number greater than 4 are formed, this must be through direct hydration of the central atom. When reduced to a flat background through removal of the Rayleigh background, the laser-Raman spectra of the aqueous solutions of both the Sb(V) and As(V) ions contain at least five bands in the 200–300-cm^{-1} region. The occurrence of five peaks is independent of separation from the Rayleigh background and of curve resolution. The choice of background level and the details of curve resolution do have some effect on the relative intensities of the vibrations, however, and the illustrated resolution is that which we regard as providing the most accurate fit to the total curve envelope. The spectra are somewhat more complex than that of $(C_6H_5)_4SbCl$ in methanol, and they show greater similarity to that of methanolic $(C_6H_5)_4SbF$—an x fundamental occurs at *ca.* 195 cm^{-1}, and solvent broadening[29] may prevent resolution of additional low-frequency components of mode u from the strong polarized lines at 220 and 242 cm^{-1} in the spectra of Sb(V) and As(V) compounds, respectively. It thus seems possible that distortions from tetrahedral symmetry may occur through first-coordination-sphere hydration to form five-coordinate species in the aqueous solutions, although the evidence for this is not unambiguous.

Acknowledgment.—This research was supported in part by NSF grant GP-8679 to M. D. M.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

Substituted Fluorophosphine Base Adducts of Triborane(7) and Diborane(4)[1]

BY E. R. LORY AND D. M. RITTER*[2]

Received September 8, 1970

Dimethylaminodifluorophosphine and difluorophosphine have been combined as the bases in adducts with triborane(7) and with diborane(4). These were made in sequential and essentially reversible reactions with tetraborane(10). The three new substances $[(CH_3)_2NPF_2]_2 \cdot B_2H_4$, $F_2PH \cdot B_3H_7$, and $(F_2PH)_2 \cdot B_2H_4$ have been characterized by analysis, mass spectrometry, infrared spectroscopy, and nmr. New data have been found for $(CH_3)_2NPF_2 \cdot B_3H_7$.

This paper reports the preparation of new acid–base derivatives of diborane(4) and some chemistry concerning adducts of triborane(7), namely, (1) their preparation from other triborane(7) adducts, (2) their transformation into diborane(4) adducts, and (3) their preparation from tetraborane(10).

Some bases (*e.g.*, PF_3 and CO) will not convert tetraborane to triborane(7) adducts; others (notably ethers and amines) do so with results for which the literature was summarized in a previous paper.[3] Of the triborane(7) adducts so formed some are subject to base displacement reactions, but at least two, $(CH_3)_3N \cdot B_3H_7$ and $(CH_3)_2O \cdot B_3H_7$, have been found to undergo borane adduct displacement by triphenylphosphine[4] and by trifluorophosphine,[3] respectively, with formation of diborane(4) adducts. Intuitively rather than deductively, the query arose whether there might be found bases of intermediate strength that would sequentially be the forming reagents with tetraborane(10) and the displacing reagents to give the diborane(4) adducts (*cf.* eq 1 and 2). Dimethylaminodifluorophosphine was known to give $(CH_3)_2NPF_2 \cdot B_3H_7$ from tetraborane(10)[5] under conditions so mild as to preclude further reaction, and the newly discovered difluorophosphine[6] seemed a similar substance. The speculation proved fruitful, since both the bases reacted with tetraborane(10) reversibly as described by the following equations, where b represents one of the bases

$$B_4H_{10} + 2b \rightleftarrows b \cdot B_3H_7 + b \cdot BH_3 \qquad (1)$$

$$b \cdot B_3H_7 + 2b \rightleftarrows b_2 \cdot B_2H_4 + b \cdot BH_3 \qquad (2)$$

Though one product in each forward reaction according to eq 2 was not diborane, but a borane adduct, diborane was used to accomplish the reversal. The best preparative method for the difluorophosphine adducts was not this process but one in which the first displacement reaction had dimethyl ether–triborane(7) as a reactant

$$(CH_3)_2O \cdot B_3H_7 + 2PF_2H \longrightarrow PF_2H \cdot B_3H_7 + (CH_3)_2O \qquad (3)$$

$$PF_2H \cdot B_3H_7 + 2PF_2H \longrightarrow (PF_2H)_2 \cdot B_2H_4 + PF_2H \cdot BH_3 \qquad (4)$$

