# Hydrolysis Mechanism of BH_4^- in Moist Acetonitrile. 2. The Nature of the Intermediate

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Abstract: The intermediate which accumulates in the reaction of BH_4^- with acetic acid in moist acetonitrile is now shown to be the acetic acid complex of $CH_3COOBH_3^-$, rather than the acetic acid complex of BH_4^- itself.[2] Other partially hydrolyzed hydridic species are observed, but shown not to be kinetically significant. Salts of $CH_3COOBH_3^-$ react at exactly the same rate as salts of BH_4^-, so the latter is rapidly converted to the former under the conditions of the kinetic experiments. When BH_4^- reacts with an amount of $CH_3COOD-D_2O$, which leaves some of it chemically intact, substantial but incomplete isotope exchange is observed. This suggests a transient complex of CH_3COOH with BH_4^-, in which isotope exchange can take place and which also decays to give the longer lived $CH_3COOBH_3^-$.

Kinetic evidence from the reaction of tetrahydroborate ion, BH_4^-, with acetic acid and water in moist acetonitrile requires the accumulation of an intermediate.[2] At acetic acid concentrations above 0.02 M and BH_4^- concentration about 10^{-3} M, substantially all of the BH_4^- must be converted to this intermediate before further reaction takes place. Because ^{11}B NMR studies detected no boron species other than BH_4^- in solutions in which BH_4^- had been treated with less than equivalent quantities of acid, it was concluded that this intermediate must be formed reversibly.[2] Since no species in which hydridic hydrogen has been lost from boron is likely to revert to BH_4^-, the intermediate was assigned the structure **1**. New

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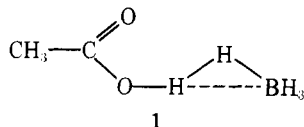
^{11}B NMR experiments have now revealed substantial quantities of trihydroacetoxyborate ion ($CH_3COOBH_3^-$) and, under some conditions, several other partially reacted species as well, in incompletely reacted acetonitrile solutions of BH_4^- and acetic acid. These, and a number of other observations, now show that the main intermediates which accumulate are $CH_3COOBH_3^-$ and its further complex with an additional acetic acid molecule. Positive evidence for the intermediacy of **1** has also been found, but **1** does not accumulate to significant concentrations. In the present paper the evidence leading to these conclusions is presented. With the exception of the NMR spectra, all the previously reported observations are shown to be consistent with the new formulation.

A separate publication[3] presents evidence that the water-promoted reaction, reported by Modler and Kreevoy, proceeds via a nucleophilic displacement by water on the acetic acid complex of $CH_3COOBH_3^-$. The nature of the "spontaneous" path is less clear, but it also leads to some form of solvated or complexed borane.

Experimental Section

Materials. The sources, preparation, and/or purification of most of the reagents and solvents used in these experiments are described in an accompanying paper.[3] THF-borane (1 M) and cesium acetate, ultrapure, were obtained from the Alfa Division of Ventron Corp. and used as received. Except as noted elsewhere, all tetrahydroborate, BH_4^-, used in this study was in the form of its bis(triphenylphosphine)iminium salt, $PNP^+BH_4^-$.[3]

Kinetic Method. The kinetic experiments were patterned as closely as practical on the methods we have described elsewhere.[3]

NMR Experiments. ^1H NMR was carried out with a Varian Associates Model HFT-80 spectrometer, with acetonitrile-d_3 and/or D_2O as solvent. The ^{11}B NMR was carried out in 12-mm tubes with a Varian Associates Model XL-100 spectrometer in FT mode with initial concentrations of boron compounds about 0.02 or 0.2 M. Chemical shifts were measured from the BH_4^- quintet.

Results

It would be highly desirable to carry out NMR studies under conditions very similar to the conditions used in the kinetic studies. This has not proved to be possible. ^1H NMR, which is much more sensitive than ^{11}B NMR, requires initial borohydride concentrations several times those used in the kinetic studies in order that BH_4^- still be observable after partial reaction. Line broadening by boron in species of lower symmetry than BH_4^- effectively makes them undetectable by ^1H NMR. ^{11}B NMR requires still higher concentrations. At the relative concentrations of BH_4^-, acid, and water employed in the kinetic experiments, the half-life of all B–H bonds is too short for spectra to be obtained. Hence, under the very different conditions employed in the NMR studies, there are observed a variety of B–H species, Figure 1, that probably are not present in significant concentrations in the kinetic experiments nor even involved in any important reaction pathway when water is present. At least ten B–H species intermediate between BH_4^- and final product were observed in sufficient concentrations to determine signal multiplicity and approximate coupling constants.

