constants; in particular the very slight increase in the bond angle on going from compounds of lighter to heavier elements is correctly predicted; (3) the results are somewhat more accurate for compounds of the lighter than of the heavier elements.

It is important to note that in all cases, the quantities calculated by our method are quite comparable in accuracy to those that would be expected from a comparable full SCF calculation. This finding is in accord with our previous study of the series of group 4 homonuclear, diatomic molecules.[1] The cost advantage of the pseudopotential method may be estimated on the assumption that the computation time increases as the fourth power of the size of the basis set. This means that an exactly equivalent full SCF computation for PF_3 would take about 5 times longer than the pseudopotential computation, whereas, for PI_3, the increase in time would be around 1300-fold!

Conclusions

The NOCOR method is found to give results that agree well with equivalent full SCF calculations for the PF_3 molecule and that compare usefully with experiment for all of the phosphorus halides. These results plus our previous findings[1] on the group IV diatomics indicate that the NOCOR method is appropriate for obtaining useful information for inorganic compounds which because of the large number of electrons involved were previously inaccessible to SCF calculations.

Acknowledgment. We wish to acknowledge the technical assistance of Mr. Eugene Thune and also thank the Air Force Office of Scientific Research for supporting this work under Grant AFOSR-72-2265.

Registry No. PF_3, 7783-55-3; PCl_3, 7719-12-2; PBr_3, 7789-60-8; PI_3, 13455-01-1.

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Hydrogen-1, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Spectral Studies of Some Phenyl- and Perflurorphenyl-Substituted Aminophosphines and Aminophosphonium Salts

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Received December 26, 1974 AIC40855Z

^1H, ^{13}C, and ^{31}P NMR data have been acquired for the aminophosphine $(i\text{-}C_3H_7)NHP(C_6H_5)_2$, **1**, the new aminophosphines $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, **2**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2$, **3**, and the new aminophosphonium salts, $(i\text{-}C_3H_7)NHP(C_6H_5)_2(CH_3)I$, **4**, $(i\text{-}C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4$, **5**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2(CH_3)BF_4$, **6**. Particular interest is associated with the following aspects of the NMR data: (1) the appearance and solvent dependence of the chemical shifts of the amino proton resonances, (2) the long-range (five-bond) coupling between the ortho fluorines of the C_6F_5 groups and the phosphonium methyl protons of **5** and **6**, and (3) the nonidentical *P*–N–C–*C* couplings in **2** and **5**.

The stereochemistry of aminophosphines[2] and related compounds[3] is a subject which is eliciting increasing attention. The focal points of these studies comprise the frequent occurrence of planar nitrogenous geometries, the electronic character of the P–N linkage, and the trends in the P–N torsional barriers. The aminophosphines $(i\text{-}C_3H_7)NHP(C_6H_5)_2$,[4] **1**, $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, **2**, and $(i\text{-}C_3H_7)NHP(C_6F_5)_2$, **3**, and the aminophosphonium salts $(i\text{-}C_3H_7)NHP(C_6H_5)_2(CH_3)I$, **4**, $(i\text{-}C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4$, **5** and $(i\text{-}C_3H_7)NHP(C_6F_5)_2(CH_3)BF_4$, **6**, which are described in the present work were synthesized as precursors to the corresponding iminophosphoranes. However, during routine characterization of these compounds by ^1H, ^{13}C, and ^{31}P NMR spectroscopy certain interesting spectral features were revealed such that separate publication of this aspect appeared to be warranted. The points of emphasis in the present paper are (1) the appearance and solvent dependence of the chemical shifts of the amino proton resonances, (2) the long-range (five-bond) coupling between the ortho fluorines of the C_6F_5 groups and the phosphonium methyl protons of **5** and **6**, and (3) the nonidentical *P*–N–C–*C* couplings in **2** and **5**.

