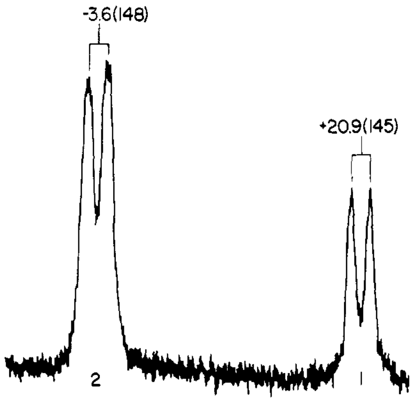

Figure 1. The 80.64-MHz ^{11}B nmr spectrum of $(C_5H_5)_2Co_2C_2B_6H_8$ taken in chloroform-*d*. Chemical shifts [ppm, relative to $BF_3 \cdot O(C_2H_5)_2$] and coupling constants (Hz) are indicated. Relative areas appear beneath the peaks.

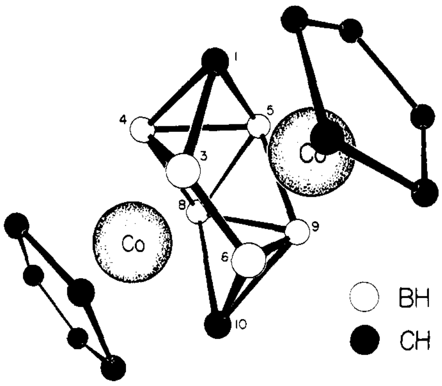

Figure 2. The proposed structure of $(C_5H_5)_2Co_2C_2B_6H_8$.

42.45; B, 18.02; H, 5.36; Co, 34.51. The mass spectrum exhibited a cutoff at *m/e* 346 which corresponds to the $^{59}Co_2{}^{12}C_{12}{}^{11}B_6{}^{1}H_{18}{}^{+}$ ion. The electronic spectrum determined in acetonitrile was as follows: [λ_{max}, mμ (ϵ): 233 (24,100), 324 (24,400), 548 (sh) (440), 652 (733)]. Figure 1 presents the 80.64-MHz ^{11}B nmr spectrum of I in chloroform-*d* solution. The spectrum exhibits doublets of relative area 2 and 1. The 60-MHz ^{1}H nmr spectrum consisted of a broad singlet of relative area 1 at τ 1.38 and a sharp singlet of area 5 at τ 4.92 which were assigned to polyhedral C–H and cyclopentadienyl protons, respectively. The proposed structure of I, presented in Figure 2, is consistent with the data if one assumes coincidental overlap of the resonances of the 4,9 and 5,8 boron atoms and resembles a bicapped Archimedian antiprism. Other possible structures cannot be excluded, however.

Finally, we wish to point out that the work reported herein represents the first example of the formation of a carborane ligand by direct electron addition to a closed polyhedral carborane. We are presently examining the scope of these reactions.

Acknowledgment. The authors wish to thank Drs. L. F. Warren for helpful discussion and R. J. Wiersema for measuring the 80-MHz ^{11}B nmr spectra. We also thank Professor F. A. L. Anet and his coworkers for the use of the 80-MHz ^{11}B nmr instrument. This research was supported in part by the Office of Naval Research.

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Evidence For A Small Ultraphosphate Molecule In Solution[1]

Sir:

During the last 20 years, a great deal has been learned[2,3] about the structure and properties of the condensed phosphates, which formerly made up one of the more confused and misunderstood areas of chemistry. There is, however, one region of composition—the ultraphosphates—about which there is still little known.

The ultraphosphates (which are defined as those compositions for which $M_2O/P_2O_5 < 1.0$, where M stands for 1 equiv of a cation or a single function of a covalently bonded moiety, such as an alkyl group) are found as infinite-network polymers of high viscosity exhibiting very broad ^{31}P nuclear magnetic resonance (nmr) peaks, the broadness of which persists even when the viscosity is greatly diminished by addition of a nonreactive solvent. The branching PO_4 groups, which are necessarily present in the ultraphosphate region of composition, almost always give rise to cross-linked network polymers. These are the sources of the physical properties observed for the ultraphosphate mixtures produced by the usual condensation or decondensation reactions.[2,4,5]

We have recently been putting considerable effort into the investigation of reactions of biochemical interest using ^{31}P nmr, because recent advances[6] in the equipment are making ^{31}P nmr considerably more useful in attacking biochemistry. As part of this general work, we have been looking into the nonaqueous phosphate chemistry of chemical dehydrating agents, such as trichloroacetonitrile[7] and dicyclohexylcarbodiimide,[8] and have found that, given sufficient time, these dehydrating agents will bring about condensation well into the ultraphosphate region of composition.[9] Further, although it is complicated and involves a number of concurrent and sequential reactions, condensation of inorganic phosphates with these dehydrating agents is

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(1) This work was supported by the General Research Support Grant awarded to the University of Illinois, College of Medicine, a grant from the Research Board of the Graduate College, University of Illinois at the Medical Center, and Grants No. USPHS-11702, NSF-6403, and NSF-GP9525.

