3)$$

In a separate experiment designed to produce $B_3H_8^-$ ion, it was found that continued heating of the reaction mixture for 40 h after the stoichiometric amount of $BF_3{\cdot}O(C_2H_5)_2$ had been added (eq 2) did not greatly alter the relative amounts of boron-containing species present. These results, coupled with the fact that we have shown that $B_{11}H_{14}^-$ ion can be prepared directly from $B_3H_8^-$ and $BF_3{\cdot}O(C_2H_5)_2$ (eq 4),

$$17B_3H_8^- + 16BF_3{\cdot}O(C_2H_5)_2 \rightarrow 5B_{11}H_{14}^- + 12BF_4^- + 33H_2 + 16O(C_2H_5)_2 \qquad (4)$$

suggest that the production of $B_{11}H_{14}^-$ ion was due to "excess" $BF_3{\cdot}O(C_2H_5)_2$ and not due to thermal decomposition of the intermediate $B_3H_8^-$ ion.

Experimental Section

Diglyme (Ansul 141) was heated over sodium and benzophenone until dark blue color was obtained and then distilled at 67 °C, 13 mmHg. Sodium borohydride was obtained from Ventron Corp. and boron trifluoride diethyl etherate (98)% was obtained from Matheson Coleman and Bell; both were used without further purification. Tetraethylammonium bromide was obtained from R.S.A. Corp. Tetraethylammonium octahydrotriborate was prepared by the method of Beall et al.[5] All other reagents were used as supplied. The temperatures were controlled with a Therm-O-Watch, I^{2}R Co., and $BF_3{\cdot}O(C_2H_5)_2$ was added with a Minipump, Milton Roy Co. The ^{11}B NMR spectra were measured using a Brucker Model HFX-90 spectrometer operating at 28.87 MHz. A Brucker Model B-SVZ proton decoupler operating at 90 MHz was used. Infrared spectra were measured as Nujol mulls using a Beckman IR 5A spectrophotometer. The analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Synthesis of $(C_2H_5)_4NB_{11}H_{14}$ from $B_3H_8^-$ Ion Prepared in Situ from $NaBH_4$. The apparatus (Figure 1) consisted of a 2000-mL, three-neck flask equipped with a mechanical stirrer, a tube through which $BF_3{\cdot}O(C_2H_5)_2$ could be pumped from a reservoir (a pressure equalized dropping funnel could be used), and a side tube connected to a dry ice condenser and from there to an acetone-filled scrubber. The condensate was collected in a flask fitted to the side tube. A thermometer was passed through the side tube and into the reaction mixture and attached to the Therm-O-Watch. Under a slow stream of nitrogen the flask was charged with 500 mL of diglyme and 60.0 g (1.59 mol) of $NaBH_4$. With stirring, the contents of the flask was heated to 105 °C and $BF_3{\cdot}O(C_2H_5)_2$ was added at 40 mL/h (250 mL, 2.04 mol). After the addition was complete (6 h), the flask and contents were allowed to cool to ambient temperature. The condensate consisted of 121.1 g (1.64 mol) of ethyl ether. The contents of the flask were filtered in air using a medium frit. The solid (141.6 g, 1.29 mol, $NaBF_4$, identified by IR) was washed twice with 50 mL of dry diglyme. The combined diglyme solution was evaporated to an oil using a rotary evaporator (1 mmHg, 67 °C). The oil was taken up in 500 mL of water and added in one portion to a solution of 100 g (0.475 mol) of $(C_2H_5)_4NBr$ in 200 mL of water. The mixture was allowed to stand 15 min and filtered. The filter cake was dissolved in 300 mL of acetone (slight degassing) and heated to reflux. Water was added until slight cloudiness appeared and the solution was allowed to cool slowly to ambient temperature and then cooled at 10 °C overnight. The pale yellow crystals were filtered and dried in vacuo to yield 25.7 g (0.098 mol, 52.4%) of $(C_2H_5)_4NB_{11}H_{14}$. The liquor was evaporated to about half the original volume and water added to cloudiness. The solution was cooled as above and the yellow crystals were filtered. The crystals were washed with ethyl ether to remove the yellow impurity to yield 5.1 g (0.019 mol, 10.2%) of tan crystals. The pale yellow and tan materials were indistinguishable by ^{11}B NMR and IR spectroscopy. The ^{11}B NMR spectrum of $(C_2H_5)_4NB_{11}H_{14}$ measured in acetone solution consisted of an asymmetric doublet at +16.4 ppm (134 Hz) [reported chemical shift relative to $BF_3{\cdot}O(C_2H_5)_2$ +16.1 ppm and coupling constant 139 Hz].[6] The infrared spectrum of $(C_2H_5)_4NB_{11}H_{14}$ (cm^{-1}; vs = very strong, m = medium, w = weak): 2940 (vs), 2850 (vs), 2560 (vs), 2535 (vs), 2500 (vs), 1490 (vs), 1465 (m), 1455 (m), 1440 (m), 1418 (w), 1395 (m), 1380 (m), 1176 (s), 1074 (m), 1034 (m), 1005 (s), 926 (w), 788 (s), 735 (w), 722 (w). Anal. Calcd: B, 45.25; C, 36.50; H, 12.93; N, 5.32. Found: B, 44.52; C, 36.49; H, 13.29; N, 4.98.