Experimental Section

Isopropylaminodiphenylphosphine, **1**, was prepared according to the method of Hart and Sisler.[4]

Preparation of Pentafluorophenylmagnesium Bromide. To a flame-dried apparatus consisting of a 250-ml round-bottomed flask equipped with a mechanical stirrer and a Claisen head topped by a dropping funnel with a gas inlet adapter were added 5.35 g (0.22 g-atom) of magnesium turnings and 60 ml of dried ether. The flask and its contents were cooled to −15° prior to adding 49.4 g (0.20 mol) of pentafluorobromobenzene in 60 ml of dried ether from the dropping funnel to the stirred reaction mixture. A dry N_2 atmosphere was maintained throughout the reaction. After 2 hr of stirring (during which time the mixture was allowed to warm to 0°) the reaction mixture was transferred back into the dropping funnel in preparation for the synthesis of the phenyl(pentafluorophenyl)halophosphine mixture.

Preparation of Phenyl(pentafluorophenyl)halophosphine Mixture.

Into the reaction vessel used for the preparation of pentafluorophenylmagnesium bromide (vide supra) were added 36 g (0.20 mol) phenyldichlorophosphine and 80 ml of dry ether. To this reaction mixture was added the previously prepared Grignard solution in a dropwise fashion while the reaction mixture was maintained below room temperature with a water bath. Rapid stirring was maintained throughout the addition and for 1 hr thereafter. After standing overnight the reaction mixture was filtered and the solids washed with fresh dry ether. The washings were combined with the filtrate, the solvent was stripped off, and the resulting oil was distilled at 95–106° (0.25 Torr). This product, which was reported previously by Fild, Glemser, and Hollenberg[5] is a mixture of the chloro- and bromophosphines which solidified and melted at 45–48°. Mass spectral analysis indicated minor contamination by perfluorobiphenyl and a yield (60 g) of the order of 85%.

Preparation of Isopropylaminophenyl(pentafluorophenyl)phosphine, 2. To the reaction vessel consisting of an apparatus arranged and prepared as in the previous two steps were added 17.7 g (0.3 mol) of isopropylamine and 50 ml of dry ether. The dropping funnel was then charged with 48.6 g (0.13 mol) of the halophosphine mixture as prepared in the previous step and 70 ml of ether. The reaction vessel was cooled to 0° before a dropwise addition to the stirred solution under a dry nitrogen blanket was begun. After the addition the reaction mixture was allowed to attain ambient temperature overnight. The ammonium salts were removed by filtration and washed several times with small portions of dry ether. The ether washings were combined with the filtrate which was concentrated to afford white crystalline solid, **2**, mp 48.5–50° after sublimation. The yield based on the estimated halophosphine used is essentially quantitative (43.33 g). Anal. Calcd. for $C_{15}H_{13}F_5NP$: C, 54.06; H, 3.93. Found: C, 53.79; H, 3.85.

Preparation of Isopropylaminobis(pentafluorophenyl)phosphine, 3. A 0.1-mol amount of the bis(pentafluorophenyl)halophosphine mixture was prepared by the action of C_6F_5MgBr on PCl_3 using the procedure described above. A small amount of this material which distilled at 98–104° (0.25 Torr) was removed for identification. The remainder was diluted with benzene and placed in a 125-ml dropping funnel which was attached by a Claisen head to a 250-ml round-bottomed flask. The shaft of a mechanical stirring unit passed through the other opening of the head. To this flame-dried apparatus was added 11.89 (0.2 mol) of isopropylamine and 40 ml of benzene. The mixture in the flask was stirred while the halophosphine solution was added very slowly. After 2 hr of stirring the apparatus was disassembled, the solid was filtered and washed, the solvent was evaporated, and colorless liquid, **3**, was distilled at 97–99° (0.05 mmHg) to give a 62% yield based on the pentafluorobromobenzene used. Anal. Calcd for $C_{15}H_8F_{10}NP$: C, 42.57; H, 1.90. Found: C, 42.38; H, 1.81.