(2) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, N. Y., 1958, pp 706–716, 773–775.

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(4) A. V. Kroll, *Z. Anorg. Allg. Chem.*, **76**, 387 (1912); **77**, 1 (1912); **78**, 95 (1912).

(5) E. J. Griffith and C. F. Callis, *J. Amer. Chem. Soc.*, **81**, 833 (1959).

(6) J. R. Van Wazer and T. Glonek in "Analytical Chemistry of Phosphorus Compounds," M. Halmann, Ed., Interscience, New York, N. Y., in press.

(7) F. Cramer and G. Weimann, *Chem. Ber.*, **94**, 966 (1961).

(8) G. Weimann and H. G. Khorana, *J. Amer. Chem. Soc.*, **84**, 4329 (1962).

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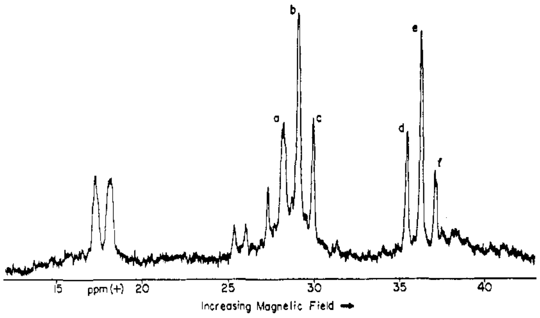

Figure 1. ^{31}P nmr spectrum of the product of the reaction of 50 ml of 2.0 M H_3PO_4 in tetramethylurea with 200 mmol of molten dicyclohexylcarbodiimide, 0.5 hr after the start of the reaction. The resonances from +25 to +31 ppm and from +35 to +40 ppm lie in the middle and branch phosphate regions, respectively.[10] The spectrum was obtained with a Bruker HFX-5 nmr spectrometer at 36.43 MHz with heteronuclear ^1H field-frequency stabilization, using 13-mm high-resolution spinning sample tubes.

kinetically controlled,[9–11] as evidenced by the fact that, when condensation has ceased (because the dehydrating agent was used up in the reaction), a rather slow reorganization to equilibrium[11] is observed—a process which may be accelerated by heating.

In a particular study in which an excess of dicyclohexylcarbodiimide was employed to condense crystalline orthophosphoric acid in tetramethylurea[12] the condensation of the phosphate proceeded to produce after about 0.5 hr an ultraphosphate composition exhibiting the surprisingly narrow-peaked spectrum shown in Figure 1. The condensation reaction gave off enough heat to warm the sample to *ca.* 80°; and, as the temperature rose, a dense, readily settleable, white precipitate was formed. This precipitate was shown to contain some phosphate but consisted predominantly of dicyclohexylurea. The spectrum of Figure 1 was taken on the supernatant liquid after the precipitate had been compacted by centrifugation.

Previous studies[11] on phosphates in various stages of condensation in tetramethylurea have shown that the orthophosphate resonance occurs in the neighborhood of −2 ppm, the end (or monofunctional) PO_4 group resonances in the range of +10–+14 ppm, the middle (or difunctional) PO_4 group resonances at +21–+31 ppm, and branched (or trifunctional) PO_4 group resonances at +34–+42 ppm. Small variations in the amount of water introduced with different samples of phosphoric acid or of the carbodiimide lead to the same general nmr pattern with somewhat different peak areas. This is also true when diisopropylcarbodiimide is employed as the condensing agent. However, even though the relative peak areas may change from one preparation to another, the peaks labeled a–f always seem to exhibit the same area relationships. This would indicate that these six peaks are attributable to the same phosphate molecule, that must be an ultraphosphate because of the high upfield position of peaks d–f, which thereby lie in the branch-group region.