$CH_3COOBH_3^-$. In all cases in which BH_4^- solutions in acetonitrile were treated with acetic acid in quantity insufficient to destroy all the BH_4^-, the principal remaining reducing species was characterized in the ^{11}B NMR spectrum by a strong 1:3:3:1 quartet located 18.3 ± 0.1 ppm downfield from BH_4^-, Figure 1. An identical quartet could be obtained by adding THF–borane to an acetonitrile solution of cesium acetate. THF–borane alone in acetonitrile gave a quartet 11.2 ppm downfield from BH_4^-. On this basis we identify the substance as trihydroacetoxyborate ion, $CH_3COOBH_3^-$. Kinetic measurements on the acidolysis of this substance prepared from THF–borane gave rates identical with those we observed in acidolysis of BH_4^-.[3] Thus it appears that the rate constants for acidolysis of BH_4^- in moist acetonitrile[2,3] are actually rate constants for acidolysis of $CH_3COOBH_3^-$.

BH_3OH^-. In the kinetic studies of the acidolysis,[3] aliquots of the reaction mixture are quenched in aqueous base. The concentration of BH compounds in these quenched solutions was determined by adding portions of them to excess 1-benzyl-3-carbamylpyridinium chloride (BNA). The BH compounds reduce BNA to the analogous dihydropyridinium compound (BNAH), the concentration of which was determined spectrophotometrically.[3] It was observed that these quenched aliquots react with BNA at a very much faster rate than does BH_4^-. Under the conditions used in the kinetic studies, BH_4^- undergoes a pseudo-first-order reaction with
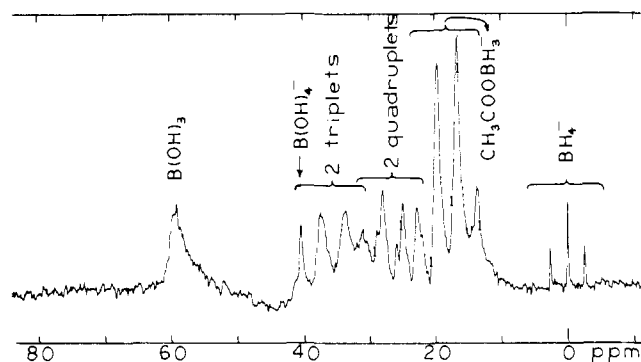
Figure 1. ^{11}B NMR spectrum of an acetonitrile solution initially 0.2 M in BH$_4^-$ and 0.25 M in CH$_3$COOH.
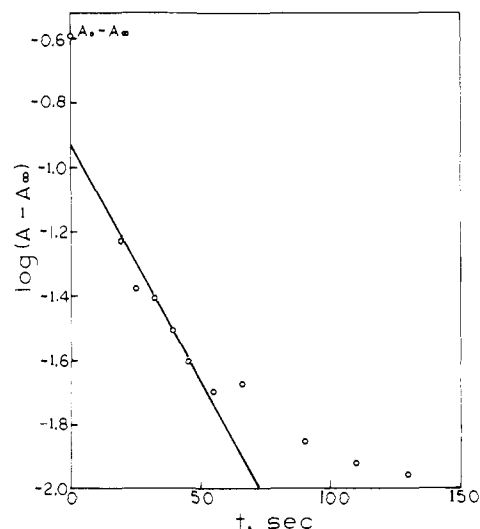

Figure 2. Semilogarithmic plot of $A - A_\infty$ vs. time in the acidolysis of a solution of composition comparable to that of Figure 1. The line has the slope expected for acidolysis of BH$_4^-$ or CH$_3$COOBH$_3^-$. If no species more reactive than CH$_3$COOBH$_3^-$ is present, the line should extrapolate to the observed $A_0 - A_\infty$. $A_\infty = 0.047$.