Preparation of Isopropylaminodiphenylmethylphosphonium Iodide, 4. To 40.5 g (0.167 mol) of **1** dissolved in 100 ml of dry benzene was added slowly with agitation a solution of 24.2 g (0.167 mol) of iodomethane in 70 ml of dry benzene. The reaction vessel was fitted with a reflux condenser and the reaction mixture brought to reflux. After a reflux period of 4 hr the solvent was removed to give 49.6 g (77% yield) of white solid **4**. This essentially uncontaminated product was recrystallized from a chloroform–ethyl acetate mixture to afford fine crystals, mp 122.5–123.5°. Anal. Calcd for $C_{16}H_{21}INP$: C, 49.88; H, 5.49. Found: C, 50.06; H, 5.45.

Preparation of Isopropylaminophenyl(pentafluorophenyl)methylphosphonium Tetrafluoroborate, 5. An apparatus consisting of a 100-ml round-bottomed flask, a magnetic stirring bar, and a gas inlet adapter was assembled and flame dried. The flask was allowed to cool with the gas adapter attached to a source of dry nitrogen. To the cooled flask was added 50 ml of dry CH_2Cl_2, 6.67 g (0.20 mol) of **2**, and ca. 0.05 ml of 2,6-di-*tert*-butylpyridine. When the solution became homogeneous, the gas inlet adapter was removed briefly for the rapid addition of trimethyloxonium tetrafluoroborate.[6] Stirring of the suspension was continued for 3 hr, after which time the solvent was removed to afford crude **5** contaminated by traces of 2,6-di-*tert*-butylpyridine and its salt. Recrystallization from ethyl acetate or a CCl_4–ethyl acetate mixture gives white crystals, mp 98–99°, in 77% yield. Anal. Calcd for $C_{16}H_{16}BF_9NP$: C, 44.17; H, 3.71. Found: C, 44.35; H, 3.60.

Preparation of Isopropylaminobis(pentafluorophenyl)methylphosphonium Tetrafluoroborate, 6. To a 25-ml round-bottomed flask equipped with a magnetic stirring bar and a Claisen head connected to a dry, prepurified N_2 source were added (after flaming) 1.320 g (3.12 mmol) of **3**, 0.462 g (3.12 mmol) of $(CH_3)_3OBF_4$,[6] and 10.0 ml of nitrogen-saturated CH_2Cl_2. After activating the stirring bar, the slurry was allowed to stir for 18 hr at ambient temperature, after which time the crystalline form of the solids had changed and the methylation was assumed to be complete. The supernatant liquor was then withdrawn carefully by means of a syringe and the residual solid washed several times with CH_2Cl_2. After drying, the solid was recrystallized from CH_3CN–C_6H_6 to afford 0.369 g (1.025 mmol) of white crystalline **6**, mp 186–189°, in 63% yield. Anal. Calcd for $C_{16}H_{11}BF_{14}NP$: C, 36.60; H, 2.11. Found: C, 36.75; H, 2.12.

NMR Spectra. The ^1H spectra were recorded on either a Varian HA-100 spectrometer operating at 100 MHz or a Bruker HFX-90 MHz instrument operating at 90 MHz. In each case the spectra were run in the CW mode with field frequency lock; sample tubes were of 5-mm diameter.

The ^{13}C and ^{31}P spectra were obtained on a Bruker HFX 90-MHz spectrometer operating at 22.63 and 36.43 MHz, respectively. The ^{13}C spectra were proton noise decoupled (FT mode, ^{19}F lock), and the ^{31}P spectra (CW mode, ^{19}F lock) were measured both with and without proton noise decoupling; in these cases 10-mm tubes were used. Further experimental details are indicated in the tables.