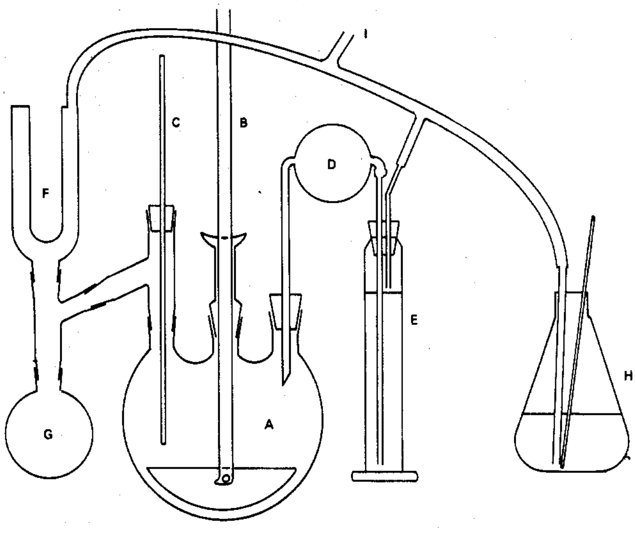

Figure 1. The apparatus used consisted of a three-neck reaction flask (A) fitted with a mechanical stirrer (B), a thermometer (C), and a pump for the addition of $BF_3{\cdot}O(C_2H_5)_2$ (D) from reservoir (E). The off-gas was passed through a dry ice condenser (F) which condensed the ether into receiver (G). The noncondensable gas passed through the condenser and into the acetone scrubber (H). The apparatus could be swept with nitrogen (I).

Synthesis of $(C_2H_5)_4NB_{11}H_{14}$ from $(C_2H_5)_4NB_3H_8$. Apparatus was assembled as shown in Figure 1 with a 1000 mL, three-neck flask. The acetone bubbler was omitted and the off-gases were passed through a trap which contained 200 mL of triethylamine and from there through a wet-test meter. The flask was charged with 18.0 g (0.105 mol) of $(C_2H_5)_4NB_3H_8$ and 500 mL of diglyme and heated to 105 °C. Over a period of 2.37 h, 15.0 mL (0.120 mol) of $BF_3{\cdot}O(C_2H_5)_2$ was added and 0.248 mol of gas was evolved. The triethylamine was stripped on a rotary evaporator to an oil which was identified by the infrared spectrum as $(C_2H_5)_3NBH_3$ (2.38 g, 0.021 mol). The contents of the flask were cooled to room temperature and filtered with a medium frit. The solids (16.6 g, 0.077 mol of $(C_2H_5)_4NBF_4$) were washed with two 50-mL portions of diglyme. The combined diglyme fractions were stripped to a yellow oil using a rotary evaporator and a mechanical pump. The oil was triturated in ethyl ether and filtered. The solids were dissolved in acetone, and water was added to the hot solution until cloudiness appeared. The hot solution was filtered and water was added until cloudiness appeared. The solution was allowed to cool and maintained at 10 °C overnight. The crystals were filtered and dried in vacuo to yield 3.55 g (0.013 mol, 42.1%) of $(C_2H_5)_4NB_{11}H_{14}$. A second crop (0.75 g, 0.003 mol, 9.7%) was obtained from the liquor in a similar manner.

Table I. Relative Concentration of Products during the Addition of $BF_3 \cdot O(C_2H_5)_2$ to $NaBH_4$

% $BF_3 \cdot O$-$(C_2H_5)_2$ added[a]	Concentration,[b] M		
	BH_4^-	$B_3H_8^-$	$B_{11}H_{14}^-$
58.9	0.420[c]	0.383	0.000
80.1	0.406	0.636	0.011
92.9	0.318	0.751	0.015
109.0	0.121	0.812	0.031
112.0	0.056	0.724	0.027
118.5	0.000	0.714	0.048
131.0	0.000	0.396	0.104
138.0	0.000	0.264	0.146
157.0	0.000	0.000	0.221
182.0	0.000	0.000	0.225
208.0	0.000	0.000	0.231

[a] Stoichiometry based upon eq 2. [b] Determined in diglyme solution by ^{11}B NMR. [c] Apparently saturated.

Table II. Extended Heating of $B_3H_8^-$ Ion Formed in Situ

Aliquot	Time elapsed, h	$[B_3H_8]$, M
1	4.8	0.516
2	6.6[a]	0.840
3	21.8	0.728
4	31.0	0.784
5	46.2	0.798

[a] Stoichiometric amount of $BF_3 \cdot O(C_2H_5)_2$ added (eq 2).