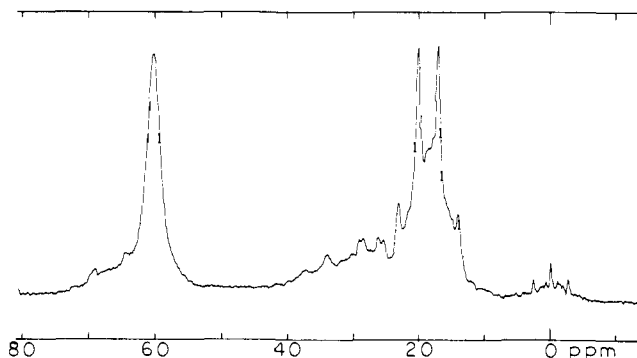Figure 3. ^{11}B NMR spectrum of an acetronitrile solution initially 0.20 M in BH$_4^-$, 0.075 M in CH$_3$COOD, and 0.60 M in D$_2$O.

BNA with a half-life of 18–18.5 s. Reaction of the quenched aliquots with BNA was at least 98% complete before any measurement could be made, and the reactions have a half-life of less than 1 s. Thus no significant BH$_4^-$ ion is present in the quenched solutions.

In order to determine what reducing species is/are present in the quenched solutions, acetonitrile solutions of BH$_4^-$ and acetic acid were mixed in a 4:5 mole ratio and immediately quenched in an equal volume of aqueous sodium hydroxide. The concentration of OH$^-$ was chosen so as to give a final concentration equal to that in the quenched aliquots of the kinetic experiments. The quartet due to the expected BH$_3$OH$^-$ was identified by comparison with the ^{11}B NMR data reported by Wang and Jolly.[4] Under the NMR conditions, with an initial (BH$_4^-$) of 0.2 M, other BH$_3$ species are present in greater concentration than BH$_3$OH$^-$. If the initial (BH$_4^-$) is reduced by an order of magnitude (this is still higher than the concentration used in the kinetic experiments) BH$_3$OH$^-$ becomes the principal reducing species, although others are still present.

Other "Downstream" B–H Species. Other quartets and triplets and one short-lived doublet are observed in partially reacted solutions, Figure 1, indicating the presence of reducing species containing from one to three B–H bonds. Similar spectra are obtained starting with either PNP$^+$BH$_4^-$ or Et$_4$N$^+$BH$_4^-$, so the principal unidentified intermediate species cannot be attributed to borane complexes with either the PNP cation or any of its decomposition products. Other than CH$_3$COOBH$_3^-$ and BH$_3$OH$^-$, we have not identified any of the downstream B–H species. It is not possible to get useful ^{11}B NMR spectra with our instrument at the concentrations used in our kinetic experiments. but, as the concentration of reactants is reduced, the concentrations of other reducing species also diminish relative to CH$_3$COOBH$_3^-$ or BH$_3$OH$^-$.

The extent to which other B–H species contribute to the rate of acidolysis of BH$_4^-$ in solutions initially prepared at high concentrations was studied as follows. A single solution was prepared, initially 0.2 M in BH$_4^-$ and 0.25 M in acetic acid. A portion was used to obtain the proton-decoupled ^{11}B NMR spectrum in order to determine relative amounts of various intermediate species. Simultaneously a second portion was diluted with acetonitrile to the usual concentration of boron compound for the kinetic experiments.[3] The rate of acidolysis was determined in the usual fashion. Four consecutive kinetic determinations were made, and the NMR spectrum was again obtained simultaneously with the last kinetic determination. The reducing power of these solutions clearly did not undergo a simple exponential decay, Figure 2. A good deal of the decay appears to take place at the rate characteristic of CH$_3$COOBH$_3^-$, as expected from the spectrum. Figure 1. The other reducing agents apparently undergo acidolysis at differing rates, some faster than CH$_3$COOBH$_3^-$ and some

slower. At least one reducing agent seems not to react appreciably within the time frame of the kinetic experiment, producing the A_∞ value of Figure 2. Apart from the fraction attributed to CH$_3$COOBH$_3^-$, the decay curves were not readily correlated with the intensities of the various NMR signals.