The extent of reaction depended upon whether the reaction time was 30 sec or 4 min. The diborane(4) adducts reacted only slowly and incompletely with diborane (50% conversion), slowly with protic solvolytic reagents, and not at all with hydrogen. This is in contrast with the rapid reactions found for $(PF_3)_2 \cdot B_2H_4$. Considering the experience with the two phosphine bases, $(CH_3)_2NPF_2$ and PF_2H, it seems likely that failure to obtain $PF_3 \cdot B_3H_7$ must arise from its very great reactivity and from its inherent instability possibly with respect to the following reactions, two of them equilibria

$$B_4H_{10} + 2PF_3 \rightleftarrows PF_3 \cdot B_3H_7 + F_3P \cdot BH_3 \qquad (5)$$

$$PF_3 \cdot B_3H_7 + 2PF_3 \rightleftarrows (PF_3)_2 \cdot B_2H_4 + F_3P \cdot BH_3 \qquad (6)$$

$$2PF_3 \cdot B_3H_7 \longrightarrow (PF_3)_2 \cdot B_2H_4 + B_4H_{10} \qquad (7)$$

---

[1] Research supported by funds from National Science Foundation Grant GP-7888.

[2] Addressee for correspondence.

[3] W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).

[4] B. M. Graybill and J. K. Ruff, *J. Amer. Chem. Soc.*, **84**, 1062 (1962).

[5] M. A. Fleming, Dissertation, University of Michigan, 1963; University Microfilms Order No. 63-6895.

[6] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

Most of the characterizations accorded the new substances were the routine determinations required to establish purity, identity, and structure. However, among these some aspects of the nmr spectroscopy are worthy of note.

Unlike the nmr spectra of some triborane(7) adducts, $B_3H_8^-$,[7] $(CH_3)_3N \cdot B_3H_7$,[8] and $C_4H_8O \cdot B_3H_7$,[8] which display equivalence among protons, the spectra of $(CH_3)_2NPF_2 \cdot B_3H_7$ and of $F_2PH \cdot B_3H_7$ show a fixity of structure in the symmetrical 2102 mode,[9] and normal magnetic coupling is found to all substituent nuclei. In the boron-11 spectra illustrated in Figure 1a and b, the downfield triplets derive from the BH_2 parts of the molecule. The upfield resonances are approximately 1:2:2:1 quartets, which doubtless are best interpreted as the X transitions of a normal ABX system.[10] The only information extractable from the spectra are the quantities $^3/_2(J_{PB} + J_{HB})$. For $(CH_3)_2NPF_2 \cdot B_3H_7$ the independently available value $J_{BP} = 132$ Hz can be used to obtain $J_{HB} = 92$ Hz. The value $J_{PB} + J_{HB} = 184$ Hz found for $F_2HP \cdot B_3H_7$ indicates much smaller individual J values for that substance. Compare this with the rather small value $J_{HB} = 84$ Hz found for $(F_2HP)_2 \cdot B_2H_4$. In a similar structural situation the spectrum observed for $PF_3 \cdot B_4H_8$[11] should be interpreted as an ABX system in which $J_{PB} = J_{HB} = 100$ Hz. As seen for $(CH_3)_2NPF_2 \cdot B_3H_7$, the two small peaks downfield from the quartet and the two downfield members of the same quartet have identical spacings. These, together with a small imbalance in intensity, suggest the presence of about 10% of a stereoisomer with the chemical shift δ 43 ppm for the upfield quartet.

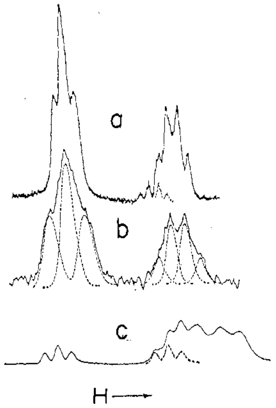

Figure 1.—Nmr spectra: (a) ^{11}B for $(CH_3)_2NPF_2 \cdot B_3H_7$; (b) ^{11}B for $F_2PH \cdot B_3H_7$; (c) ^1H for $(F_2PH)_2 \cdot B_2H_4$.