Reaction Study Using ^{11}B NMR. Apparatus was assembled as shown in Figure 1 using a 1000 mL, four-neck flask. The fourth neck contained a tube which extended below the surface of the reaction mixture and equipped with a side inlet through which N_2 could be swept. This tube was stoppered except when aliquots were taken. The flask was charged with 500 mL of diglyme and 60 g (1.59 mol) of $NaBH_4$. The mixture was heated to 105 °C and a total of 250 mL (2.04 mol) of $BF_3 \cdot O(C_2H_5)_2$ was added at the rate of 30 mL/h. Aliquots (~2 mL) were withdrawn from the mixture and placed into screw cap vials and allowed to stand. When the reaction was complete, the supernatant in each vial was placed into an NMR tube and the spectrum measured. Each spectrum was calibrated, and peak areas were determined by comparison to the peak due to $B(OCH_3)_3$ contained in a capillary tube successively placed into each sample. The capillary had been previously calibrated against various known concentrations of purified $(C_2H_5)_4NB_3H_8$ in diglyme solution. The results are shown in Table I.

Extended Heating of $B_3H_8^-$ Ion Formed in Situ. Apparatus was assembled as shown in Figure 1 with a 500-mL, four-neck flask. The fourth neck contained a tube for the withdrawal of aliquots (vide supra). The flask was charged with 250 mL of diglyme and 30 g (0.79 mol) of $NaBH_4$. The mixture was heated to 105 °C and $BF_3 \cdot O(C_2H_5)_2$ (78 mL, 0.64 mol) was added in 6.6 h. Aliquots were withdrawn and analyzed by ^{11}B NMR as above. The results are shown in Table II.

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Registry No. $(C_2H_5)_4NB_{11}H_{14}$, 12555-78-1; $B_3H_8^-$, 12429-74-2; $NaBH_4$, 16940-66-2; $BF_3 \cdot O(C_2H_5)_2$, 109-63-7; $(C_2H_5)_4NB_3H_8$, 12555-74-7.

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Contribution from the Departments of Chemistry, University of Wisconsin—Madison,
Madison, Wisconsin 53706, and University of Strathclyde, Glasgow G1 1XL, Scotland

The Chemistry of Beryllaboranes. Characterization and Reactions of Beryllium Bis(tetrahydroborate), $Be(BH_4)_2$, and Beryllium Bis(octahydrotriborate), $Be(B_3H_8)_2$

DONALD F. GAINES,*[1a] JERRY L. WALSH,[1a] JOHN H. MORRIS,[1b] and DAVID F. HILLENBRAND[1a]

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Gas-phase ^{11}B and ^1H NMR spectra of $Be(BH_4)_2$ show that only one monomeric species is present. A linear B–Be–B framework is inferred, and the hydrogens of each tetrahydroborate undergo rapid local internal exchange. The preparation and characterization of beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$, cyclopentadienylberyllium octahydrotriborate, $C_5H_5BeB_3H_8$, and methylberyllium octahydrotriborate, $(CH_3BeB_3H_8)_2$, are described. The $B_3H_8^-$ derivatives of beryllium exhibit a range of fluxional character as identified by variable-temperature NMR studies. The ^{11}B NMR spectrum of cyclopentadienylberyllium tetrahydroborate consists of a quintet of quartets indicating ^{11}B–H and ^{11}B–^9Be coupling, with the tetrahydroborate hydrogen atoms undergoing rapid intramolecular exchange. The reaction chemistry of BH_4^- and $B_3H_8^-$ derivatives of beryllium is discussed.

Introduction

The chemistry of beryllium–boron compounds, the beryllaboranes, has not been extensively studied. Several of the simple beryllaboranes, however, have been structurally characterized. For example, the structure of $C_5H_5BeBH_4$ is proposed, on the basis of electron diffraction[2] and infrared[3] data, to contain a η^5-cyclopentadienyl ring and a tetrahedral tetrahydroborate group attached to beryllium by two hydrogen bridges; infrared data[4] for $(CH_3BeBH_4)_2$ are consistent with a structure containing bridging methyl groups between the beryllium atoms and a terminal tetrahydroborate group attached to each beryllium with two bridging hydrogens.

The structural characterization of gas-phase, monomeric $Be(BH_4)_2$, however, has a controversial history, and its structure cannot be unequivocally defined. Electron diffraction data have been interpreted in terms of linear D_{2d},[5] triangular C_{2v},[6] and linear C_{3v} or D_{3d}[7] structures (Figure 1a, b, and c or d, respectively). Another such study[8] suggested the presence of two unidentified structures depending on the sample history. Vibrational data for $Be(BH_4)_2$ have been interpreted in terms of linear D_{2d},[9] triangular C_2,[10] and triangular C_{2v}[11] structures (Figure 1a, b, and e, respectively), as well as in terms of a

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