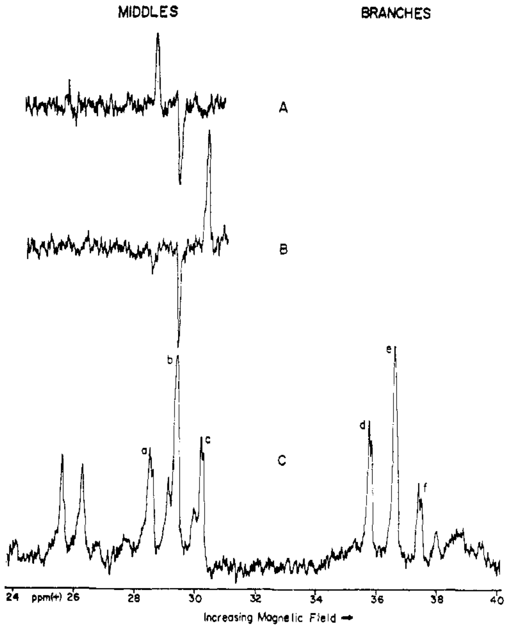

Figure 2. ^{31}P nmr spectra, taken at 36.43 MHz 3 weeks later, on the sample used for Figure 1. Only the resonances shown in the figure were detected, and it is seen that those centered at +18 ppm (see Figure 1) had disappeared. C is the usual ^{31}P nmr spectrum, while A and B are indor spectra. Spectra A through C are aligned with respect to chemical shift.

Homonuclear ^{31}P decoupling of the multiplets labeled a–f in Figure 1 is beyond the capabilities of existing instrumentation. Therefore, as shown in Figure 2, an indor[13] experiment was carried out. To obtain spectrum A, the frequency and power level of the measuring oscillator was adjusted so that it was detecting but not saturating the signal from peak f. This signal was amplified to give the y deflection of an xy recorder. A second sweep oscillator covering the same frequency range as the measuring oscillator was used to sweep the remaining spectra, and the x coordinate of the recorder was synchronized with the sweep of this oscillator. The positive and negative peaks of the resulting indor spectrum occur at positions of resonance which upon irradiation perturb signal f. Spectrum B was obtained in a similar manner by tuning in on peak d rather than peak f. A third study (not shown) involving the indor spectrum of peak e showed that this resonance is coupled with all three of the resonances a, b, and c. Similarly, indor spectra of peaks a, b, and c exhibited the expected coupling with peaks d, e, and f.

These indor results, the relatively narrow nmr line widths, and the chemical shifts indicate the presence of an ultraphosphate molecule which is not a macromolecular structure and is based on equivalent numbers of middle and branch groups, with all middles being in chemically equivalent positions, with the same being true of all branches. Further, the doubled-triplet structure of the nmr pattern shows that each middle is directly connected to two branches and each branch to two middles and an equivalent branch

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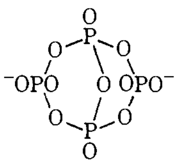
(10) T. Glonek, J. R. Van Wazer, and T. C. Myers, *Bioinorg. Chem.*, in press.

(11) T. Glonek, Ph.D. Thesis, University of Illinois at the Medical Center, Chicago, 1969. A microfilm copy of this thesis can be obtained from University Microfilms, Ann Arbor, Mich. 48106, Order No. 70-1659.

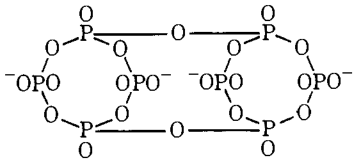
(12) P. Z. Han, M.S. Thesis, University of Illinois at the Medical Center, Chicago, 1970. A microfilm copy of this thesis can be obtained from University Microfilms, Ann Arbor, Mich. 48106.

(13) V. J. Kowalewski, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 1 (1969).

group. The requirement of chemical equivalence supports a rather simple cage structure such as I and II.



I



II

From reaction of P_4O_{10} with diisopropylurea in tetramethylurea (and thus reversing the carbodiimide condensation), it is found that the doubled-triplet nmr pattern discussed above appears with some other nmr signals, while the particles of phosphorus pentoxide are observed to be readily dispersible and not gummy.[14] This finding supports the choice of structure I for the subject compound. Although this particular $M_2P_4O_{10}$ structure (I) has been postulated many times[15,16] with respect to the solvolyses of the P_4O_{10} molecule, this is the first evidence for its existence.

(14) J. R. Van Wazer and S. Norval, *J. Amer. Chem. Soc.*, **88**, 4415 (1966).

(15) See p 694 of ref 2.

(16) G. Burkhardt, M. P. Klein, and M. Calvin, *J. Amer. Chem. Soc.*, **87**, 591 (1965). (The reader is referred to ref 14 for a reinterpretation of the findings of this paper.)

