that the transients decompose via reaction 2 and not via reaction 6. (In the latter case a linear dependence on $1/[[(\mathrm{nta})(\mathrm{H_2O})_2\mathrm{M^{II}}]^-]^2$ is expected.) The observed rate of decomposition, k_d, according to reaction 2 is given by eq 8. k_2 can be

$$k_d = \frac{2k_2K_1}{\epsilon_\lambda([(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^-)\ l}\ \frac{1}{[[(\mathrm{nta})(\mathrm{H_2O})_2\mathrm{M^{II}}]^-]} \qquad (8)$$

calculated from the slope of the dependence of k_d on $1/[[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{II}}]^-]$ and from ϵ_λ and K_1. Thus, $2k_2 = (3.2 \pm 0.6) \times 10^9$ and $(1.1 \pm 0.3) \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ for M = Mn and Fe respectively are obtained. GC analysis points out that indeed over 90% of the $^\bullet\mathrm{CH_3}$ free radicals formed by the pulse yield $\mathrm{C_2H_6}$.[9]

The specific rates of reaction of $^\bullet\mathrm{CH_3}$ with $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{II}}]^-$ are of the same order of magnitude as those reported for the oxidation of the same complexes by $\mathrm{Br_2}^-$, $(\mathrm{NCS})_2^-$, $\mathrm{O_2}^-$, and $^\bullet\mathrm{O_2CH}{\cdot}(\mathrm{CH_3})_2\mathrm{OH}$.[10] All these reactions occur via the inner-sphere mechanism. It is unclear at present whether reaction 1 follows an $\mathrm{S_N1}$ or an $\mathrm{S_N2}$ mechanism.

The values of $K_1 = 8.3 \times 10^{-4}$, 4.3×10^{-4}, and 1.4×10^{-8} M for M = Mn, Fe, and Co respectively clearly indicate that $\Delta G°$ depends only slightly on the nature of the central cation. One should remember that reaction −1 involves a loss of a water ligand and therefore $\Delta G°$ for the metal–carbon bond dissociation is considerably larger than $\Delta G_1°$. The free energy of reaction 9 is

$$[(\mathrm{nta})(\mathrm{H_2O})_2\mathrm{M^{II}}]^- \rightleftharpoons [(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{II}}]^- + \mathrm{H_2O} \qquad (9)$$

not known. However, it is reasonable that the effect of the nature of the central cation on $\Delta G_9°$ is analogous to that observed for $\Delta G_{10}°$

$$\mathrm{M(H_2O)_6}^{2+} \rightleftharpoons \mathrm{M(H_2O)_5}^{2+} + \mathrm{H_2O} \qquad (10)$$

i.e. that $\Delta G_9°(\mathrm{Co(II)}) > \Delta G_9°(\mathrm{Fe(II)}) > \Delta G_9°(\mathrm{Mn(II)})$. Thus, it is reasonable to assume that the metal–carbon bond dissociation energy indeed decreases considerably from $\mathrm{Co^{III}{-}CH_3}$ to $\mathrm{Fe^{III}{-}CH_3}$ and $\mathrm{Mn^{III}{-}CH_3}$ as expected.

It is unclear at present whether the $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^-$ complexes have a low- or high-spin configuration. The absorption spectrum of the cobalt complex[1] suggests that at least in this case the transient complex has the low-spin configuration.

The role of the ligand nta in enabling the observation of these transients, which are not observed for the analogous aqueous complexes,[11] is not fully understood. Several factors have to be considered:

1. The ligand enhances the rate of the aquo ligand exchange, thus increasing k_{-1}.[13] Only if $k_{-1}[\mathrm{L(H_2O)}_n\mathrm{M^{II}}][^\bullet\mathrm{CH_3}] > k_6[^\bullet\mathrm{CH_3}]^2$ is the observation of the transients feasible.
2. The ligand lowers the redox potential of the M(III/II) couple. As reaction −1 is at least formally an oxidation process, it is expected that the stability of the transient will be enhanced by lowering the redox potential of the central cation.
3. The ligand lowers the water–metal bond dissociation energy.

The relative importance of these factors is under study. For this purpose the effect of ligands other than nta on K_1 is being studied.

Finally we would like to point out that reaction 2, which leads to the formation of a carbon–carbon bond, approaches the diffusion-controlled limit in the three systems studied.

Acknowledgment. This study was supported by grants from the Israel Academy of Sciences and Humanities, the Ministry of Energy and Infrastructure and the Planning and Granting Committee of the Council of Higher Education, and the Israel Atomic Energy Commission. D.M. wishes to express his thanks to Irene Evens for her continuous interest and support.