Results and Discussion

The spectral feature which first attracted our attention was the appearance of the amino proton resonance of **2** (Table I). The "triplet" pattern of this resonance could result from a long-range coupling between the ortho fluorines of the C_6F_5 group and the amino proton of **2** or from the near degeneracy of J_{PNH} and J_{HCNH}. However, the effect is obviously due to the near degeneracy of J_{PNH} and J_{HCNH} for the following reasons: (i) the same "triplet" structure persists in the phosphonium salt **4** which does not bear any C_6F_5 substituents; (ii) in **1** and **6** the amino proton resonance is a well-resolved doublet of doublets (Table I); (iii) in the bis(pentafluorophenyl) compound **3** the amino proton resonance is a triplet rather than the anticipated quintet. This conclusion was confirmed by $^1H\{^1H\}$ homonuclear double-resonance experiments on **2** and **4**.[7] In each case irradiation of the methine proton collapsed the "triplet" amino proton resonance to a doublet with J_{PNH} = 9.1 and 9.2 Hz, respectively (Table I). (Analogous double-resonance experiments were not possible with **3** and **5** because of an insufficient chemical shift difference between the C*H* and N*H* resonances). It is interesting to note, however, that the "triplet" appearance of the NH resonance of the aminophosphine, **2** persists in the aminophosphonium salt **4** despite the fact that the coordination number at phosphorus has increased from 3 to 4. Two-bond phosphorus couplings are well known[8] to be sensitive to, inter alia, the valence of the phosphorus atom and it may therefore be inferred that the near degeneracy of the *P*–N–*H* and *H*–C–N–*H* couplings in **2** and **4** is maintained by the sign of J_{PNH} changing from negative in **2** to positive in **4**. Support for this view is provided by the observation[9] that J_{PNH} is −14.21 Hz in the phosphine $(CF_3)_2P^{15}NH_2$ and +14.51 Hz in the phosphorane $F_3P(^{15}NH_2)_2$.

Compounds **2** and **5** both possess phosphorus chiral centers. This chirality[10] renders the isopropyl methyl groups diastereotopic and is responsible for the observed anisochrony[10] of these moities in **2** and **5** (Table I). Note that in both compounds the couplings between the methine proton and the anisochronous methyl groups are identical (vide infra).

Long-range (five-bond) coupling between the *P*-methyl protons and the ortho fluorines of the pentafluorophenyl groups is detectable in the phosphonium cations **5** and **6**. The *P*-methyl region of **5** exhibits a triplet pattern while the fine structure in **6** is a quintet. No further splitting by the amino or methine protons is apparent. Examination of molecular models reveals that the *P*-methyl protons of **5** and **6** are within close proximity of the ortho fluorines of the C_6F_5 groups. This raises the possibility of a through-space interaction between the coupled nuclei. However, the present evidence does not