The boron-11 and phosphorus-31 nmr spectra of $(CH_3)_2NPF_2 \cdot B_2H_4$ show no evidence of coupling between boron and any other nucleus, but in $(F_2PH)_2 \cdot B_2H_4$ coupling is found for boron nucleii with protons, but not with phosphorus-31.[12] Considering the spectra found for the triborane(7) adducts, phosphorus coupling seems unlikely to appear missing from spectra of the diborane(4) adducts through being overlooked.

Experimental Part

The usual glass vacuum system equipped with greased stopcocks and mercury float valves was used. Unless otherwise indicated, all preparative reactions were conducted in Pyrex glass heavy-walled tubes (volume 5–7 cm³) fitted with Teflon-plug glass stopcocks.[13] The amounts of volatile materials used were determined by pressure measurements in calibrated volumes and materials of low volatility were weighed. Melting point values below 23° were determined by the collapsing-ring, dropping-plunger method. Starting materials were purified by glpc,[3] and their purity was confirmed by infrared spectra and vapor pressure measurements. Unless noted otherwise all nmr spectra were obtained on a Varian DA60-IL spectrometer (Model 4311) operated at the following frequencies (MHz): ^1H, 60; ^{19}F, 56.4; ^{11}B, 19.25; ^{31}P, 19.25. Chemical shift values were calculated relative to the following external standards: ^1H, $Si(CH_3)_4$; ^{19}F, CCl_3F; ^{11}B, $(CH_3)_2O \cdot BF_3$; ^{31}P, H_3PO_4 (85%).

Reaction of Tetraborane(10) with Dimethylaminodifluorophosphine. A. Preparation and Reactions of Dimethylaminodifluorophosphine–Triborane(7).[14]—Tetraborane(10)[15] (2.00 mmol) and dimethylaminodifluorophosphine (3.20 mmol)[16] were condensed into the reaction tube at −196°. The tube was rapidly warmed to 25° and kept at this temperature for 10 min. The tube was then opened to the vacuum system, and the volatile components were separated by fractional condensation through traps cooled to −24, −80, and −196°. A small amount of bis(dimethylaminodifluorophosphine)–diborane(4) remained in the reaction tube. Of the traps, that at −80° contained dimethylaminodifluorophosphine–borane, and the one at −196° contained unreacted starting materials. The product in the trap at −24°, dimethylaminodifluorophosphine–triborane(7), was purified by distillation out of a trap kept at 0° into one kept at −24° (1.34 mmol, 67% yield). An excess of tetraborane(10) (<1:1) produced a similar yield of the triborane(7) adduct, but no diborane(4) adduct was observed.

Dimethylaminodifluorophosphine–triborane(7) did not react with hydrogen during a period of 2.5 hr at 40°. Approximately 80% of a sample of the adduct was recovered after storage at 23° for 5 days. Noncondensable gas, diborane, dimethylaminodifluorophosphine–borane (major product), and a nonvolatile oil were observed as decomposition products. The triborane(7) adduct (0.06 mmol) reacted completely with dimethylaminodifluorophosphine (0.79 mmol) in 24 hr at 25° to produce an 82% yield (0.042 mmol) of bis(dimethylaminodifluorophosphine)–diborane(4).

B. Preparation and Reactions of Bis(dimethylaminodifluorophosphine)–Diborane(4).—Tetraborane(10)[15] (1.80 mmol) was treated with dimethylaminodifluorophosphine[16] (4.00 mmol) for 24 hr at 25°. The reaction mixture was separated by fractional condensation through a trap kept at 0°. Unreacted starting materials and dimethylaminodifluorophosphine–borane passed through this trap, and the product in the trap was purified by vacuum sublimation (1.50 mmol, 80% yield, mp 43°). The diborane(4) adduct can also be prepared by reaction between dimethylaminodifluorophosphine and the triborane(7) adduct (see above).

Bis(dimethylaminodifluorophosphine)–diborane(4) (0.618 mmol) reacted with diborane (2.75 mmol) at 30° for 19 hr

---

[7] D. Marynick and T. Onak, *J. Chem. Soc. A*, 1160 (1970), and ref 1 and 2 in that paper.

[8] M. A. Ring, E. F. Witucki, and R. C. Greenough, *Inorg. Chem.*, **6**, 395 (1967).

[9] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 45.

[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, p 357 ff.

[11] A. D. Norman and R. Schaeffer, *J. Amer. Chem. Soc.*, **88**, 1146 (1966).

