Table I. Comparison of the Nb(IV) Melt Spectrum with the K_3NbF_7 Spectrum[a,d]

Nb(IV) in LiF-BeF_2 (66-34 mol %)	K_3NbF_7 Position	K_3NbF_7 Assignment[b]
5500 (0.39)	2150	e_1'' [(*yz*), (*zx*)][c]
13500 (0.44)	16556 (1.8)	e_2' [(x^2-y^2), (*xy*)]
19700 (1.1)	19762 (2.3)	
26300 (2.1)	28570	a_1' (z^2)

[a] K_3NbF_7 data taken from ref 2. [b] Assignment based on D_{5h} symmetry. [c] The e_1'' degenerate state is split to give a ground electronic state and the one indicated here. [d] All values are given in cm^{-1}. Molar extinction coefficients in l. mol^{-1} cm^{-1} are given in parentheses.

The melt spectrum of Figure 1, with bands similar in intensity to those of the crystal (cf. Table I), is consistent with this interpretation and represents the type of spectrum expected from a completely disordered seven-coordinated Nb(IV) ion.

Evidence in support of the implication that the coordination number remains seven on dissolution of K_3NbF_7 in the melt can be derived from the coordination behavior studies of similar tetravalent transition metal ions in fluoride melts. These studies[5] which include Zr(IV), Th(IV), and U(IV) ions, show that a variety of species ranging from eight to six coordination are possible in the melts. It was observed that the coordination number of the ion in the fluoride solvent is dependent on both the availability of "free fluoride"[6] ions with which to associate and the size of the metal ionic radius. Therefore, lower coordination numbers will occur for Nb(IV) and Zr(IV) in comparison with U(IV) and Th(IV). Because a seven–eight coordination equilibrium was observed for U(IV) in LiF–BeF_2 melts, any decrease in the size of the metal ion would tend to favor the lower coordination, i.e., seven.

In conclusion, the spectrum of Nb(IV) in fluoride melts is interpreted as arising from a $NbF_7{}^{3-}$ species which has very low symmetry. The spectrum represents the very interesting case of a simple d^1 ion in which the degeneracy of the 4d subshell is completely removed.

Registry No. K_3NbF_7, 57049-46-4; NbF_4, 13842-88-1.

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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Reduction of Trimethyl Phosphite–Borane. Formation of a New Type of Diphosphine Derivative

L. A. Peacock and R. A. Geanangel*

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The reactions of phosphine–boranes have not been widely investigated as compared, for example, to those of amine–boranes. We have recently studied some of the chemical characteristics of alkyl phosphite–boranes to compare these with amine–borane systems. In particular the reactions of phosphine–boranes and their derivatives with alkali metals were considered. We wish to report here on the reaction of trimethyl phosphite–borane with sodium naphthalide.

Experimental Section

Equipment and Materials. Standard vacuum-line techniques were employed[1] with greaseless stopcocks on all parts and reaction equipment. A LabConCo glovebox equipped with a recirculating pump and drying train and flushed with dry nitrogen gas was used for intert-atmosphere manipulations.

Ir spectra were obtained on a Beckman Model 4250 IR spectrophotometer. A Cary 14 spectrophotometer was employed for the uv spectra. A Varian Model E-3 spectrometer was used to obtain EPR spectra. Conductivity measurements were made on a Yellow Springs Model 31 conductivity bridge. Proton NMR data were obtained on a Varian Model T-60 NMR spectrometer while ^{11}B spectra were obtained using a Varian Model HA-100 instrument at 32.1 MHz and a Bruker Scientific Model WH-90 spectrometer at 28.89 MHz (FT mode). The latter instrument was also used to obtain ^{31}P spectra at 36.4 MHz in the FT mode. A Varian Model CFT-20 spectrometer was employed for the ^{13}C spectra. A cryoscopy cell similar to that described by Shriver[1] was employed for molecular weight measurements.

Carbon and hydrogen analyses were carried out by Heterocyclic Chemical Corp. Boron and phosphorus determinations were made by literature methods.[2,3]

All starting materials were reagent grade except trimethyl phosphite which was practical grade. Naphthalene, sodium borohydride, and trimethyl phosphite were purchased from MCB and sodium metal was from J. T. Baker. Deuterium oxide (99.8%) was obtained from Diaprep. Alumina of activity "1" was purchased from EM Reagents.