The fact that the quantities of the unidentified B–H intermediates, relative to quantity of CH$_3$COOBH$_3^-$, diminish both with a decrease in initial concentrations of reactants and with an increase in initial water concentration, together with the deviation of the kinetic data in Figure 2 from the normal straight line for acidolysis of BH$_4^{-\,3}$ or CH$_3$COOBH$_3^-$, indicates that these unidentified species are of little importance in the "spontaneous" reaction pathway under the conditions of the kinetic experiments and are probably nearly nonexistent in the water-promoted pathway.

Exchange Experiment. An 8:3:24 mole ratio of BH$_4^-$–DOAc–D$_2$O in acetonitrile was allowed to react for 2 h. Both coupled, Figure 3, and proton-decoupled spectra were obtained. In the borohydride region of the coupled spectrum, Figure 4a, the expected quintet ($J_{BH} = 83$ Hz) of unreacted BH$_4^-$ was clearly discernible. Additionally the quartet of triplets ($J_{BH} = 83$, $J_{BD} = 12.7$ Hz) expected of BH$_3$D$^-$ was discernible, centered 5.7 Hz upfield from the BH$_4^-$ quintet. The noisy background does not permit unambiguous identification of more highly exchanged products, but further splitting is apparent, indicating that exchange did continue to more highly exchanged products. Background noise prevents precise
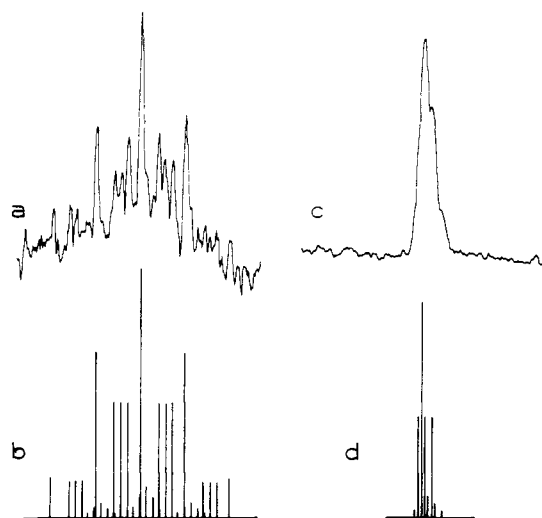
Figure 4. (a) Expansion of the borohydride region of the spectrum in Figure 3. (b) Simulated line spectrum "expected" for a 1:1.4:0.30 ratio of BH_4^-, BH_3D^-, and $BH_2D_2^-$. It is assumed that $J_{BH} = 83$ Hz, $J_{BD} = 12.7$ Hz,[6] and the chemical shift is 5.7 Hz upfield for each D atom bonded to boron. The effect of H–D coupling on the boron spectrum is unknown and therefore ignored. (c) Expansion of the borohydride region of the proton-decoupled spectrum of the same solution. (d) Simulated line spectrum corresponding to (c).

quantitative comparison of BH_4^- and BH_3D^-, but they are clearly of comparable intensities in the spectra. The lines expected of the partially exchanged material are shown in Figure 4b for comparison. The differences between Figures 4a and 4b may be attributable in part to the small effect expected in the ^{11}B spectrum as a consequence of H–D coupling.

The borohydride region of the proton-decoupled spectrum, Figure 4c, shows a single broad peak with several shoulders of varying intensity. This peak is consistent with a BH_4^- singlet, a BH_3D^- triplet of comparable intensity 5.7 Hz upfield from BH_4^-, and a much weaker $BH_2D_2^-$ quintet another 5.7 Hz upfield. In the coupled spectrum, Figure 3, the $CH_3COOBH_3^-$ quartet has shoulders representing the triplet of triplets expected of $CH_3COOBH_2D^-$ located 5.7 Hz upfield from $CH_3COOBH_3^-$. Similar features are evident in one of the unidentified quartets in the spectrum.
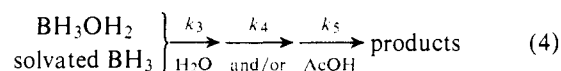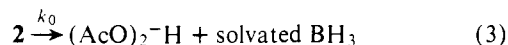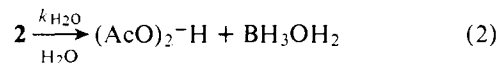
Discussion

