Table II. Selected Infrared Bands in the 3500–1400-cm^{-1} Region

Compd	N–H str	C=O str	N–H def	N–H bend; C–N, C–O str
Primary amides[b]	3350, 3180	1650	1650–1620	1420–1400
Secondary amides[b]	3330–3060	1640	1570–1515	1305–1200
2-$B_{10}H_9NH_3^-$ [c]	3250		1580	1400
$B_{12}H_{11}NH_3^-$	3250, 3200		1590	1400
1-$B_{10}H_9NH_2COCH_3^-$ [d]	3280, 3100	1645		
$B_{10}H_9NH_2COC_6H_5^-$ [d]	3300, 3200	1640	1570	
$B_{10}H_8(NH_2COCH_3)_2 \cdot 2ROH$[a]	3250	1650	1480, 1460	1425, 1280
$B_{10}H_8(NH_2COCH_3)_2$	3440, 3330	1655	1600	1425
$B_{12}H_{11}NHCOCH_3^{2-}$ [e]	3220	1600		
$B_{12}H_{11}NH_2COCH_3^-$	3300, 3100	1640	1590	1420
$B_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)^-$	3430, 3340	1650	1600	1450, 1420
$B_{12}H_{10}NH_3(NH_2COCH_2SO_3C_6H_5)$	3410, 3320, 2900, 2830	1660	1600, 1580	1415
$B_{12}H_{10}(NHCOCH_2CONH_2)_2^{2-}$	3450–3250	1650, 1620	1600, 1570	1450–1425, 1400

[a] See the discussion in the text for alternative assignments of bands in this type of derivative. [b] Reference 16. [c] Reference 15. [d] Reference 2. [e] Reference 3.

trile gave a tlc pattern of spots corresponding to products III, II, $B_{12}H_{12}^{2-}$, I, VIII, and VI in order of ascending R_f.

Conclusion

The work reported in this paper indicates that $FeCl_3$ can be used for the purpose of attaching bifunctional nitriles to polyhedral boranes in a one-step reaction without the loss of the second function. A free ester and amide groups can be converted to a -COOH group and removal of the benzenesulfonate ion will leave behind an alcoholic -OH group. It is noteworthy that a thorough examination of tlc and ir data failed to detect any appreciable amount of either $B_{12}H_{11}OH^{2-}$ or $B_{12}H_{10}(OH)_2^{2-}$ among the reaction products. Apparently in the absence of strong protonic acids and at moderate temperatures neither the C=O nor the S=O bonds succeed in establishing a boron–oxygen link to $B_{12}H_{12}^{2-}$, in marked contrast with the reactivity of such bonds in acid-catalyzed additions.[2,7]

Though the yields of organic derivatives were disappointingly low, they compare favorably with the yields of similar compounds synthesized by some of the methods mentioned in the Introduction. Improving the yields of $B_{10}H_{10}^{2-}$ derivatives will be difficult due to the serious competition from coupling and decomposition. Such competition is insignificant in the case of $B_{12}H_{12}^{2-}$. Here the low yields reflect lower reaction rates, which are partly the result of low solubilities of most borane salts in the nitriles. Addition of a common solvent proved counterproductive, since in addition to diluting the reagents most of the highly polar solvents competed with the nitriles and interfered with the reduction of $FeCl_3$. A more promising, though initially tedious, approach involves finding for each nitrile an inert cation capable of solubilizing $B_{12}H_{12}^{2-}$. The separation and purification of monosubstituted derivatives, which accounted for a good portion of the unrecovered reaction products, would have been easier and taken less time in the absence of a large amount of starting material, which tended to coprecipitate with them. Consequent reduction in the length of exposure to aqueous acids and bases would have cut down the losses caused by hydrolysis.

