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# ORGANOPHOSPHORUS MOLECULES OF THE STOICHIOMETRY $B_9H_{11}CPR$ *

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## Summary

The reaction of 7,8- or 7,9- $B_9H_{11}CP^-$ with alkyl halides (RX) resulted in molecules of the stoichiometry $B_9H_{11}CPR$. NMR spectra of the products are reported and these data indicate that the R groups are bonded to the phosphorus.

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## Introduction

Base degradations of the polyhedral phosphacarbaundecaboranes(11), 1,2- and 1,7- $B_{10}H_{11}CP$, have been shown to result in the eleven atom *nido* carbaphosphaboranes, 7,8- and 7,9- $B_9H_{11}CP^-$. In these, the phosphorus atoms are in the open face of the cage fragment [1], and they function as Lewis bases. Reactions of these anions with $M(CO)_6$ (M = Cr, Mo, W) yield complexes $B_9H_{11}CP—M(CO)_5{}^-$ in which the cage phosphorus functions as a monodentate phosphine [2]. Similarly, reactions of these with $[(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(cyclohexene)]^+$ and $[(\pi\text{-}C_7H_7)Mo(CO)_3]^+$ yield neutral complexes in which the phosphorus atoms function as sigma donors [3]. The reactions of $B_9H_{11}CP^-$ with methyl iodide yield neutral molecules of the stoichiometry $B_9H_{11}CPCH_3$ which also confirm the donor properties of the phosphorus atoms [1]. In order to gain insight into the properties of these unusual phosphorus atoms we have prepared and studied a series of neutral derivatives of the type $B_9H_{11}CP—R$ (R = $CH_3CH_2$—, $CH_2CHCH_2$—, $C_6H_5CH_2$—, $C_6H_5CHCHCH_2$—).

## Experimental

The boron hydrides 7,8- and 7,9- $B_9H_{11}CP^-$ were prepared using literature methods [1]. The acetonitrile was distilled from phosphorus pentoxide and stored over type 4A molecular seives. All reactions were carried out under a positive pressure of prepurified nitrogen or argon.

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The proton NMR spectra were recorded using a Varian Associates T-60 spectrometer with TMS as an internal standard. Boron ($^{11}B$) NMR spectra at 70.6 MHz were recorded at Indiana University with a Varian HR-220 spectrometer, and the chemical shifts are referred to $BF_3 \cdot O(C_2H_5)_2$ = 0 ppm. Low resolution mass spectra were obtained with an Atlas CH-7 instrument. Melting points were obtained in evacuated sealed capillaries and are uncorrected. Elemental analyses and molecular weights were obtained from Galbraith Laboratories, Knoxville, Tennessee.

*Handling of material*

The neutral compounds described in this paper are very malodorous. The allyl derivative is particularly offensive and is detectable in minute amounts. These compounds must be handled in a fume hood and stored in sealed containers.

*General procedure for the preparation of $B_9H_{11}CPR$*

Equimolar amounts of $[(CH_3)_4N][B_9H_{11}CP]$ and the organohalide were stirred and refluxed in dry acetonitrile for a period of 1-5 h. During the reaction period, $[(CH_3)_4N]X$ precipitated. After cooling to room temperature, the acetonitrile was removed in vacuo leaving colorless gummy residues. The $C_6H_5CH_2$— derivatives were purified by chromatography on a silica gel column using benzene as eluent, followed by a high vacuum sublimation. The $C_6H_5$-$CHCHCH_2$— derivative was purified by a high vacuum sublimation, and the $CH_3CH_2$— and $CH_2CHCH_2$— products by high vacuum distillations. The products were handled in an atmosphere of prepurified nitrogen or argon. Additional information is summarized in Table 1.

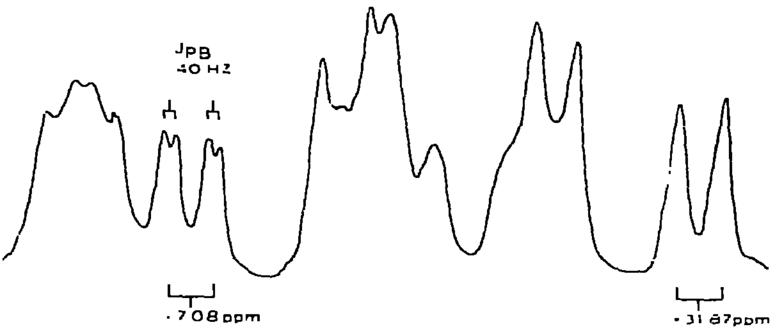
**Results and discussion**

The tetramethylammonium salt of 7,9-$B_9H_{11}CP^-$ reacts with $\alpha$-bromotoluene (benzyl bromide), 3-bromopropene (allyl bromide), 1-phenyl-3-bromopropene (cinnamyl bromide), or iodoethane —RX— in refluxing acetonitrile to give $(CH_3)_4NX$ and moderate yields of formally neutral and covalent molecules of the stoichiometry 7,9-$B_9H_{10}CHPR$. The 7,8-isomer also reacts with $\alpha$-chlorotoluene to yield an analogous compound 7,8-$B_9H_{11}CPCH_2C_6H_5$. All products are moderately soluble in chloroform and benzene but insoluble in hexane.