[12] The nmr spectra of $(PF_3)_2 \cdot B_2H_4$ are not well known. The 19.3-MHz spectrum for boron-11 at −90° shows two broad peaks of nonintegral proportions which could be interpreted in terms of stereoisomerism arising from restricted rotation. The 60-MHz proton spectrum at −30° shows a quartet as might be expected, but the coupling constant has a somewhat low value, $J_{BH} = 49 \pm 6$ Hz. The coupling appears to be B–H but not B–P: W. R. Deever, Ph.D. Thesis, University of Washington, 1968; *Diss. Abstr. B*, **29**, 918 (1969). The boron-11 spectrum of $[(C_6H_5)_3P]_2 \cdot B_2H_4$ seems likely to be interpretable in the same terms.[4]

[13] Fisher and Porter Co. Catalog No. 795-120-0004.

[14] This compound was first prepared by M. A. Fleming by a more complicated procedure. As shown in ref 5 the phosphorus–boron bonded character of the compound was correctly deduced from infrared data.

[15] Prepared from diborane at high pressure: G. Kodama, Dissertation, University of Michigan, 1967, p 60; University Microfilms Order No. 58-3690.

[16] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964); *cf.* ref 5.

TABLE I

MASS SPECTRA[a]

$((CH_3)_2$-$NF_2P\cdot BH_2)_2$[b]		(CH_3)-$NF_2P\cdot B_3H_7$[c]		$HF_2P\cdot B_3H_7$[b]		$(HF_2P\cdot BH_2)_2$[b]	
m/e	Intens[d]	*m/e*	Intens	*m/e*	Intens	*m/e*	Intens
252	1	152	2	109	5	166	5
251	1	151	8	108	91	165	5
250	9	150	6	107	65	164	100
249	4	149	2	106	43	163	49
248	1	113	100	105	19	162	26
238	10	112	97	94	45	152	12
113	100	94	35	93	20	151	81
112	80	82	23	70	100	150	21
94	15	81	14	69	42	95	16
42	32	69	18	51	64	94	94
		56	25	50	11	93	44
		42	72	45	11	83	27
		28	12	44	17	82	19
				43	10	70	59
				39	60	69	46
				38	67	63	28
				37	50	62	17
				36	29	51	56
				35	20	45	27
				28	19	44	21
				27	29	43	22
				26	14	33	24
						31	24
						28	29
						13	13

[a] Spectra recorded on an AEI MS-9 mass spectrometer purchased with funds supplied under National Science Foundation Instrument Grant GP-5418. [b] Ionizing potential 20 V. [c] Ionizing potential 25 V. [d] Intensity values shown have been normalized to the most intense peak in the spectrum. Except for peaks consituting the parent ion envelope, peaks with normalized intensity values less than 10 have not been included.

TABLE II

NMR DATA[a]

	Boron-11	Proton, 60 MHz	Phosphorus-31	Fluorine-19, 56.4 MHz
$[(CH_3)_2NPF_2]_2\cdot B_2H_4$	19.25 MHz, 26°; s; δ 51.4 ppm	d of 1:2:1 t; δ -2.7 ppm; $J_{FPNCH} = 2.6$ Hz; $J_{PNCH} = 9.7$ Hz; H on B resonance broad and unresolved	19.25 MHz; 1:2:1 t; δ -131 ppm; $J_{FP} = 1133$ Hz	d; δ 76.3 ppm; $J_{PF} = 1140$ Hz
$(CH_3)NPF_2\cdot B_3H_7$	32.1 MHz, $-30°$; t;[b] δ 12 ppm; $J_{HB} = 114$ Hz; ~1:2:2:1 q;[b] δ 50 ppm; $J_{PB} + J_{HB} = 224$ Hz; Figure 1a	d of 1:2:1 t; δ -1.6 ppm; $J_{FPNCH} = 3.2$ Hz; $J_{PNCH} = 10.5$ Hz; H on B resonances broad and unresolved	40.5 MHz; 1:2:1 t of 1:1:1:1 q; δ -116 ppm; $J_{FP} = 1160$ Hz; $J_{BP} = 132$ Hz	D; δ 76.5 ppm; $J_{PF} = 1159$ Hz
$(F_2PH)_2\cdot B_2H_4$[d]	19.25 MHz, 26°; t; δ 56 ppm; $J_{HB} = 84$ Hz	$^1/_2$ d of 1:2:1 t; δ -11.8 ppm, 25°; $J_{PH} = 595$ Hz, $J_{PH} \gg J_{FPH}$; $^1/_2$ d of 1:2:1 t; δ ~ -1.9 ppm; ~1:1:1 q; δ 0.8 ppm; $J_{BH} = 84$ Hz; Figure 1c		d of d; δ -53.8 ppm; $J_{PF} = 1147$ Hz; $J_{HPF} = 50.3$ Hz
$F_2PH\cdot B_3H_7$[d]	19.25 MHz, 26°; t;[b] δ 22 ppm; $J_{HB} = 117$ Hz; ~1:2:2:1 q;[b] δ 60 ppm; $J_{PB} + J_{HB} = 184$ Hz; Figure 1b	$^1/_2$ d of 1:2:1 t, low field; overlapping H on B resonances at high field		d of d; δ 59.5 ppm; $J_{PF} = 110$ Hz; $J_{HPF} = 56$ Hz