Table I. ^{1}H NMR Data for Aminophosphines and Aminophosphonium Salts

Compd	Group	Chem shift[a]	Multiplicity[b]	Coupling constants, Hz
(i-C_3H_7)NHP(C_6H_5)$_2$ (1)	CH_3	8.76 (CH_2Cl_2)	d	J_{HCCH} = 5.5
	CH	6.53 (CH_2Cl_2)	m	
	NH	8.12 ($CDCl_3$)	d of d	J_{HCNH} = 6.1
		7.94 (CH_2Cl_2)	d of d	J_{PNH} = 8.1
	CH(Ar)	2.5 (CH_2Cl_2)	m	
(i-C_3H_7)NHP(C_6F_5)C_6H_5 (2)	CH_3	8.86 (CD_2Cl_2)	d	J_{HCCH} = 6.4
	CH_3'	8.74 (CD_2Cl_2)	d	$J_{HCCH'}$ = 6.4
	CH	6.61 (CD_2Cl_2)	m	
	NH	7.45 (CD_2Cl_2)	t	Separation 9.2
	CH(Ar)	2.7 (CD_2Cl_2)	m	[DR:[c] J_{PNH} = 9.1]
i-C_3H_7NHP(C_6F_5)$_2$ (3)	CH_3	8.78 (CD_2Cl_2)	d	J_{HCCH} = 6.3
	CH	6.67 (CD_2Cl_2)	m	
	NH	6.89 (CD_2Cl_2)	t	Separation 9
		6.04 (DMSO-d_6)	t	
(i-C_3H_7)NHP(C_6H_5)$_2CH_3I$ (4)	CH_3	8.68 (CD_3COCD_3)	d	J_{HCCH} = 6.4
		8.72 (CD_2Cl_2)	d	J_{HCCH} = 6.3
		8.66 ($CDCl_3$)	d	J_{HCCH} = 6.3
		8.71 (CD_3CN)	d	J_{HCCH} = 6.3
	CH_3(P)	7.16 (CD_3COCD_3)	d	J_{PCH} = 13.8
		7.35 (CD_2Cl_2)	d	J_{PCH} = 13.6
		7.29 ($CDCl_3$)	d	J_{PCH} = 13.2
		7.37 (CD_3CN)	d	J_{PCH} = 13.8
	CH	6.49 (CD_3COCD_3)	m	
		6.66 (CD_2Cl_2)	m	
		6.61 ($CDCl_3$)	m	
		6.57 (CD_3CN)	m	
	NH	3.62 (CD_3COCD_3)	t	Broad
		3.80 (CD_2Cl_2)	t	Separation 9.4
		3.93 ($CDCl_3$)	t	Separation 9.6
		4.31 (CD_3CN)	t	Separation 9.3
				[DR:[c] J_{PNH} = 9.2]
	CH(Ar)	2.1 (CD_3COCD_3)	m	
		2.2 (CD_2Cl_2)	m	
		2.2 ($CDCl_3$)	m	
		2.2 (CD_3CN)	m	
(i-C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4 (5)	CH_3	8.80 (CD_2Cl_2)	d	J_{HCCH} = 6.1
	CH_3'	8.76 (CD_2Cl_2)	d	$J_{HCCH'}$ = 6.1
	CH_3(P)	7.40 (CD_2Cl_2)	d of t	J_{PCH} = 14.0
				J_{FCCPCH} = 2.5
	CH	6.66 (CD_2Cl_2)	m	
	NH	5.03 (CD_2Cl_2)	t	Separation ≅9 (broad)
	CH(Ar)	2.2 (CD_2Cl_2)	m	
(i-C_3H_7)NHP(C_6F_5)$_2$(CH_3)BF_4 (6)	CH_3	8.75 (DMSO-d_6)	d	J_{HCCH} = 6.5
	CH_3(P)	6.97 (DMSO-d_6)	d of q	J_{PCH} = 14.8
				J_{FCCPCH} = 2.0
	CH	6.3 (DMSO-d_6)	m	
	NH	2.86 (DMSO-d_6)	d of d	J_{PNH} = 11.0[d]
				J_{HCNH} = 9.0

[a] Chemical shifts in τ relative to internal TMS. [b] Key: d, doublet; m, multiplet; t, triplet; q, quintet. [c] Double resonance (see text). [d] Tentative assignment.

permit a distinction to be made between a through-space or through-bond mechanism.[11]

Compounds **1**–**6** were characterized further on the basis of noise-decoupled ^{31}P NMR spectroscopy. Note that with the aminophosphines **1**, **2**, and **3** a progressive increase of ^{31}P chemical shift is observed as the central atom is substituted by pentafluorophenyl groups (Table II). This shielding effect has been observed previously[12] and appears to be a general feature of pentafluorophenyl-substituted phosphorus compounds. Compounds **2** and **3** exhibit the anticipated coupling between the phosphorus and ortho fluorine nuclei. Measurement of the triplet and quintet spacings in the ^{31}P spectra of **2** and **3**, respectively, yields values of J_{PCCF} (Table II) which are comparable to those which have been published for other perfluorophenyl-substituted phosphorus(III) compounds.[13] In compounds **5** and **6** the greater multiplicity of the ^{31}P resonances is due to additional coupling from the meta and para fluorines of the C_6F_5 groups.

The ^{13}C NMR spectra of **1**–**6** were also measured (with the exception of the aromatic carbon atoms). The ^{13}C chemical shifts and various carbon–phosphorus coupling constants are presented in Table III. The salient feature of these data is

Table II. ^{31}P NMR Data for Aminophosphines and Aminophosphonium Salts

Compd	Chem shift[a]	Multiplicity[b]
(i-C_3H_7)NHP(C_6H_5)$_2$ (1)	−30.43[c]	s[g]
(i-C_3H_7)NHP(C_6F_5)C_6H_5 (2)	−15.99[c]	t[h]
(i-C_3H_7)NHP(C_6F_5)$_2$ (3)	+2.06[c]	q[i]
(i-C_3H_7)NHP(C_6H_5)$_2$(CH_3)I (4)	−34.42[d]	s
(i-C_3H_7)NHP(C_6F_5)(C_6H_5)(CH_3)BF_4 (5)	−32.58[e]	m
(i-C_3H_7)NHP(C_6F_5)$_2$(CH_3)BF_4 (6)	−21.2[f]	m