TABLE 1

REACTIONS OF 7,8- AND 7,9- $B_9H_{11}CP^-$ WITH ORGANOHALIDES

| RX | Reaction time (h) | Product | Yield (%) | Mmole of each reagent |
|---|---|---|---|---|
| $C_6H_5CH_2Br$ | 4 | 7,8-$B_9H_{11}CPCH_2C_6H_5$ | 30 | 5.30 |
| $C_6H_5CH_2Br$ | 4 | 7,9-$B_9H_{11}CPCH_2C_6H_5$ | 52 | 1.10 |
| $CH_2CHCH_2Br$ | 2 | 7,9-$B_9H_{11}CPCH_2CHCH_2$ | 71 | 3.97 |
| $C_6H_5CHCHCH_2Br$ | 2 | 7,9-$B_9H_{11}CPCH_2CHCHC_6H_5$ | 60 | 2.21 |
| $CH_3CH_2I$ | 4 | 7,9-$B_9H_{11}CPCH_2CH_3$ | 60 | 2.21 |



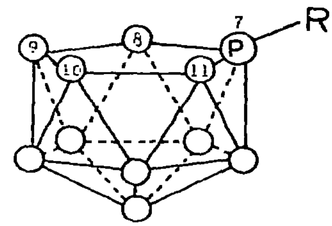




Fig. 1. A 70.6 MHz $^{11}B$ NMR spectrum of 7,9-$B_9H_{11}CPCH_2C_6H_5$ measured in benzene.

Fig. 2. Proposed structure of $B_9H_{11}CPR$ derivatives. The carbon atoms are either in the 8 (7,8-isomer) or 9 (7,9-isomer) position. Hydrogen atoms have been omitted for clarity.

These derivatives are colorless and all are solids at room temperature with the exception of the allyl derivative, which is a liquid when freshly distilled. In accord with the neutral formulation, these products readily distill or sublime at reduced pressure. All are exceedingly malodorous. These derivatives can be stored in an inert atmosphere but show detectable borate formation when stored in air for several days.

The $^{11}B$ NMR spectra of the 7,9-benzyl (see Fig. 1) and cinnamyl derivatives have been recorded in benzene and, as expected, the spectra are essentially identical. Both spectra consist of five multiplets of relative area (low to high field) 2/1/3/2/1/ which are consistent with the eleven atom framework shown in Fig. 2*. The most prominent feature of the spectra is a sharp doublet of doublets (at +7.08 ppm in Fig. 1) which corresponds to one boron. A similar coupling pattern has been observed for the previously reported 7,9-$B_9H_{11}$-$CPCH_3$ and the additional coupling has been shown to result from $^{31}P$—$^{11}B$ coupling rather than from the $^{1}H$—$^{11}B$ coupling due to the single, acidic eleventh hydrogen [1]. For the isoelectronic and isostructural carborane 7,9-$[B_9H_{12}C_2]^-$ the $^{11}B$ spectrum displays a coupling of 40 Hz in a multiplet at +25.4 ppm which has been assigned to the single acidic hydrogen which occupies a static bridging position between two boron atoms in the open face of the carborane framework [4]. It is reasonable to assume that the corresponding acidic hydrogen in the $B_9H_{11}CPR$ derivatives is similar in character and thus additional $^{1}H$—$^{11}B$ coupling should be observable in the spectrum displayed in Fig. 1. Such coupling, however, is not readily detectable in the spectrum of either the benzyl or cinnamyl derivative, but additional NMR experiments should reveal the unobserved coupling.

The $^{1}H$ NMR spectra (see Table 3) of the $B_9H_{11}CPR$ strongly support the conclusion that the R groups are attached to the phosphorus atoms in the phosphacarborane framework as shown in Fig. 2. Accordingly, the spectra of all derivatives display spin coupling characteristic of R groups attached to phos-

* Ideally the $^{11}B$ spectrum should consist of nine doublets corresponding to the nine unique B—H groups. Additional coupling due to the "extra" hydrogen and the phosphorus is also expected.