Registry No. $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Co^{III}CH_3}]^-$, 116053-28-2; $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Mn^{III}CH_3}]^-$, 116053-29-3; $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Fe^{III}CH_3}]^-$, 116053-30-6; $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Co^{II}}]^-$, 116053-31-7; $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Mn^{II}}]^-$, 116053-32-8; $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{Fe^{II}}]^-$, 116053-33-9; $\mathrm{CH_3}$, 2229-07-4; $\mathrm{C_2H_6}$, 74-84-0.

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(9) At pH >8.0 the kinetics observed for M = Fe depend on the pH. (These measurements cannot be carried out for M = Mn due to precipitation.) At pH 10.5 $k_{-1} = (5.3 \pm 0.8) \times 10^6$ $\mathrm{M^{-1}\ s^{-1}}$, $k_1 = (1.05 \pm 0.20) \times 10^3$ $\mathrm{s^{-1}}$, and $K_1 = (2.0 \pm 1.2) \times 10^{-4}$ M are observed. The results thus suggest that both k_{-1} and k_1 decrease with increasing pH; K_1 seems to decrease slightly, but due to the large error limits this result is not significant. (In the alkaline region the rate of autoxidation of the Fe(II) complex increases and thus the accuracy of the measurements decreases.) The observed rate of decomposition, k_d, decreases by a factor of ca. 30 from pH 8.0 to pH 10.5. This result clearly indicates that k_2 decreases with increasing pH. However, we cannot calculate k_2 accurately in the alkaline region as reaction 6 competes with reaction 2 under the experimental conditions.

(10) Lati, J.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1105.

(11) The observation of $\mathrm{(H_2O)_5Fe^{III}CH(CH_3)_2OH^{2+}}$ was reported.[12] However, we were unable to reproduce the experimental results.

(12) Pribush, A. G.; Brusenseva, S. A.; Shubin, V. N.; Dolin, P. I. *High Energy Chem. (Engl. Transl.)* **1975**, *9*, 206.

(13) Langford, C. H.; Sastri, V. S. In *Reaction Mechanisms in Inorganic Chemistry*; MTP International Review of Science (Inorganic Chemistry, Series One); Butterworths: Oxford, England, 1972; Vol. 9, p 203.

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Preparation and Characterization of Phosphine-Tetraborane(8)

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Only a few phosphine ($\mathrm{PH_3}$) adducts of boranes have been reported in the literature. Phosphine–borane(3), $\mathrm{BH_3{\cdot}PH_3}$, represents a classical example of the compounds. The unique reaction of this adduct with ammonia was first reported by Gamble and Gilmont,[1] and later the reaction and its product were elucidated by Parry and co-workers.[2] The phosphine adduct of triborane(7), $\mathrm{B_3H_7{\cdot}PH_3}$, was prepared in this laboratory,[3] and its properties were investigated to compare with those of $\mathrm{BH_3{\cdot}PH_3}$. The effect of stronger acidity of the $\mathrm{B_3H_7}$ fragment was apparent: the phosphine hydrogens are more acidic and the B–P bond in $\mathrm{B_3H_7{\cdot}PH_3}$ is stronger than those in $\mathrm{BH_3{\cdot}PH_3}$.

To further investigate the properties of phosphine adducts of other borane fragments, the next higher borane adduct, $\mathrm{B_4H_8{\cdot}PH_3}$, was prepared by cleaving pentaborane(11) ($\mathrm{B_5H_{11}}$) with $\mathrm{PH_3}$. The characterization of $\mathrm{B_4H_8{\cdot}PH_3}$ and the formation of a reaction intermediate ($\mathrm{B_5H_{11}{\cdot}PH_3}$) are reported in this note.

Results and Discussion

A. Phosphine–Tetraborane(8). When $\mathrm{B_5H_{11}}$ and $\mathrm{PH_3}$ were mixed in dichloromethane at −95 °C, a reaction occurred immediately and $\mathrm{B_5H_{11}{\cdot}PH_3}$ was formed. At −80 °C in the presence of excess $\mathrm{PH_3}$ a further reaction proceeded, and $\mathrm{B_4H_8{\cdot}PH_3}$ and $\mathrm{BH_3{\cdot}PH_3}$ were produced. The tetraborane (8) adduct was separated from the reaction mixture as a white solid by evaporating the solvent and then by subliming out $\mathrm{BH_3{\cdot}PH_3}$ from the residual solid at −23 °C under vacuum. The compound melted at −6 to −5 °C and decomposed above 0 °C. It was soluble in most organic solvents including dichloromethane, chloroform, diethyl ether, and tetrahydrofuran.