[a] Chemical shifts relative to external H_3PO_4 in ppm. [b] Under conditions of proton noise decoupling. Key: s, singlet; t, triplet; q, quintet; m, multiplet. [c] 50% v/v in C_6H_6. [d] In $CHCl_3$. [e] In CH_3CN. [f] In DMSO. [g] Decoupling of aromatic protons only gives a d of d with J_{PNH} = 8.7 Hz and J_{PNCH} = 6.2 Hz. [h] J_{PCF} = 35.5 Hz. [i] J_{PCF} = 35.0 Hz.

the existence of nonequivalent *PNCC* couplings (and, of course, anisochronous methyl carbon atoms) in **2** and **5** (Figure 1). It will be noted that **2** and **5** possess chiral centers at phosphorus and, furthermore, when this is not the case (as in **1**, **3**, **4**, and **6**) the couplings are degenerate. A priori one anticipates both the chemical shifts and coupling constants to

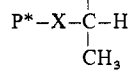
Table III. ^{13}C NMR Data for Aminophosphines and Aminophosphonium Salts

Compd[a]	$\delta(CH)^b$	$\delta(CH_3)$	$\delta(CH_3P)$	$J_{PC(CH_3)}{}^c$	J_{PNC}	J_{PNCC}
$(C_6H_5)_2PNHCH(CH_3)_2$ (1)	49.1	26.3			23.2	6.8
$C_6F_5(C_6H_5)PNHCH(CH_3)_2$ (2)	50.5	26.5, 26.1			29.8	5.6, 8.3
$(C_6F_5)_2PNHCH(CH_3)_2$ (3)	51.8	26.0			37.2	8.5
$[CH_3(C_6H_5)_2PNHCH(CH_3)_2][I]$ (4)	47.0	25.4	13.7	69.6	2.4	5.1
$[CH_3(C_6F_5)(C_6H_5)PNHCH(CH_3)_2][BF_4]$ (5)	47.8	25.2, 24.7	14.4[d]	71.5	3.7	5.4, 5.1
$[CH_3(C_6F_5)_2PNHCH(CH_3)_2][BF_4]$ (6)	49.8	27.2	15.6	73.2	4.5	6.1

[a] In CH_2Cl_2 solution (1-5) or in DMSO (6). [b] Relative to internal (1-5) and external (6) TMS in ppm. [c] All J values in Hz. [d] Triplet, $J_{FCCPC} = 4.6$ Hz.

Figure 1. ^{13}C NMR spectrum of $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, 2, in the isopropyl methyl region.

be nonidentical when, within the generalized fragment



a prochiral moiety (e.g., an isopropyl group) is attached to a chiral center,[14] where X can be nothing or a "transmitting group" such as O, S, NR, etc., and P* represents a phosphorus chiral center. However, most of the stereochemical studies of conformationally mobile phosphorus systems which have been executed thus far have involved chirality assay by means of ^1H NMR.[15] Here, chemical shift nonequivalence is generally detectable; however, in those cases where X is a transmitting group *PXCCH* coupling constants are not observable, whereas in our compounds J_{PNCC} is clearly resolvable and found to be different for the two methyl environments. Presumably this is a ramification of the fact that the protons within the $P\text{–}X\text{–}CH(CH_3)_2$ moiety are somewhat remote from the phosphorus chiral center, and, therefore in general, the question of observability of coupling constant nonequivalence relates to their magnitudes. Evidently the methyl carbons, being one bond nearer to the phosphorus atom, are more sensitive to its chirality and consequently exhibit different *PNCC* couplings. The degree of proximity of the isopropyl group to the asymmetric center on the magnitude of the chemical shift difference in carbon systems has already been noted and a monotonic decline was found.[16]

Other examples of this effect in open-chain, mobile systems have recently been provided by the compounds $[(CH_3)_2CH]_2NP(Cl)C_6H_5$ and $[(CH_3)_2CH]_2NP(S)(Cl)C_6H_5$ which show two different *PNCC* couplings at ambient temperatures.[17] Similar observations have been made for *POCC* couplings in phosphonates.[18]

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X), the Robert A. Welch Foundation, and the Deutsche Forschungsgemeinschaft for generous financial support. A.H.C. is grateful to the Deutscher Akademischer Austauschdienst for a fellowship.