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet. [b] t:q area ratio 2:1. [c] Dissolved in $CFCl_3$. [d] Neat samples.

in toluene as a solvent to produce the following products (amounts in mmol): dimethylaminodifluorophosphine–triborane(7), 0.142; tetraborane(10), 0.169. These represent about 50% conversion of the diborane(4) adduct. Noncondensable gas, 0.011 mmol, and trace amounts of pentaborane(9) and pentaborane(11) were found and 1.70 mmol of diborane was recovered. No reaction between hydrogen and bis(dimethylaminodifluorophosphine)–diborane(4) was observed over a 4-day period at 25°.

Reaction of Tetraborane(10) with Difluorophosphine.—Tetraborane(10)[15] (0.945 mmol) and difluorophosphine[17] (2.92 mmol) were allowed to react for 12 min at 23°.[18] Under the conditions of the reaction both reactants were present as liquids. The volatile components were separated by glpc,[19] and the following materials were recovered (amounts in mmol): tetraborane(10), 0.687; difluorophosphine–borane, 0.223; difluorophosphine–triborane(7), 0.168 (yield 16%); bis(difluorophosphine)–diborane(4), 0.023 (yield 2%). Decomposition of difluorophosphine during the reaction prevented a determination of the amount consumed. Reactions conducted on the same scale, but in the gas phase, resulted in much smaller conversions of tetraborane(10) to products. Larger amounts of the triborane(7) and the diborane(4) adducts were prepared from difluorophosphine (2.39 mmol) and (dimethyl ether)–triborane(7)[20] (1.33 mmol). After the mixing of reagents at −196° the reaction tube was quickly warmed to about 20°. As this temperature was approached, the solid disappeared ((dimethyl ether)–triborane(7) mp 10.5°), and the liquid rapidly became yellow. The tube was cooled to −196° after a reaction time of about 30 sec had passed. The volatile materials recovered, excluding dimethyl ether, were as follows (amounts in mmol): difluorophosphine, 0.32; bis(difluorophosphine)-diborane(4), 0.239 (yield 18%); difluorophosphine–triborane(7), 0.592 (yield 45%); difluorophosphine–borane, 0.368; difluorophosphine–tetraborane(8), 0.04. If a reaction period of 4 min was allowed, the amount of the triborane(7) adduct recovered decreased sharply, and the yield of the diborane(4) adduct increased to 73%. Bis(difluorophosphine)–diborane(4) did not react with hydrogen overnight at 23° or with diborane in the gas phase. However, the reaction of 0.62 mmol of the diborane(4) adduct with 2.75 mmol of diborane for 16 hr at 23° with 3 ml of toluene as a solvent produced the following volatile products (amounts in mmol): difluorophosphine–triborane(7), 0.142; tetraborane(10), 0.17; hydrogen, 0.10; and a small amount of higher boron hydrides. This corresponds to about 50% conversion of the diborane(4) adduct. The substance was stable for 3 weeks at −80°.