All aprotic solvents were dried over sodium and distilled prior to use. Trimethyl phosphite–borane was prepared according to the method of Reetz.[4] Sodium naphthalide was formed by placing measured quantities of sodium and naphthalene (with an excess of sodium) in a dry vessel on the vacuum line and condensing in a quantity of dried 1,2-dimethoxyethane. In a typical preparation 62.8 mg-atoms of sodium and 47.8 mmol of naphthalene were placed in a 100-ml glass bulb and cooled to −196° whereupon about 25 ml of solvent was vapor-transferred into the vessel. Slow warming and stirring gave the dark green solution indicative of sodium naphthalide.

Preparation of $Na_2[(CH_3O)_3P{\cdot}BH_3]_2$. In the reaction of sodium naphthalide with trimethyl phosphite–borane, nitrogen was first admitted into the vessel containing the former, which was then removed from the vacuum line port and attached via an O-ring connector to a vacuum-line filtration apparatus. The bulb was cooled with liquid nitrogen and 8.7 g (63 mmol) of $(CH_3O)_3P{\cdot}BH_3$ was added. The entire apparatus was then evacuated and the reaction bulb was allowed to warm slowly to room temperature with stirring. Near 0°C the reaction mixture became red but after stirring overnight the mixture was light brown with some white precipitate. The product was precipitated by condensing in 25 ml of dry petroleum ether (bp 30–60°) and warming again to room temperature with stirring. The light brown solid was separated from the light yellow solution by filtration in vacuo followed by several washings with petroleum ether to help remove naphthalene. Solvents were removed by vapor transfer and the near-white solid was dried under dynamic vacuum for several hours. Dry nitrogen was admitted and the apparatus removed to a glovebox where the solid product was transferred to a preweighed vial. A crude yield of 8.00 g (79%) based on trimethyl phosphite–borane was obtained.

Further purification was accomplished by column chromatography using alumina and 1,2-dimethoxyethane. A glass column was filled with a slurry of alumina and allowed to stand overnight. The entire product (8.00 g) in 75 ml of 1,2-dimethoxyethane was added to the solvent reservoir and the solution was eluted under 10 psi of dry nitrogen. The separation was followed by ^1H NMR as fractions were collected. The first 100 ml contained naphthalene and was discarded. The next 150 ml was collected and the solvent was stripped off using a rotary evaporator yielding a light yellow solid. The solid was placed in 100 ml of dichloromethane and stirred for 2 hr. Filtration gave the white solid product (2.3 g) in about 23% yield.

An attempted melting point determination on the product showed color changes to yellow near 228° and to orange near 330° but no melting was observed up to 400°. Anal. Calcd for $C_3H_{12}BO_3NaP$:

C, 22.39; H, 7.52; B, 6.72; P, 19.25. Found: C, 22.49; H, 7.61; B, 6.80; P, 19.88.

Molecular weights were measured cryoscopically in distilled water at concentrations of at least 0.05 *m*. (Lesser concentrations gave erratic, nonreproducible results in our apparatus). The apparent molecular weights for 0.057, 0.083, and 0.143 *m* solutions were 112.4, 101.2, and 110.2, respectively. For a three-ion electrolyte this corresponds to an average formula weight of 324 ± 18.

Conductivity measurements were made on a 2.9×10^{-3} *M* solution of the product in distilled water. The cell constant was determined to be 1.301×10^{-2} using a 0.02 *M* KCl solution whose specific conductance was 2.768×10^{-3} ohm^{-1}. From this the molar conductivity of the product solution was calculated to be 230 ohm^{-1} which may be compared to a range of 235–273 ohm^{-1} found typically for uni-bivalent electrolytes.[5]

Reaction with Bromine. A 0.34-g (1.06-mmol) sample of the product was dissolved in 50 ml of anhydrous 1,2-dimethoxyethane and a solution of 0.25 g (1.56 mmol) of Br_2 in the same solvent was added dropwise under N_2. The bromine was decolorized and a white precipitate was formed. The reaction mixture was filtered and the solvent was removed in vacuo leaving a viscous liquid which was redissolved in dichloromethane. Its proton NMR spectrum indicated the presence of $(CH_3O)_3P\cdot BH_3$ (δ 3.64, $J_{HCOP} = 11.6$ Hz) accompanied by several minor resonances attributable to borane bromination products.