The $^{11}\mathrm{B}$ NMR spectrum of $\mathrm{B_4H_8{\cdot}PH_3}$ consists of two sets of resonance signals, α and β, each having the general common pattern of $\mathrm{B_4H_8{\cdot}L}$ spectra. (See Figure 1 and Table I.) The presence of the two sets of signals is attributed to two isomeric forms of $\mathrm{B_4H_8{\cdot}PH_3}$, endo and exo forms, as many $\mathrm{B_4H_8}$ adducts are known to exist in these two geometrical isomers.[4] The $^{31}\mathrm{P}$

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(1) Gamble, E. L.; Gilmont, P. *J. Am. Chem. Soc.* **1940**, *62*, 717.

(2) Gilje, J. W.; Morse, K. W.; Parry, R. W. *Inorg. Chem.* **1967**, *6*, 1761. Dietz, E. A.; Morse, K. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 1.

(3) Bishop, V. L.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 2724.

(4) (a) Centofanti, L. F.; Kodama, G.; Parry, R. W. *Inorg. Chem.* **1969**, *8*, 2072. Paine, R. T.; Parry, R. W. *Inorg. Chem.* **1972**, *11*, 1237. (b) Stampf, E. J.; Garber, A. R.; Odom, J. D.; Ellis, P. D. *Inorg. Chem.* **1975**, *14*, 2446. Odom, J. D.; Moore, T. F.; Dawson, W. H.; Garber, A. R.; Stampf, E. J. *Inorg. Chem.* **1979**, *18*, 2179. Odom, J. D.; Moore, T. F. *Inorg. Chem.* **1980**, *19*, 2651. Odom, J. D.; Zozulin, A. J. *Inorg. Chem.* **1981**, *20*, 3740.

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Table I. NMR Data for $B_4H_8\cdot PH_3$ in CD_2Cl_2 at -40 °C

	α-isomer shift, ppm (J_{XY}, Hz)	β-isomer shift, ppm (J_{XY}, Hz)	assgnt
^{11}B	-54.8 ($J_{BP} \approx 75$) ($J_{BH} = 106$)	-57.0 ($J_{BP} = 105$) ($J_{BH} = 118$)	B_1
	-4.2 ($J_{BH} = 117$)	-3.5	$B_{2,4}$
	+1.6 ($J_{BH} = 118$)	+5.1 ($J_{BH} = 140$)	B_3
^{31}P	-85.7 ($J_{BP} = 80$) ($J_{HP} = 397$)	-73.8 ($J_{BP} = 102$) ($J_{HP} = 420$)	
^{1}H	-2.02	*a*	H_μ
	+1.47	*a*	H_1
	+2.20	*a*	$H_{2,4}$ (ax or eq)
	+2.33	*a*	$H_{2,4}$ (ax or eq)
	+2.69	*a*	H_3
	+4.66 ($J_{HP} = 396$)	+5.27 ($J_{HP} = 420$)	H (PH_3)

[a] The signal may be overlapped with the corresponding signal of the α isomer and could not be identified.

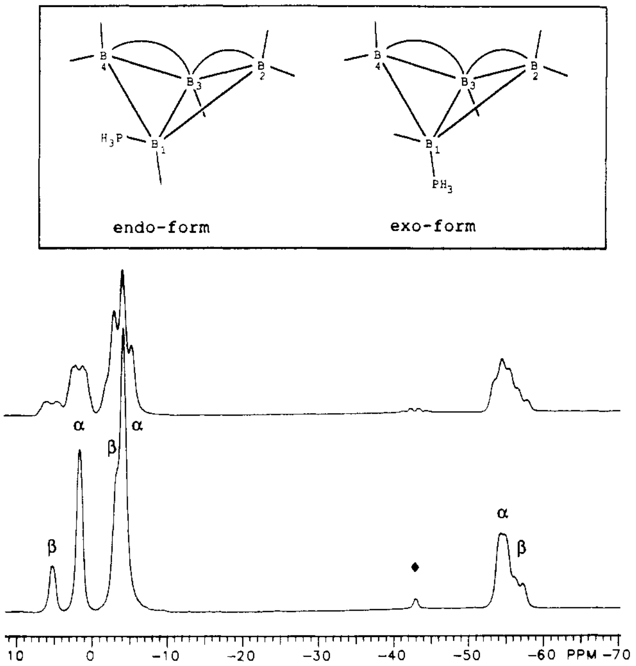


Figure 1. Geometrical isomers of $B_4H_8\cdot PH_3$ (in the box) and ^{11}B NMR spectra (96.2 MHz) of $B_4H_8\cdot PH_3$ in CD_2Cl_2 at -40 °C. The upper spectrum is normal; the lower spectrum is proton-spin-decoupled. The signal indicated by ♦ is due to $BH_3\cdot PH_3$.