Characterization of Substances. Bis(dimethylaminodifluorophosphine)–Diborane(4).—*Anal.* Calcd for $((CH_3)_2NF_2P\cdot BH_2)_2$: B, 8.56; N, 11.00. Found: B, 8.67; N, 11.08. Hydrolysis of the compound in ethanolic hydrogen chloride with a small amount of 1,2-dimethoxyethane (monoglyme)[21] added as solvent[22] for 24 hr at 100° gave 99% of the hydrogen calculated for the reaction

$$((CH_3)_2NF_2P\cdot BH_2)_2 + 6C_2H_5OH \xrightarrow{H^+} 5H_2 + 2B(OC_2H_5)_3 + 2(CH_3)_2NF_2P$$

Bis(dimethylaminodifluorophosphine)–diborane(4) is a white

---

[17] R. W. Rudolph and H. Schiller, *J. Amer. Chem. Soc.*, **90**, 3581 (1968).

[18] *Caution!* Difluorophosphine has a vapor pressure of 21.2 ± 0.3 atm at 21.6°.

[19] $HF_2P\cdot B_3H_7$: $(HF_2P\cdot BH_2)_2$ relative retention times 1.2:1.

[20] W. R. Deever and D. M. Ritter, *Inorg. Chem.*, **7**, 1036 (1968).

[21] Ansul Co., Marinette, Wis.

[22] F. J. Mettille and D. J. Burton, *J. Inorg. Nucl. Chem.*, **30**, 333 (1968).

solid (mp 43° with slight decomposition), which is sensitive to air and water. It is soluble in carbon tetrachloride, trichlorofluoromethane, and benzene but insoluble in butane.

The infrared spectrum (4000–200 cm^{-1}) in carbon tetrachloride showed the following absorbances (cm^{-1}): 2935 (m), 2864 (w), 2189 (w), 2370 (s), 2335 (s), 2215 (w), 1740 (m), 1483 (m), 1452 (m), 1315 (s), 1182 (w), 1120 (w), 1072 (w), 1004 (s), 862 (vvs), 770 (s), 743 (vs), 590 (w), 527 (w), 449 (w).

The mass spectrum is given in Table I, and the results of nmr measurements are found in Table II.

Dimethylaminodifluorophosphine–Triborane(7).—*Anal.* Calcd for $(CH_3)_2NF_2P\cdot B_3H_7$: B, 21.4; N, 9.19. Found: B, 21.3; N, 9.32. Hydrolysis of the compound in ethanolic potassium hydroxide gave 96% of the hydrogen calculated for the reaction

$$(CH_3)_2NF_2P\cdot B_3H_7 + 9C_2H_5OH \xrightarrow{OH^-} 8H_2 + B(OC_2H_5)_3 + (CH_3)_2NF_2P$$

A molecular weight of 154 ± 4 (calcd 153) was found by a rapid gas density measurement at 92°; mp −35.5°.

The mass spectrum of the compound is given in Table I, and the results from the nmr spectra are to be found in Table II.

Bis(difluorophosphine)–Diborane(4).—*Anal.* Calcd for $(F_2PH\cdot BH_2)_2$: B, 13.05. Found: B, 13.9. Hydrolysis of the compound yielded 100% of the hydrogen calculated for the reaction

$$(PHF_2\cdot BH_2)_2 + 5H_2O \xrightarrow{H^+} 5H_2 + 2B(OH)_3 + 2PF_2H$$

The vapor pressure is 19 mm at 0°; mp −53.2°.

The infrared spectrum (4000–600 cm^{-1}) showed the following absorbances (cm^{-1}): 2440 (s), 2400 (m), 2325 (w), 2310 (w), 2200 (vw), 1110 (w), 1035 (s), 975 (w), 875 (vs), 820 (s), 780 (m), 720 (w), 650 (vw).

The mass spectrum of the adduct is given in Table I and the results from the nmr spectra are to be found in Table II.

Difluorophosphine–Triborane(7).—*Anal.* Calcd for $PF_2H\cdot B_3H_7$: B, 29.8. Found: B, 31.8. Hydrolysis of the compound yielded 99% of the hydrogen calculated for the reaction

$$PF_2H\cdot B_3H_7 + 9H_2O \xrightarrow{H^+} 8H_2 + 3B(OH)_3 + PF_2H$$

The adduct melted at −82.9°. The vapor pressure was 21 mm at 0°.

The infrared spectrum (4000–600 cm^{-1}) showed the following absorbances (cm^{-1}): 2550 (s), 2480 (m), 2320 (vw), 1995 (vw), 1575 (w), 1160 (m), 1050 (m), 1005 (w), 920 (s), 880 (s), 790 (vvw), 730 (vw).