Spectra. The ir spectrum of $(CH_3O)_3P\cdot BH_3$ obtained as a neat film exhibited the following bands (cm^{-1}): 3010 (w); 2954 (s), $\nu(CH_3)$; 2850 (m), $\nu(CH_3)$; 2394 (vs), $\nu(BH_3)$; 2353 (m), $\nu(BH_3)$; 1458 (m), $\delta(CH_3)$; 1446 (m), $\delta(CH_3)$; 1182 (s), $\nu(POC)$; 1133 (m), $\delta(BH_3)$; 1095 (m,sh), $\delta(BH_3)$; 1050 (vvs, br), $\nu(POC)$; 1024 (vvs), $\nu(POC)$; 1010 (vvs); 834 (vs); 823 (vs); 794 (vvs), $\nu(BP)$; 598 (w). Assignments were taken in part from Heitsch and Verkade.[6]

The ir spectrum of $Na_2[(CH_3O)_3P\cdot BH_3]_2$ obtained as a KBr pellet contained the following bands (cm^{-1}): 3018 (w); 2996 (w); 2955 (m), $\nu(CH_3)$; 2852 (m), $\nu(CH_3)$; 2412 (s), $\nu(BH_3)$; 2368 (s), $\nu(BH_3)$; 2355 (sh); 1460 (m), $\delta(CH_3)$; 1453 (m), $\delta(CH_3)$; 1386 (w); 1188 (s), $\nu(POC)$; 1158 (sh); 1133 (vs), $\delta(BH_3)$; 1078 (vs), $\delta(BH_3)$; 1045 (vs), $\nu(POC)$; 1020 (vs), $\nu(POC)$; 810 (s), $\nu(BP)$; 775 (vs), $\rho(BH_3)$; 748 (s); 723 (m); 608 (w); 468 (m); 425 (m).

The Raman spectrum of $Na_2[(CH_3O)_3P\cdot BH_3]_2$ obtained on the powdered solid in a sealed capillary tube contained the following bands (cm^{-1}): 3049 (m); 2940 (m), $\nu(CH_3)$; 2423 (s), $\nu(BH_3)$; 2363 (s), $\nu(BH_3)$; 2115 (m); 1866 (m); 1622 (m); 1567 (m); 1011 (m), $\nu(POC)$; 965 (m); 806 (s), $\nu(BP)$; 774 (m), $\rho(BH_3)$; 746 (m); 661 (m); 499 (m), $\nu(PP)$; 290 (s); 235 (m); 206 (s).

The product, $Na[(CH_3O)_3P\cdot BH_3]_2$, exhibited two uv bands (λ 262, 287 nm) in 1,2-dimethoxyethane solution (cutoff 260 nm) and three bands [λ 275 (ϵ 7.8), 226 (ϵ 15.4), 213 nm (ϵ 19.9)] in aqueous solution. Trimethyl phosphite–borane is not appreciably soluble in water; its spectrum in 1,2-dimethoxyethane contains two bands (λ 273, 282 nm).

An EPR spectrum of $Na_2[(CH_3O)_3P\cdot BH_3]_2$ failed to give an observable resonance indicating that the solid is probably diamagnetic. This was confirmed by magnetic susceptibility measurements.

NMR measurements on the product in D_2O solution were obtained for ^1H, ^{13}C, ^{11}B, and ^{31}P nuclei. The ^1H resonance consisted of a symmetrical doublet at δ 3.48 ($J_{HCOP} = 10.2$ Hz) for methyl protons and a quartet of doublets centered at δ −0.95 (upfield from TMS) ($J_{HB} = 88.8$ Hz, $J_{BP} = 21.6$ Hz). *p*-Dioxane was employed as an internal standard.

The ^{11}B spectrum consisted of a symmetrical octet resulting from two overlapping quartets centered at +59.1 ppm from external trimethyl borate ($J_{BH} = 88.1$ Hz, $J_{BP} = 147.3$ Hz). Upon proton decoupling the spectrum collapsed to a symmetrical doublet at +59.7 ppm ($J_{BP} = 144.4$ Hz).

The ^{13}C spectrum (proton decoupled) consisted of a doublet at −51.1 ppm (relative to TMS) with a coupling constant, J_{COP}, of 4.3 Hz. *p*-Dioxane was used as an internal standard.

The ^{31}P spectrum of the product consisted of four equally spaced, broad bands centered at +40 ppm (P_4O_6). Proton decoupling sharpened the peaks giving a coupling constant, J_{PB}, of 149.3 Hz.

Results and Discussion

Phosphite–boranes, although reasonably stable adducts,[4] have received less attention than some more familiar phosphine–boranes. Frisch, Heal, Mackle, and Madden[7] have studied the reactions of triphenylphosphine–borane hydrogens. Their results support the proposition[8] that those hydrogens are somewhat electropositive. They prepared but did not fully characterize a sodium salt, thought to be of the form $(C_6H_5)_3PBH_2^-Na^+$.