The proposal of Modler and Kreevoy[2] for acidolysis of borohydride in moist acetonitrile via a rate-determining breakdown of a complex between acetic acid and borohydride ion must be modified to take into account both the newly determined kinetic isotope effects[3] and new NMR results showing that the predominant hydridic species in the kinetic experiments was $CH_3COOBH_3^-$. A reversibly formed complex between acetic acid and BH_4^-, such as **1**, accounts for extensive isotopic exchange between the reactants, Figures 3 and 4, and appreciable exchange in the $CH_3COOBH_3^-$. Such an intermediate has a precedent in the aqueous solution hydrolysis of BH_4^-.[5] Beyond this, little is known about the mechanism of the isotope exchange or the concomitant conversion of BH_4^- to $CH_3COOBH_3^-$.

Under the reaction conditions used[2,3] for most of the kinetic experiments the rate is essentially independent of acetic acid concentration and linearly dependent on water concentration, yet in the absence of acid the $CH_3COOBH_3^-$ is relatively

$$CH_3-C \begin{matrix} O^--BH_3 \\ \diagdown \\ O \end{matrix} + AcOH \overset{K}{\rightleftharpoons} CH_3-C \begin{matrix} O-BH_3 \\ \diagdown \\ O\cdots H-OAc \end{matrix} \quad (1)$$

2
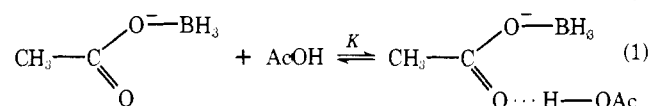
stable to water. The reversible formation of a complex, **2**, between $CH_3COOBH_3^-$ and acetic acid, followed by the rate-determining breakdown of the complex by either of two mechanisms, eq 2 and 3, yields a rate law identical with that of Modler and Kreevoy[2] and is consistent with the kinetic isotope effects.[3] The products of the rate-determining step

$$2 \underset{H_2O}{\overset{k_{H_2O}}{\longrightarrow}} (AcO)_2^-H + BH_3OH_2 \quad (2)$$

$$2 \overset{k_0}{\longrightarrow} (AcO)_2^-H + \text{solvated } BH_3 \quad (3)$$

$$\left. \begin{matrix} BH_3OH_2 \\ \text{solvated } BH_3 \end{matrix} \right\} \underset{H_2O \ \text{and/or} \ AcOH}{\overset{k_3 \quad k_4 \quad k_5}{\longrightarrow}} \text{products} \quad (4)$$

presumably break down in stages, eq 4, to give the final products, $B(OH)_4^-$ and $B(OH)_3$. If the stability of intermediates as shown by the NMR experiments is a valid indication, the later stages in acidolysis become increasingly fast. Modler and Kreevoy determined a value of $1.6 \pm 0.3 \times 10^2$ for K, although they attributed it to a different equilibrium. With this value for K, in a solution of concentration such that the excess of acetic acid over BH_4^- is not less than 0.02 M, nearly all the $CH_3COOBH_3^-$ would be converted to **2**. In our kinetic studies[3] an acetic acid excess of at least this magnitude was always used and no deviations from first-order decay rates occur until after 95% reaction. Even after 95% reaction little or no deviation is detected in experiments with (H_2O) greater than 0.3 M. Although it is not entirely compelling, this argues that **2** (in rapid equilibrium with $CH_3COOBH_3^-$) was nearly all formed from BH_4^- before the first aliquots were withdrawn, rather than being formed and decaying at comparable rates.

The nature of the "downstream" intermediates is quite unclear and merits future study. Four BH_3 species, two BH_2 species, and one BH species have been observed in acetonitrile solutions, along with trace signals of indeterminate multiplicity. Of these, only $CH_3COOBH_3^-$ is definitely identified. Most of the others are present in amounts too great to be accounted for as products derived from impurities in either reactants or solvent. Substances containing the partial structure $>BOBH$ might be postulated. Various hydrates of borane derivatives certainly must form, but the persistence of the observed substances in the presence of water and over a period of days is not consistent with the instability expected for a compound such as BH_3OH_2. Reduction of solvent by BH_4^- to ethylamine or ammonia should lead to rather stable substances of the type RNH_2BH_3, but very little such reduction should occur under the conditions employed in the kinetic studies.