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Reactions of Hexaborane(10) with Molecular Lewis Bases. Proton Abstraction and Molecular Addition

Sir:

Although strongly basic anions have been shown to deprotonate B_6H_{10} through removal of a bridge proton to form $B_6H_9^-$,[1,2] the effect of molecular bases on hexaborane(10) until the present study has been relatively unexamined with the exception of a previous report of an adduct with triphenylphosphine in a 1:1 molar ratio.[3] We, however, observe the formation of $B_6H_{10}[P(C_6H_5)_3]_2$. Indeed, adducts of composition $B_6H_{10}L_2$, where L = $N(CH_3)_3$, $P(CH_3)_3$, and $P(C_6H_5)_3$, have been isolated in this laboratory and are apparently molecular addition compounds. On the other hand, ammonia reacts with hexaborane(10) according to the following deprotonation reaction

$$B_6H_{10} + NH_3 \longrightarrow NH_4^+B_6H_9^-$$

This result suggests that B_6H_{10} is a significantly stronger Brønsted acid than could be inferred from earlier observations of acidity[1,2] and is further support for an earlier suggestion by Parry and Edwards[4] that the bridge hydrogens of the boron hydrides are sufficiently acidic to interact with ammonia.

Hexaborane(10) in liquid ammonia (−78 to −33°) and 1 NH_3:1 B_6H_{10} mixtures in THF (−78 to −45°) and $(C_2H_5)_2O$ (−78 to −70°) produced boron-11 nmr spectra which revealed the presence of only $B_6H_9^-$ over the temperature ranges indicated. At more elevated temperatures in THF and $(C_2H_5)_2O$ a competing reaction involving bridge cleavage of the B_6 framework predominated. This competing reaction, details of which will be reported at a later date, is believed to be analogous to the reaction of NH_3 with B_5H_9, recently reported by Kodama,[5] in which $BH_2(NH_3)_2^+B_4H_7^-$ was formed. It is of interest to note that Johnson and Shore[6] have recently shown that competing reactions occur between B_4H_{10} and NH_3 in $(C_2H_5)_2O$. Depending upon reaction conditions chosen either $NH_4^+B_4H_9^-$ or $BH_2(NH_3)_2^+B_3H_8^-$ can be made to be the predominant product.

In addition to the nmr data indicating deprotonation of B_6H_{10} by NH_3, further evidence was obtained through the following metathesis reaction in which NH_4Br precipitated and from which $N(n\text{-}C_4H_9)_4B_6H_9$ was isolated from the filtrate.

$$NH_3 + B_6H_{10} + N(n\text{-}C_4H_9)_4Br \xrightarrow[\text{(small amount of THF)}]{CH_2Cl_2} N(n\text{-}C_4H_9)_4B_6H_9 + NH_4Br\downarrow$$

To a reaction vessel fitted with a glass frit, 2.03 mmol of B_6H_{10} and 4.12 mmol of NH_3 were distilled into a solution of 2.07 mmol of $N(n\text{-}C_4H_9)_4Br$ in 25 ml of CH_2Cl_2 and 5 ml of THF. A white precipitate formed which was always maintained between −78 and −45°. Filtration on the vacuum line allowed isolation (98% theory) and identification of the precipitate which was shown to be NH_4Br from its X-ray powder diffraction pattern. Volatiles were distilled from the filtrate and separated. A 2.06-mmol quantity of NH_3 was recovered, thereby indicating a reaction ratio of 1.00 NH_3:1.00 B_6H_{10}. The solid which remained upon removal of volatiles from the filtrate was shown to be $N(n\text{-}C_4H_9)_4B_6H_9$ from its X-ray powder pattern compared with that of an authentic sample of this salt.[7] This metathesis reaction is the simplest method available for preparing $N(n\text{-}C_4H_9)_4B_6H_9$.

Attempts to prepare $N(n\text{-}C_4H_9)_4B_5H_8$ through an equivalent metathesis reaction involving equimolar mixtures of B_5H_9, NH_3, and $N(n\text{-}C_4H_9)_4Br$ in methylene chloride in the presence of THF failed, presumably because of the weaker Brønsted acidity of B_5H_9 than B_6H_{10}. On the other hand, B_5H_9 can apparently be deprotonated by NH_3 in liquid NH_3.[8]

The bis-$N(CH_3)_3$ and bis-$P(CH_3)_3$ adducts of B_6H_{10} were best prepared in hydrocarbon solvents such as

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(1) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

(2) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

(3) R. E. Williams and F. J. Gerhart, *J. Amer. Chem. Soc.*, **87**, 3513 (1965).

(4) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).

(5) G. Kodama, *ibid.*, **92**, 3482 (1970).

(6) H. D. Johnson, II, and S. G. Shore, *ibid.*, in press.

(7) Authentic samples of $N(n\text{-}C_4H_9)B_6H_9$ were prepared through the following metathesis reaction which was developed by Mr. Vincent Brice of this laboratory

$$N(n\text{-}C_4H_9)_4I + KB_6H_9 \xrightarrow{CH_2Cl_2} N(n\text{-}C_4H_9)_4B_6H_9 + KI\downarrow$$

(8) G. Kodama and R. W. Parry, private communication.