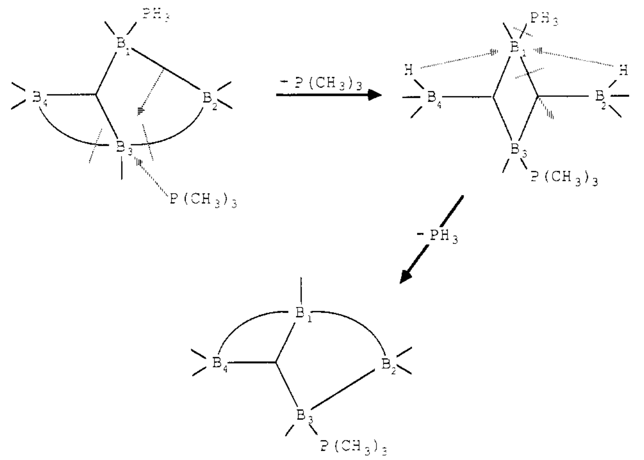
and ^1H NMR spectra also supported the presence of two isomeric forms. The signals of set β were either absent or very weak in the spectrum of a freshly prepared sample solution at -80 °C. As the sample was allowed to warm to -40 °C, the β signals grew rapidly to finally give the spectrum shown in Figure 1. This change was irreversible with respect to the temperature. However, if the solvent was removed completely from the solution at -23 °C by pumping to ensure the formation of "dry" $B_4H_8\cdot PH_3$ and then the solid was redissolved in dichloromethane at -95 °C, the β signals were absent again in the spectrum. Apparently, the compound crystallizes preferentially in the α-isomer form.

The conformational assignment of the isomers (α and β) has yet to be determined. An X-ray structural study by La Prade and Nordman[5] revealed that $B_4H_8\cdot PF_2N(CH_3)_2$ in the solid phase was of endo conformation. If one assumes that the endo conformation is the form preferred by B_4H_8 adducts in solid phases, the α isomer would have to be *endo*-$B_4H_8\cdot PH_3$. On the other hand, a series of extensive NMR studies on various fluorophosphine adducts of B_4H_8 by Odom and co-workers[4b] indicated that the shift values of the B_3 atoms are less negative and the J_{BP} values are larger for the endo isomers than they are for exo isomers. This result suggests that the α isomer of B_4H_8 is in the exo form if the same relations are to be held by the two $B_4H_8\cdot PH_3$ isomers. Clearly, a single-crystal X-ray structural study of $B_4H_8\cdot PH_3$ is desired.

The observed B-P coupling constants (75-80 and 100 Hz) are greater than those in $B_3H_7\cdot PH_3$ (70 Hz) and $BH_3\cdot PH_3$ (27 Hz) and are consistent with the trend of increasing borane acid strength with the size of borane fragment. A parallel relationship between the B-P bond strengths and the magnitudes of B-P coupling constants has been reported.[6]

Certain base adducts of tetraborane(8), $B_4H_8\cdot L$, combine with Lewis bases (L′) to form bis(base) adducts, $B_4H_8\cdot L\cdot L'$. The stability of a bis(base) adduct with respect to the dissociation of its second ligand base is dependent upon the nature of the bases involved. For example, $B_4H_8\cdot 2P(CH_3)_3$[7] is a stable solid at room temperature, whereas $B_4H_8\cdot N(CH_3)_3\cdot P(CH_3)_3$[8] and $B_4H_8\cdot 2N(CH_3)_3$[9] dissociate one (weaker one) of the two bases at room temperature. When $B_4H_8\cdot PH_3$ was mixed with a large excess of PH_3 in dichloromethane, no evidence for the formation of $B_4H_8\cdot 2PH_3$ could be found in a temperature range from -80 to -30 °C. When treated with $P(CH_3)_3$, $B_4H_8\cdot PH_3$ was converted into $B_4H_8\cdot P(CH_3)_3$ or into $B_4H_8\cdot 2P(CH_3)_3$ if excess $P(CH_3)_3$ was used. Here again, no evidence for the formation of $B_4H_8\cdot PH_3\cdot P(CH_3)_3$ could be found in the process of the displacement reaction. Conversely, $B_4H_8\cdot P(CH_3)_3$ did not react with PH_3. Phosphine (PH_3) is not a strong enough base to add to $B_4H_8\cdot PH_3$ or $B_4H_8\cdot P(CH_3)_3$.

Scheme I



The above mentioned displacement of PH_3 with $P(CH_3)_3$ occurs readily at -80 °C, whereas the displacement of PH_3 from $BH_3\cdot PH_3$ with $P(CH_3)_3$ proceeds only slowly at -50 °C, though the B-P bond in $BH_3\cdot PH_3$ is weaker than that in $B_4H_8\cdot PH_3$. To explain this observed low barrier to the displacement of PH_3 from $B_4H_8\cdot PH_3$, a mechanism is suggested as illustrated in Scheme I.[10] The basal boron atoms ($B_{2,3,4}$) of $B_4H_8\cdot PH_3$ are considered to be the site of the $P(CH_3)_3$ attack to form an unstable reaction intermediate "$B_4H_8\cdot PH_3\cdot P(CH_3)_3$". The weak base PH_3 is eliminated from this intermediate to complete the facile displacement reaction. This mechanism is similar to the one that was proposed earlier by Ritter and co-workers[11] and by Paine and Parry[12] for displacement reactions of $B_3H_7\cdot L$.