Regardless of the nature of these unidentified "downstream" intermediates that appear in the NMR spectra, the kinetic evidence referred to in the Results section indicates that they are not formed to an important degree at the dilute concentrations of reactants used in the regular kinetic experiments. They must, therefore, not be a part of the principal reaction path followed under kinetic conditions. It seems reasonable to ignore them in discussing the mechanism of the reaction under the kinetic conditions employed.[3]

References and Notes

(1) Department of Chemistry, Moorhead State University, Moorhead, Minn. 56560.
(2) R. F. Modler and M. M. Kreevoy, *J. Am. Chem. Soc.*, **99**, 2271 (1977).
(3) B. S. Meeks and M. M. Kreevoy, *Inorg. Chem.*, in press.
(4) F. T. Wang and W. L. Jolly, *Inorg. Chem.*, **11**, 1933 (1972).
(5) M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.*, **94**, 6371 (1972).
(6) $J_{BD} = J_{BH} \times \gamma_D/\gamma_H = 83$ Hz (obsd) $\times 1/6.514 = 12.74$. See: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, p 90.

A Tris(dialkylamino)phosphine with Pyramidal Nitrogens

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Abstract: Syntheses for the unstable symmetrical tricyclic aminophosphine **1** and its relatively stable O=P (**2**), S=P (**3**), and Se=P (**4**) derivatives are reported. The failure of **1** to form a stable BH_3 adduct contrasts with that observed for $P(NMe_2)_3$, $P(MeNCH_2)_3CMe$, and $P(\overline{NCH_2CH_2})_3$ and is rationalized in terms of electronic differences on the nitrogen which are imposed by structural constraints. The trend in $^1J_{PSe}$ for these compounds is shown to be consistent with this idea. The structure of **3**, determined by X-ray means, substantiates our earlier postulate that constraint in $P(ZC)_3$ systems decreases the PZC angle before the ZPZ angle is affected.

Introduction

Owing to the lack of unambiguous structural and PES data, the assignment of the conformational preference of acyclic tris(dialkylamino)phosphines remains unsettled.[1] Complicating this problem is the question of planarity or pyramidality of the nitrogens in the PNR_2 moiety. In the absence of steric factors, nitrogen is found from X-ray diffraction studies to be generally planar or nearly so (i.e., the sum of the angles around nitrogen is >355°) in PN<, O=PN<, and S=PN< systems.[2] Evidence that subtle steric and/or electronic forces may be operative can be seen in the 348° sum of the angles about nitrogen deduced from an electron diffraction study of Me_2NPF_2[3] (although microwave[4] and X-ray diffraction[5] work revealed a planar nitrogen) and in the <340° for the angle sum determined by X-ray means for one nitrogen in tris(morpholino)- and two nitrogens in tris(piperidinyl)-phosphine.[6]

The preparations of the compounds in Scheme I were carried out in order (1) to examine a rigid tris(dialkylamino)phosphine

Scheme I
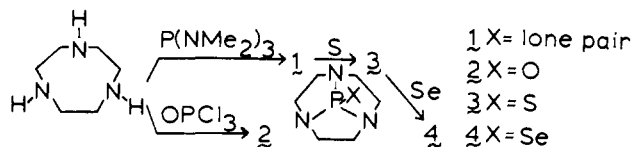
1 which might closely duplicate the C_{3v} structure proposed to be the dominant conformer of $P(NMe_2)_3$ on the basis of PES spectral studies,[7] (2) to assess the electronic consequences of forcing the nitrogen lone pairs to be cis to X in the compounds in Scheme I as opposed to their geometry in **5–9** wherein all the nitrogen lone pairs are orthogonal to P–X,[2,8,9] and (3) to further test[10] our hypothesis[11] that the ZPZ angles around a bridgehead phosphorus in $P(ZC)_3$ systems are not nearly so
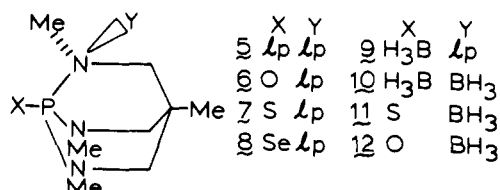
sensitive to constraint as are the PZC angles around the phosphorus substituent atom Z.

Experimental Section