The mass spectrum of the adduct is given in Table I, and the results from the nmr measurements are to be found in Table II.

Acknowledgment.—We wish to thank Professor A. B. Burg of the University of Southern California, Los Angeles, Calif., for his assistance given by observing several nmr spectra on the Varian HA-100 spectrometer modified for boron, phosphorus, and fluorine.

CONTRIBUTION NO. 1907, FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401, AND FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Elucidation of the Boron-11 Nuclear Magnetic Resonance Spectra of Some B_9H_{13}(ligand) Derivatives

BY G. M. BODNER,[1a] F. R. SCHOLER,[1a] L. J. TODD,*[1a] L. E. SENOR,[1b] AND J. C. CARTER[1b]

Received October 16, 1970

The ^{11}B nmr spectra at 32.1, 70.56, and 80.2 MHz of a series of specifically labeled B_9H_{13}(ligand) compounds with both neutral and negatively charged ligands have been examined. This has provided an assignment of the ^{11}B nmr of these compounds which is compatible with the known solid-state structure of this class of boron compounds.

Introduction

In recent years, through an investigation of the proper derivatives, the nmr spectra of several boron hydrides have been assigned. The ^{11}B nmr spectra of $B_{10}H_{14}$[2] and $B_{10}H_{12}$(ligand)$_2$[3] have been elucidated along with the more complex ^1H nmr spectrum of $B_{10}H_{14}$.[4]

We wish to report a similar study of the ^{11}B nmr spectrum of B_9H_{13}(ligand) derivatives. A single-crystal X-ray study of the $B_9H_{13}\cdot NCCH_3$ derivative by Wang, Simpson, and Lipscomb[5] yielded the structure shown in Figure 1.[6]

A previous investigation[7] of the ^{11}B nmr of $B_9H_{13}\cdot NH_3$ at 19.3 MHz showed a poorly resolved but characteristic pattern of two overlapping doublets at −10.3 and −0.5 ppm (each of area 1), a broad multiplet of area 5 at +18.4 ppm and a high-field doublet of area 2 at +39.3 ppm. These authors noted that upon decoupling the two low-field doublets collapsed to singlets.

We have studied the ^{11}B nmr spectra at 32.1, 70.56, and 80.2 MHz of a series of specifically labeled B_9H_{13}(ligand) compounds with both neutral and negatively charged ligands. This has provided an assignment of the ^{11}B nmr of these compounds which is compatible with the known geometry shown in Figure 1.

Experimental Section

2-Bromodecaborane was prepared as described previously, mp 107–108°.[8] The 1,2,3,4-decarborane-d_4 prepared by a literature method[9] was kindly supplied by L. G. Sneddon, Indiana University. The B_9H_{13}(ligand) compounds and their substituted derivatives were prepared by the procedure of Graybill, Pito-

---

[1] (a) Indiana University. (b) University of Pittsburgh.

[2] R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc., London*, 402 (1964); P. C. Keller, D. Maclean, and R. O. Schaeffer, *Chem. Commun.*, 204 (1965).

[3] D. E. Hyatt, F. R. Scholer, and L. J. Todd, *Inorg. Chem.*, **6**, 630 (1967).

[4] G. M. Bodner and L. G. Sneddon, *ibid.*, **9**, 1421 (1970); R. L. Williams, N. N. Greenwood, and J. H. Morris, *Spectrochim. Acta*, **21**, 1579 (1965).

[5] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961).

[6] We have used the numbering system proposed by the Council of the American Chemical Socity, *Inorg. Chem.*, **7**, 1945 (1968). This is not the same system which has been used in the past. Several workers in the field have numbered this compound as a derivative of $B_{10}H_{14}$, in which the B(6) position has been removed. To convert to this system renumber as follows: B(1) in Figure 1 = 4, B(2) = 1, B(3) = 3, B(4) = 9, B(5) = 10, B(6) = 5, B(7) = 2, B(8) = 7, B(9) = 8.

[7] E. L. Muetterties and F. Klanberg, *Inorg. Chem.*, **5**, 315 (1966).

[8] M. S. Cohen and C. E. Pearl, U. S. Patent 2,990,239 (1961).

[9] J. A. DuPont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **84**, 1804 (1962).