B. Phosphine-Pentaborane(11). As noted earlier in section A, mixing of B_5H_{11} and PH_3 in dichloromethane at -95 °C resulted in the formation of an unstable compound. A tensimetric

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(5) La Prade, M. D.; Nordman, C. E. *Inorg. Chem.* **1969**, *8*, 1669.

(6) Rudolph, R. W.; Schultz, C. W. *J. Am. Chem. Soc.* **1971**, *93*, 6821. Cowley, A. H.; Damasco, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 6815.

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(9) Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1979**, *18*, 1465.

(10) In this scheme the B_3 atom is taken as the site of $P(CH_3)_3$ attack. An alternative mechanism, which involves the attack on the B_2 (or B_4) atom followed by a skeletal rearrangement and the elimination of PH_3, is equally valid. At present no evidence is available to differentiate the two pathways.

(11) Deever, W. R.; Lory, E. R.; Ritter, D. M. *Inorg. Chem.* **1969**, *8*, 1263.

(12) Paine, R. T.; Parry, R. W. *Inorg. Chem.* **1975**, *14*, 689.

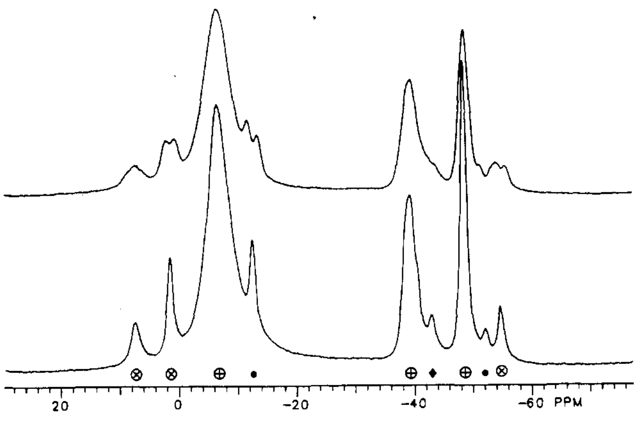

Figure 2. ^{11}B NMR spectra (96.2 MHz) of a 1:1 mixture of B_5H_{11} and PH_3 in CH_2Cl_2 at −95 °C. The upper spectrum is normal; the lower spectrum is proton-spin-decoupled: ⊕; $B_5H_{11}\cdot PH_3$, ⊗; B_5H_{11}, ♦; $BH_3\cdot PH_3$; ●; B_5H_9 impurity in the B_5H_{11} sample.

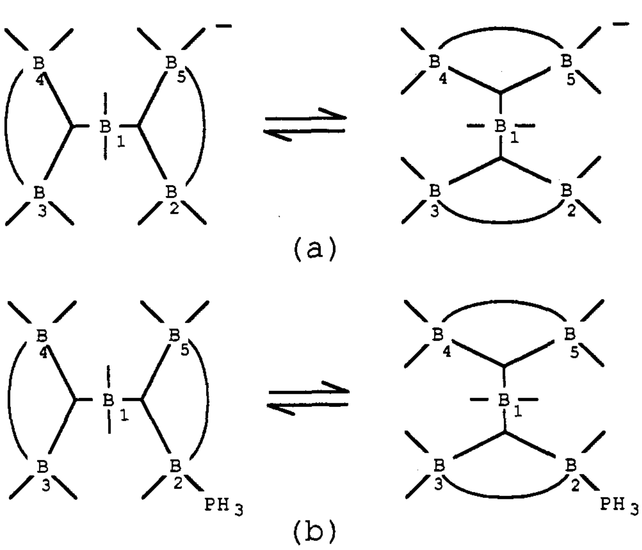

Figure 3. Structures and tautomerism of (a) $B_5H_{12}^-$ and (b) $B_5H_{11}\cdot PH_3$.

titration of a B_5H_{11} solution in dichloromethane with PH_3 at −95 °C indicated the reaction stoichiometry to be 1:1. The ^{11}B NMR spectrum of the reaction solution showed signals, which were attributable to the adduct, at −48.6, −39.4 ($J_{BP} \approx 70$ Hz[13]), and −6.7 ppm in an approximately 1:1:3 intensity ratio. The −6.7 ppm signal was broad ($\nu_{1/2}$ = 480 Hz at −95 °C, $\{^1H\}$). (See Figure 2.) The ^{31}P spectrum of the solution showed a well-defined quartet (1:3:3:1, J_{PH} = 415 Hz) of partially collapsed quartets (1:1:1:1, $J_{PB} \approx 70$ Hz) at −93.5 ppm. The signal of free PH_3 (−238 ppm) was present in the ^{31}P spectrum. These observations suggested that the compound was an adduct with the formula $B_5H_{11}\cdot PH_3$.