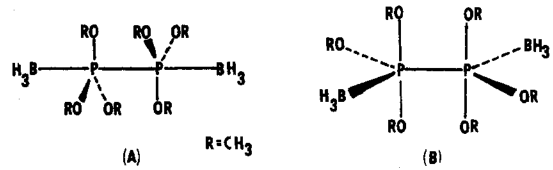


Figure 1. Possible structures for $(CH_3O)_3P(BH_3)P(BH_3)(OCH_3)_3^{2-}$.

This work encouraged us to attempt to prepare an analogous salt from trimethyl phosphite–borane, $(CH_3O)_3P\cdot BH_3$ (I). The source of sodium in our metalation reaction was sodium naphthalide prepared in 1,2-dimethoxyethane (glyme) solution. When such a solution was allowed to react with an equimolar quantity of I, rapid decolorization ensued, resulting in the formation of naphthalene and a new compound (II) in crude yield of 79%. After chromatographic purification (see Experimental Section) a final yield of 23% was obtained.

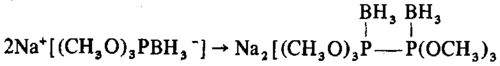
The product is a hygroscopic white solid which is stable at room temperature but, on heating, becomes yellow at about 238°C. However, it does not melt or volatilize up to 400°C. There is no evidence that II hydrolyzes appreciably in aqueous solution over long periods of time.

We believe that the compound II is the first representative of a new type of diphosphine compound. Several observations form the basis for our conclusion. First, no appreciable quantities of noncondensable gas (H_2) accumulated during any of the reactions by which II was prepared. Second, the elemental analyses (C, H, P, and B), although requiring careful purification to ensure the removal of all traces of naphthalene from the compound, indicated the composition $C_3H_{12}BO_3PNa$. The product was diamagnetic by careful EPR and magnetic susceptibility measurements in the solid state. Conductivity measurements on a 0.0029 *M* aqueous solution gave a value of 230 ohm^{-1}, consistent with a uni-bivalent electrolyte.[5] Cryoscopic molecular weight measurements in the same solvent gave an average apparent molecular weight of 108 ± 6 which, when adjusted for the presence of three ions, gives 324 ± 18 which corresponds to the dimer, $Na_2[(CH_3O)_3P\cdot BH_3]_2$ (mol wt 321.8).

A plausible rationale for these observations is that sodium naphthalide initially deposits an electron with the phosphite–borane adduct, forming an intermediate salt containing the adduct as a radical anion

$$NaC_{10}H_8 + (CH_3O)_3PBH_3 \rightarrow Na^+[(CH_3O)_3PBH_3^{\cdot -}] + C_{10}H_8$$

One may speculate that the electron is localized on the phosphorus atoms which is probably the only site possessing relatively low-energy (3d) orbitals which it may occupy. The radical anion may then couple producing a phosphorus–phosphorus bonded dianion



$$2Na^+[(CH_3O)_3PBH_3^{\cdot -}] \rightarrow Na_2[(CH_3O)_3\overset{\overset{BH_3}{|}}{P}-\overset{\overset{BH_3}{|}}{P}(OCH_3)_3]$$

Figure 1 shows the proposed structures of two geometric isomers of the dianion. The geometry around each phosphorus is expected to be approximately trigonal bipyramidal corresponding to dsp^3 phosphorus hybridization. Including the two electrons derived from sodium naphthalide, there are a total of ten electrons around each phosphorus: one pair forming the P–P bond, one forming the P–B coordinate link, and three pairs making P–O bonds.

The isomeric forms A and B (Figure 1) represent two of the several ways the substituents can be arranged in the trigonal-bipyramidal sites around each phosphorus. The structure of A is consistent with ^1H, ^{13}C, and ^{11}B NMR spectra which indicate only one environment for each respective type of nucleus. However the spectra do not absolutely rule out isomer B or a mixture of isomers since five-coordinate phosphorus compounds are often stereochemically nonrigid. Unfortunately we have not yet been able to confirm or eliminate this possibility with low-temperature NMR studies.

The ^{11}B NMR spectrum of II consists of an octet of relative intensities 1:3:1:3:3:1:3:1 which results from a quartet due to three hydrogens coupled to boron ($J = 88$ Hz) doubled in turn by splitting due to ^{31}P ($J = 147$ Hz). (The spectrum has a substantially different appearance from that of the symmetrical quintet of $(CH_3O)_3P{\cdot}BH_3$.) The assignment is confirmed by the ^{31}P spectrum which, under broad-band proton decoupling, is a symmetrical 1:1:1:1 quartet due to spin coupling with the ^{11}B nucleus ($J = 149$ Hz). Long-range coupling between nonadjacent phosphorus and boron atoms, if present, could not be resolved. These spectra as well as ^1H and ^{13}C spectra described in the Experimental Section are consistent with structures of the proposed isomers of II, assuming in the case of isomer B that a rapid exchange occurs at 35° among phosphorus coordination sites.