Registry No. $(i\text{-}C_3H_7)NHP(C_6H_5)_2$, 31036-96-1; $(i\text{-}C_3H_7)NHP(C_6F_5)C_6H_5$, 54844-79-0; $(i\text{-}C_3H_7)NHP(C_6F_5)_2$, 54844-80-3; $(i\text{-}C_3H_7)NHP(C_6H_5)_2CH_3I$, 54844-81-4; $(i\text{-}C_3H_7)NHP(C_6H_5)_2CH_3I$, 54844-82-5; $(i\text{-}C_3H_7)NHP(C_6F_5)(C_6H_5)CH_3BF_4$, 54844-76-7; $(i\text{-}C_3H_7)NHP(C_6F_5)_2(CH_3)BF_4$, 54844-78-9; C_6F_5MgBr, 828-72-8; phenyl(pentafluorophenyl)chlorophosphine, 13649-07-5; phenyl(pentafluorophenyl)bromophosphine, 13648-82-3; isopropylamine, 75-31-0; bis(pentafluorophenyl)chlorophosphine, 5032-90-6; bis(pentafluorophenyl)bromophosphine, 13648-79-8; ^{13}C, 14762-74-4; ^{31}P, 7723-14-0.

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Synthesis of Novel Fluorine-Containing Small Carboranes and Bis(difluoroboryl)methane

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Received December 17, 1974

AIC408392

The first fluorine-containing smaller carboranes and bis(difluoroboryl)methane have been prepared. The controlled reaction of $C_2B_5H_7$ with elemental fluorine yields the new compounds $BF_2CH_2BF_2$ (I), 3-$FC_2B_5H_6$ (II), 1-$FC_2B_5H_6$ (III), 5-$FC_2B_5H_6$ (IV), 1,5-$F_2C_2B_5H_5$ (V), 1,3-$F_2C_2B_5H_5$ (VI), and 5,6-$F_2C_2B_5H_5$ (VII). These new carboranes were characterized by ^{11}B NMR spectroscopy, mass spectroscopy, and infrared spectroscopy.

Introduction

Electrophilic and photochemical halogenations of *o*-$C_2H_2B_{10}H_{10}$ have been reported.[2] In the electrophilic chlorination, only four boron atoms of the cage are substituted. These four positions (boron atoms 8, 9, 10, 12) correspond to the most negative atoms in the cage as predicted by non-empirical molecular orbital theory. The monochloro derivative has been found to be mainly 9-Cl-*o*-$C_2H_2B_{10}H_9$ with a small amount of 8-Cl-*o*-$C_2H_2B_{10}H_9$.[2b] Electrophilic bromination and iodination appear to give similar results.[3] Photochemical chlorinations and brominations are much less selective. Exhaustive photochemical chlorination of *o*-carborane yields *o*-$C_2H_2B_{10}Cl_{10}$. The monofluorinated compounds 3-F-*o*-$C_2H_2B_{10}H_9$ and 2-F-*m*-$C_2H_2B_{10}H_9$ have been prepared from *o*-$C_2H_2B_{10}H_{10}$[4a] and the lithiated carboranes,[4b] respectively. Direct fluorination of *o*-, *m*-, and *p*-$C_2H_2B_{10}H_{10}$ in liquid HF gave *o*-, *m*-, and *p*-$C_2H_2B_{10}F_{10}$.[5] Perfluoro-*m*-carborane, $C_2F_2B_{10}F_{10}$, was prepared by the fluorination of *m*-$C_2F_2B_{10}H_{10}$.[5] In the earlier work with this direct fluorination technique, Lagow and Margrave fluorinated *m*-$C_2H_2B_{10}H_{10}$ to *m*-$C_2F_2B_{10}F_{10}$ directly.[6]

Much less work has been done on the halogenation of the small carboranes. 2,4-Dicarba-*closo*-heptaborane(7) has been chlorinated with and without an $AlCl_3$ catalyst.[7] With the catalyst, only 5-$ClC_2B_5H_6$ was found, while without the catalyst, the chlorination gave 1-, 3-, and 5-$ClC_2B_5H_6$, results reminiscent of the halogenations of the large carboranes.