A possible structure of this adduct can be derived from the structure proposed by Shore for the $B_5H_{12}^-$ anion,[14] which is isoelectronic with $B_5H_{11}\cdot PH_3$. (See Figure 3.) Replacement of H^- by PH_3 at a basal position of the anion gives a structure for $B_5H_{11}\cdot PH_3$. On the basis of this structure, the signal at −48.6 ppm can be assigned to the apex boron atom (B_1) and the signal at −39.4 ppm to the phosphine-attached boron atom (B_2). The broad signal at −6.7 ppm is probably an overlap of the $B_{3,5}$[15] and B_4 signals. A mechanism involving a rapid interchange of the B_3, B_4, and B_5 atoms that renders the three basal boron atoms equivalent, however, cannot be ruled out.

The adduct $B_5H_{11}\cdot PH_3$ decomposes above −80 °C in dichloromethane solutions. Generally, B_5H_{11}, $BH_3\cdot PH_3$, $B_4H_8\cdot PH_3$, B_2H_6, and B_4H_{10} were found in the solution after the decomposition of the adduct, but free PH_3 was absent. The relative amounts of these decomposition products varied from one sample to another. No effort was made to define the conditions of decompositions. If B_5H_{11} and PH_3 were mixed in a 1:2 molar ratio to prepare $B_4H_8\cdot PH_3$ and if the reaction mixture was warmed rapidly, the decomposition of the initially formed $B_5H_{11}\cdot PH_3$ will contaminate the desired product. Therefore, the use of *excess* PH_3 and reaction temperature −80 °C is recommended for the preparation of pure $B_4H_8\cdot PH_3$.

Experimental Section

A. Chemicals and Instruments. Conventional vacuum-line techniques were used throughout for the handling of air-sensitive, volatile compounds. Phosphine (PH_3) was prepared by a literature method.[16] Pentaborane(11) and $P(CH_3)_3$ were our laboratory stock.[17] These chemicals were fractionally distilled on vacuum lines before use. The NMR spectra were recorded on Varian XL-100-15 and XL-300 spectrometers. References for chemical shift values are $BF_3\cdot O(C_2H_5)_2$ and 85% orthophosphoric acid for ^{11}B and ^{31}P, respectively. For proton shifts, the signal of dichloromethane was taken as 5.28 ppm. A VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG Data System 2000 was used for the mass spectrum acquisition of $B_4H_8\cdot PH_3$.

B. Reaction of B_5H_{11} with PH_3. (a) Tensimetric Titrations at −63 and −95 °C. A 0.375-mmol sample of B_5H_{11} was dissolved in 3 mL of dichloromethane in a 25 mm o.d. Pyrex reaction tube, and the tube was thermostated at −63 °C (chloroform slush bath). Then, measured quantities of PH_3 were introduced stepwise into the tube. The solution was stirred continuously and allowed to stand until the pressure came to equilibrium (about 10 min) after each addition of the PH_3. The pressure of the system was read on a mercury manometer that was attached to the reaction system. A pressure rise was observed when the PH_3:B_5H_{11} molar ratio reached 2:1.

Similarly, a dichloromethane solution containing 0.438 mmol of B_5H_{11} was tensimetrically titrated at −95 °C (toluene slush bath). A pressure rise was observed at a PH_3:B_5H_{11} ratio of 1:1.

(b) Reaction As Monitored by NMR Spectra. A 0.64-mmol sample of B_5H_{11} was dissolved in ca. 2 mL of dichloromethane in a 10 mm o.d. Pyrex reaction tube equipped with a stopcock, and 2.58 mmol of PH_3 was condensed above the solution at −197 °C. The tube was shaken in a −80 °C bath to mix the solution, and then it was placed in the cold probe of NMR spectrometer. The initial spectrum (^{11}B) at −80 °C contained the signals of B_5H_{11}, $BH_3\cdot PH_3$, and $B_4H_8\cdot PH_3$ and, in addition, three other signals due to $B_5H_{11}\cdot PH_3$. At this temperature intensities of the $BH_3\cdot PH_3$ and $B_4H_8\cdot PH_3$ signals were slowly increasing at the expense of other signals. When the sample was allowed to warm to 0 °C over a period of 60 min, only the signals of $BH_3\cdot PH_3$ and $B_4H_8\cdot PH_3$ had remained in the spectrum.