The high-field shift of the carbons as well as of the methyl and borane protons on formation of II from I may be an indication of increased electron density around those nuclei in II as expected for anion formation. The marked upfield shift seen in the ^{31}P spectrum probably arises from the increase in coordination number of phosphorus.[9]

Evidence indicating the presence of a phosphorus–phosphorus bond in the product comes from vibrational spectra. The characteristic stretching frequency range for P–P bonds is about 400–600 cm^{-1}.[10] For example the frequency assigned for the P–P stretch in diphosphine is 437 cm^{-1}.[11] This type of stretching vibration is expected to be ir inactive but Raman active. The Raman band at 499 cm^{-1} meets the requirements and we tentatively assign that as the P–P stretch. Other spectral assignments are made only by analogy to earlier assignments.[12-16]

Another indication sometimes used for detecting the presence of diphosphine moieties is a uv absorption near 216 nm or higher.[17] Although there are obviously many possible interferences, an aqueous solution of II gave three absorptions in this region at 275, 226, and 213 nm while I in glyme solution gave only two bands at 282 and 273 nm. Again these spectra are consistent with the presence of a P–P bond.

Although we know of no other examples of compounds with this specific type of diphosphine structure, it does not appear to violate the rules of valence. It is possible that the borane groups, in removing electron density from the phosphorus atoms, play an important role in stabilizing the dimeric anion. This may explain why no such dimers have been prepared from phosphites alone where lone-pair orbitals might interact unfavorably.

The proposed structure of II suggests that it should be possible to reoxidize the compound and recover I. When bromine and II were combined in glyme solvent, a white precipitate was formed and ^1H NMR of the product solution confirmed the formation of trimethyl phosphite–borane

$$Na_2[(CH_3O)_3P{\cdot}BH_3]_2 + Br_2 \rightarrow 2NaBr + 2(CH_3O)_3P{\cdot}BH_3$$

If our assessment of the structure of $Na_2[(CH_3O)_3P{\cdot}BH_3]_2$ is correct, its synthesis represents a new method for obtaining P–P linkages. We are currently investigating the reactions of other phosphine–boranes to determine whether additional examples of this type of structure can be found.

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Registry No. $Na_2[(CH_3O)_3P{\cdot}BH_3]_2$, 57325-21-0; $NaC_{10}H_8$, 3481-12-7; $(CH_3O)_3P{\cdot}BH_3$, 6867-39-6.

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Contribution from the Istituto di Chimica Generale ed
Inorganica, Università di Venezia, Venice, Italy,
and the Istituto di Chimica Organica,
Università di Padova, Padua, Italy

Chloroauric Acid as Oxidant. Stereospecific Oxidation of Methionine to Methionine Sulfoxide[1]

Giovanni Natile, Emilio Bordignon,* and Lucio Cattalini

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Gold(III) halides have been known for many years to be able to oxidize sulfides to sulfoxides, but the redox reaction has never been fully investigated, nor its potentiality widely exploited. Herrmann[2] reported many years ago that benzyl sulfide could be oxidized stoichiometrically to the corresponding sulfoxide by gold trichloride in the presence of water, the gold(III) being reduced to gold(I).[2,3] Phillips[4] reported in 1901 that gold trichloride reacted with dimethyl sulfide to give a complex of gold(I) but he did not isolate or detect dimethyl sulfoxide. Since the oxidative process is most probably consequent to the coordination of the organic sulfide to gold in a sterically controlled process, we thought that optically active products could be obtained in this way. The results obtained in the oxidation of the amino acid methionine, which contains a thioether function, by gold(III) chloride are reported in this paper.

Experimental Section

Chloroauric acid was purchased from Johnson Matthey and Co. and used without further purification. The amino acids were available from Fluka AG.; all other chemicals were reagent grade.

Optical rotation was measured with a Perkin-Elmer 141 polarimeter, and a Carlo Erba 3A27 amino acid analyzer was used to test the reaction products. The kinetics were followed spectrophotometrically with an Optica CF4R instrument equipped with a thermostated cell compartment.

Reaction of Methionine with Chloroauric Acid. In a typical experiment, the stoichiometric amount of (*S*)-methionine (10^{-3} mol in 10 cm^3 of water) was added under stirring to a 10-ml water solution