TABLE 2

ANALYTICAL DATA FOR $B_9H_{11}CPR$

| | Analysis found (calcd.)(%) | | | M.p. (°C) | Mol. wt. found (calcd.) | |
|---|---|---|---|---|---|---|
| | C | H | P | | Mass spec. | Osmometry[a] |
| 7,8-$B_9H_{11}CPCH_2C_6H_5$ | 39.70 | 7.95 | | | 244 | |
| | (39.62) | (7.48) | (12.77) | 50-51 | (244) | (242.5) |
| 7,9-$B_9H_{11}CPCH_2C_6H_5$ | 39.41 | 7.52 | 12.56 | | 244 | 244 |
| | (39.62) | (7.48) | (12.77) | 57-59 | (244) | (242.5) |
| 7,9-$B_9H_{11}CPCH_2CHCH_2$ | 25.20 | 8.33 | 15.96 | | 194 | 185 |
| | (24.97) | (8.38) | (16.10) | | (194) | (192.5) |
| 7,9-$B_9H_{11}CPCH_2CHCHC_6H_5$ | 44.74 | 7.85 | 11.57 | | 270 | 287 |
| | (44.73) | (7.51) | (11.53) | 107-109 | (270) | (268.5) |
| 7,9-$B_9H_{11}CPCH_2CH_3$ | 20.39 | 9.11 | | | 182 | |
| | (19.97) | (8.94) | (17.17) | 29-30 | (182) | (180.4) |

[a] Molecular weights were determined in benzene solution.

TABLE 3

SOME PROTON NMR DATA FOR $B_9H_{11}CPR$

| Isomer | R | Chemical shift, δ (ppm) | Assignment |
|---|---|---|---|
| 7,8- | $—CH_2C_6H_5$ | 3.83 doublet<br>$^2J$(PCH) 11.0 Hz | P—$CH_2$ group |
| | | 1.9 broad singlet | Carborane CH |
| 7,9- | $—CH_2C_6H_5$ | 3.55 doublet<br>$^2J$(PCH) 11.0 Hz | P—$CH_2$ group |
| | | 2.4 broad singlet | Carborane CH |
| 7,9- | $—CH_2CHCH_2$ | 3.04 doublet of doublets<br>$^2J$(PCH) 10.5; $^3J$(HCCH) 6.5 Hz | P—$CH_2$ group |
| | | 2.4 broad singlet | Carborane CH |
| 7,9- | $—CH_2CHC(H)C_6H_5$ | 3.17 doublet of doublets<br>$^2J$(PCH) 10.5; $^3J$(HCCH) 7.0 Hz | P—$CH_2$ group |
| | | 2.4 broad singlet | Carborane CH |
| 7,9- | $—CH_2CH_3$ | 2.37 five line multiplet<br>$^2J$(PCH) ≈ $^3J$(HCCH) ≈ 8.0 Hz | P—$CH_2$ group |
| | | 1.40 doublet of triplets<br>$^3J$(PCCH) 24.0; $^3J$(HCCH) 8.0 Hz | $CH_3$ group |

phorus [5,6] which has been noted previously for both 7,8- and 7,9-$B_9H_{11}$-$CPCH_3$ [1]. Thus the spectra of the benzyl derivatives contain a sharp doublet corresponding to the $CH_2$ resonances with $^2J$(PCH) 11.0 Hz. Similarly the spectra of both the allyl and cinnamyl derivatives display a doublet of doublets corresponding to the methylene group protons with $^2J$(PCH) 10.0 Hz and $^3J$(HCCH) 6.5 and 7.0 Hz, respectively.

For the ethyl derivatives the methylene resonances are sufficiently separated from the methyl resonances so that the spectrum is essentially first order — even at 60 MHz. The methylene resonances, however, appear as a five line pattern which can be interpreted as overlapping quartets with $^2J$(PCH) ≃ $^3J$(HCCH) ≃ 8.0 Hz. This interpretation is in accord with results from a study of $P(OCH_2CH_3)_3$ in which the five line pattern arising from the $CH_2$ protons was shown to result from overlapping quartets through a double resonance experiment*. The methyl resonances, however, clearly appear as a pair of triplets with $^3J$(FCCH) 24.0 Hz and $^3J$(HCCH) 8.0 Hz. The observation that the magnitude of the $^3J$(PCCH) is larger than the $^2J$(PCH) is consistent with a $PCH_2$-$CH_3$ grouping [5,8].

The spectra of both the cinnamyl and allyl derivatives display multiplets in the vinylic region that are more complex than those observed for the parent alkyl halides. These vinylic resonances will not be considered in detail in this paper, but their complex nature suggests the presence of coupling, $^3J$(PCCH).

It has been observed that the chemical shifts of the protons of alkyl groups attached to phosphorus depend on the formal charge of the phosphorus which is determined by the ancillary groups [5]. For a given $B_9H_{11}CPR$, the

* Discussed on page 106 of a review article by Baldeschweiler and Randall [7].

groups adjacent to the P atom in the 7,8-isomer differ from those in the 7,9-isomer in that the CH group neighbors the P only in the 7,8-derivative. Of the two environments, the P atom in the 7,8-isomer is expected to have the greater positive charge due to the adjacent CH group which is more electronegative than a BH group. The chemical shifts of the PCH protons of the benzyl and methyl [1] derivatives are in accord with this prediction with the resonances from the 7,8-isomers at lower field than those from the 7,9-isomers.

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