(c) Isolation of $B_4H_8\cdot PH_3$. A dichloromethane solution containing about 0.5 mmol of B_5H_{11} in about 2 mL of the solvent was prepared in a 10 mm o.d. Pyrex reaction tube equipped with a stopcock, and about 2 mmol of PH_3 was condensed above the solution at −197 °C. Then, the tube was placed in a −80 °C bath and allowed to stand for 1.5 h while the solution was agitated intermittently. The tube was then allowed to warm to −63 °C, and the volatile components at this temperature were pumped out. The amount of phosphine that was separated from the volatile components was always consistent with the 1:2 (B_5H_{11}:PH_3) reaction stoichiometry. Then, the tube was placed in a −23 °C bath and the pumping was continued for 6 h. The volatile materials collected were $BH_3\cdot PH_3$ contaminated with a small amount of $B_4H_8\cdot PH_3$ and traces of unidentified boron-containing compounds. The white residue in the reaction tube was dissolved in dichloromethane at −95 °C. If the freshly prepared solution was never warmed above −95 °C, its ^{11}B NMR spectrum contained only the signals of set β. The solid sample of $B_4H_8\cdot PH_3$ thus prepared melted at −6 to −5 °C, and upon standing at 0 °C it decomposed readily to give a viscous yellow oil. Mass spectral data (EI mode at 70 and 15 eV; source temperature 150 °C) were not informative. At the region of the molecular masses of $B_4H_8\cdot PH_3$ (m/z 78–89), overlapping clusters of peaks were present, and thus the $B_4H_8\cdot PH_3$ mass cutoff was obscured. When 70 eV was used, several clusters of peaks were present in the higher mass region, the highest mass cluster being centered at m/z 200. At 15 eV the highest mass appeared at m/z 111. Apparently, the compound decomposed in the probe. Anal.[18] Found:

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(13) The doublet feature of the signal was observed on a proton-spin-decoupled spectrum recorded at −75 °C.

(14) Remmel, R. J.; Johnson, H. D., II.; Jaworiwski, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

(15) The B_3 and B_5 atoms are thought to be equivalent due to a rapid tautomeric motion of the molecule, which is shown in Figure 3.

(16) Gokhale, D.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 56.

(17) B_5H_{11}; ref 9. $P(CH_3)_3$; ref 8.

H_2 (on acid hydrolysis, 72 h in 6 M HCl at 100 °C):B:P = 10.0:3.98:1.03 (molar ratio). Calcd for $B_4H_8{\cdot}PH_3$: 10.0:4.0:1.0.

C. Reaction of $B_4H_8{\cdot}PH_3$. (a) With PH_3. A sample of $B_4H_8{\cdot}PH_3$, which had been prepared by the procedure described in section B(c) with use of 0.49 mmol of B_5H_{11}, was dissolved in 1.5 mL of dichloromethane, and the solution was mixed with 2.46 mmol of PH_3. The ^{11}B spectra of the mixture were examined in a temperature range from −80 to −30 °C. Only the signals of $B_4H_8{\cdot}PH_3$ were observed.

(b) With $P(CH_3)_3$. A sample of $B_4H_8{\cdot}PH_3$ prepared from 0.60 mmol of B_5H_{11} was dissolved in 1 mL of dichloromethane, and the solution was treated with 3.04 mmol of $P(CH_3)_3$ at −80 °C. The ^{11}B NMR spectrum of the mixture indicated the formation of $B_4H_8{\cdot}2P(CH_3)_3$. When a $B_4H_8{\cdot}PH_3$ sample was treated with approximately 1 molar equiv of $P(CH_3)_3$, $B_4H_8{\cdot}P(CH_3)_3$ and a small amount of $B_4H_8{\cdot}2P(CH_3)_3$ were produced.

D. Reaction of $BH_3{\cdot}PH_3$ with $P(CH_3)_3$. A 0.5-mmol sample of $P(CH_3)_3$ was condensed at −197 °C above a 2-mL dichloromethane solution containing about 0.5 mmol of $BH_3{\cdot}PH_3$ and was mixed into the solution at −95 °C. Below −50 °C no change could be detected in the ^{11}B spectrum of the solution. At −50 °C the signal of $BH_3{\cdot}P(CH_3)_3$ was detected. At −40 °C the $BH_3{\cdot}P(CH_3)_3$ signal grew slowly at the expense of the $BH_3{\cdot}PH_3$ signal.