In view of the results of the direct fluorination of *m*-$C_2H_2B_{10}H_{10}$, it was of interest to examine the fluorination of the smaller carboranes to see if the perfluoro analogs could be prepared. Using the conditions described in the Experimental Section, only partially fluorinated derivatives of $C_2B_5H_7$ were found, along with unreacted $C_2B_5H_7$, $BF_2CH_2BF_2$, and BF_3.

Experimental Section

The direct fluorination apparatus has been described previously.[8] Mass spectra were measured on a Hitachi RMU 6D mass spectrometer at 70 eV. ^{19}F and ^1H NMR spectra were taken on a Perkin-Elmer R20-B spectrometer (60 MHz for protons and 56.4 MHz for fluorine) which could be coupled to a Digilab Fourier transform system. Chemical shifts and coupling constants were calculated using frequencies counted on a Takeda Riken-TR-3824X frequency counter. ^{11}B spectra were taken on a Bruker HFX-90 spectrometer at 28.8 MHz. The Bruker HFX-90 spectrometer was interfaced with a Digilab FTS/NMR Fourier transform data system. Typical parameters used were 2048-point transform, 5-kHz bandwidth, 35° nutation angle, 0.5 sec between repetitive pulses, 10–6000 pulses, and ^1H broad-band decoupling. The sample (in Et_2O) was contained in a 4-mm tube inserted concentrically into a 10-mm tube. The field/frequency lock was provided by C_6F_6 contained in the 10-mm tube. Chemical shifts are given with reference to TMS for protons, $CFCl_3$, CF_3COOH, or C_6F_6 for fluorine, and $BF_3{\cdot}O(C_2H_5)_2$ for boron. Positive chemical shifts refer to absorbances at higher field with respect to the reference. Gas chromatography was done using either a Varian or Bendix gas chromatograph equipped with thermal conductivity detectors and cryogenic temperature controllers. Columns were made of 10% SE-30 on Chromosorb P and 13% fluorosilicone on Chromosorb P. Both columns were 10 ft × 1/4 in. Infrared data were recorded on a Beckman IR 20A instrument. Gas-phase spectra were run in a 10-cm cell with $AgNO_3$ windows. Mulls (Nujol and fluorocarbon) were run between KBr plates. X-Ray powder patterns were run on a Norelco X-ray diffractometer. 2,4-Dicarba-*closo*-heptaborane(7) (Chemical Systems Co.) was condensed into a glass tube equipped with a vacuum stopcock and ground-glass joint. This tube could then be attached to the fluorination system by way of a Swaglok T joint placed just before the cold box. In order to condense the $C_2B_5H_7$ into the cold box, the fluorination system was evacuated to a pressure of about 25 Torr.

Table I

Zone no. (*T*, °C)	He flow, cm³/min	F_2 flow, cm³/min	Time, hr
2 (−120)	60	0.5	20
3 (−120)	60	0.5	4
3 (−120)	30	0.5	6.5
3 (−80)	60	0	10
3 (room temp)	60	0	12

Reaction I. $C_2B_5H_7$ (0.59814 g, 7.07 mmol) was condensed into the second trap of the cold reactor which was held at −120°. The fluorination conditions are given in Table I. The glass products trap was kept at −196° for the entire reaction and contained a quantity of white material at the end of the reaction. The trap was taken to the vacuum line and evacuated while kept at −196°. Then the material was transferred into the vacuum line and fractionated. The compounds which passed a −126° trap were shown to be SiF_4 and BF_3 by ^{19}F NMR,[9] mass, and ir spectroscopy.[10]