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(18) Because of the instability of $B_4H_8{\cdot}PH_3$, the analytical samples were not weighed. The amount of vaporization loss of $B_4H_8{\cdot}PH_3$ that occurred during the removal of $BH_3{\cdot}PH_3$ from the product mixture was dependent upon the length of pumping time and ranged from 10 to 25% under the conditions employed for the preparation of the samples. Therefore, only the ratio (H_2:B:P) obtained for each sample was meaningful. The NMR data of the product and the formation of B_4H_8 adducts by treatment with $P(CH_3)_3$ further supported the formulation $B_4H_8{\cdot}PH_3$ for the compound.

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Aqueous Molybdenum–Iron–Sulfur Chemistry: Enzyme-Mediated Assembly of $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ from Molybdate and Thiosulfate

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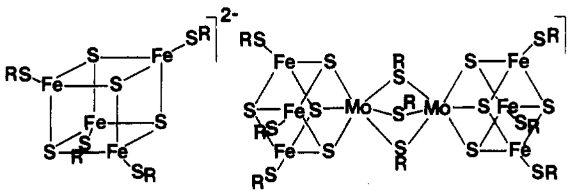
Iron–sulfur and molybdenum–iron–sulfur clusters in proteins have stimulated a large number of investigations aimed at synthesizing structural, electronic, and catalytic analogues of the biological clusters. Two prototypical "thiocubane" clusters that form by "spontaneous self-assembly" from simple iron salts, thiolates, and either sulfur or tetrathiomolybdate are $[Fe_4S_4(SR)_4]^{2-}$ [1] and $[Mo_2Fe_6S_8(SR)_9]^{3-}$.[2] (Schematic structures are shown in Chart I.) The former cluster is a synthetic analogue of those occurring in many iron–sulfur proteins. The latter "double-cubane" cluster is not an analogue of any known biological cluster, but some structural and electronic features of the $MoFe_3S_4$ core approach those of the iron–molybdenum cofactor of nitrogenase.[3] A synthetic analogue of this cofactor has so far proven elusive.

Chart I



$[Fe_4S_4(SR_4)]^{2-}$ $[Mo_2Fe_6S_8(SR)_9]^{3-}$

Recent results from this laboratory[4] have shown that salts of the water-soluble cluster $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ can be prepared in high yields from aqueous solutions containing iron salts and thiols. Sulfur, sulfide, or the outer sulfur of thiosulate can be used as the source of core sulfide. The sulfurtransferase rhodanese (thiosulfate:cyanide sulfurtransferase, EC 2.8.1.1) catalyzes the reduction of the outer sulfur of thiosulfate in the presence of thiols, especially dithiols:[5]

$$^{*}SSO_3^{2-} + 2RSH \rightarrow {}^{*}SH^- + RSSR + HSO_3^- \qquad (1)$$

We have used the rhodanese/thiosulfate/dithiol system to show that the assembly of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ can be enzyme-mediated.[4] We have also reported that reactions of MoS_4^{2-} with salts of Fe(II) in aqueous solution can, depending on the conditions, lead to formation of either the "double-cubane" cluster $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ or the novel "linear" tetranuclear cluster $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.[6] This latter cluster represents trapping of an intermediate in a previously undescribed process, namely, the Fe^{2+}-accelerated hydrolysis of MoS_4^{2-}.

Since MoO_4^{2-} is the only known biological uptake and transport form of molybdenum in nitrogen-fixing bacteria,[7] we sought an aqueous system for synthesis of Mo–Fe–S clusters using MoO_4^{2-} as the source of molybdenum. Starting from MoO_4^{2-} rather than MoS_4^{2-} would also allow the exploration of various sources of cluster sulfide, which could, in turn, influence the product distribution. Herein we report and briefly discuss some results of such explorations.

Experimental Section

Rhodanese was isolated from bovine liver according to a published procedure[8] and stored at 0–4 °C as a crystalline suspension in 2 mM sodium thiosulfate, 2 M ammonium sulfate, pH 7.6. This suspension was added as such for cluster assembly reactions, as described below. Millimolar concentrations of ammonium sulfate were thus introduced into the rhodanese-containing reaction mixtures. Concentrations and thiosulfate reductase activities of rhodanese were determined, and solutions of D,L-dihydrolipoate were prepared by previously described procedures.[4] Sodium thiosulfate and sodium sulfide were added as 1 M stock solutions in either 0.2–0.3 M Tris-sulfate or NaTAPS, pH 9.0–9.2.[9] These buffers were used for all reactions. Aqueous solutions were prepared from distilled, deionized water. Methanol was distilled from magnesium and iodine. 2-Propanol was distilled from calcium hydride.

All reactions were performed at room temperature, under a purified Ar atmosphere in either Schlenk-type glassware or septum-capped vials. Solutions were added and transferred via steel tubing or gastight syringes.

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(9) Abbreviations used: Tris, 2-amino-2-(hydroxymethyl)propane-1,3-diol; NaTAPS, sodium 3-[[tris(hydroxymethyl)methyl]amino]propanesulfonate.

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