Registry No. $Na_2B_{12}H_{12}$, 12008-78-5; $K_2B_{12}H_{11}Cl$, 52002-73-0; $[(CH_3)_4N]_3B_{24}H_{23}$, 52322-42-6; $Cs_3B_{24}H_{22}Cl$, 52002-75-2; $(CH_3)_4NB_{12}H_{11}NH_3$, 52322-45-9; $(CH_3)_4NB_{12}H_{11}NH_2COCH_3$, 52322-46-0; $B_{10}H_8(NH_2COCH_3)_2$, 12540-58-8; $(CH_3)_4NB_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)$, 52322-47-1; $Cs_2B_{12}H_{10}(NHCOCH_2CONH_2)_2$, 52002-78-5; $B_{12}H_{10}NH_3(NH_2COCH_2SO_3C_6H_5)$, 52322-44-8; $FeCl_3$, 7705-08-0; acetonitrile, 75-05-8; $[(CH_3)_4N]_2B_{12}H_{11}Cl$, 12546-13-3; $[(CH_3)_4N]_3B_{24}H_{22}Cl$, 52322-48-2; $K_2B_{10}H_{10}$, 12447-89-1; ethyl cyanoacetate, 105-56-6; cyanomethyl benzenesulfonate, 10531-13-2; malononitrile, 109-77-3.

Contribution No. 2504 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Antipodal Shielding Effects in the Boron-11, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Spectra of Icosahedral Carborane Derivatives

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A long-range shielding effect, possibly similar to that reported previously for B_5H_9 derivatives, has been observed in icosahedral carboranes and their metalloborane derivatives. This perturbation of the chemical shift upon substitution occurs at a position antipodal to the point of substitution and leads to a net shielding of endopolyhedral ^{11}B, ^{13}C, and ^{31}P nmr resonances and a net deshielding of exopolyhedral C-H ^1H nmr resonances.

Introduction

A ^{11}B nmr study of basal boron substituted B_5H_9 derivatives[2] uncovered a long-range shielding effect for the boron resonance trans to the point of substitution. In the case of the closo molecules 1-$CH_3CB_5H_6$[3a] and 1-$ClC_2B_5H_6$[3b] and

(1) (a) Procter and Gamble Fellow, 1972–1973. (b) NASA Predoctoral Fellow, 1969–1972.

(2) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 9, 1430 (1970).

(3) (a) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungerman, and T. Onak, *Inorg. Chem.*, 10, 2770 (1971); (b) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *ibid.*, 9, 2285 (1970).

Table I. Analytical Data for New Halogenated Carborane Derivatives

Compd	% carbon		% hydrogen		% halogen	
	Calcd	Found	Calcd	Found	Calcd	Found
$[(CH_3)_4N^+][(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co^-]$	13.36	13.00	4.14	4.88	44.20	44.47
$[(CH_3)_4N^+][(9\text{-}Br\text{-}1,2\text{-}B_9C_2H_{10})_2Co^-]$	16.94	16.93	5.83	6.03	28.27	28.00
$9,10\text{-}Cl_2\text{-}1,7\text{-}B_{10}C_2H_{10}$	11.27	11.41	4.69	5.05	33.33	33.26
$9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3S)_2\text{-}1,7\text{-}B_{10}C_2H_8$	12.18	12.25	3.55	3.60	16.24[a]	16.03[a]

[a] Sulfur analysis.

Table II. Nmr Chemical Shift Parameters for Some Halogenated Carborane Derivatives

Compd	$\delta(^{11}B)$[a]				$\delta(^1H)$[a]	$\delta(^{13}C)$[a]
	B(5,12)	B(9,10)	B(4,6,8,11)	B(2,3)		
$1,7\text{-}B_{10}C_2H_{12}$	6.6	10.4	12.9	16.2	−3.52	−57.7
$9\text{-}Br\text{-}1,7\text{-}B_{10}C_2H_{11}$	6.2	7.0[b] B (9)	12.4	17.2 B (3)	−3.77	−55.7
		9.2 B (10)	13.7	20.6 B (2)		
$9,10\text{-}Br_2\text{-}1,7\text{-}B_{10}C_2H_{10}$	6.0	6.2[b]	12.4	21.0	−3.88	−54.0
$9,10\text{-}Cl_2\text{-}1,7\text{-}B_{10}C_2H_{10}$	5.7	0.7[b]	13.5	22.2	−3.76	−51.6
$1,7\text{-}(CH_3)_2\text{-}1,7\text{-}B_{10}C_2H_{10}$	7.2	9.9	9.9	11.7		−72.1
$9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3)_2\text{-}1,7\text{-}B_{10}C_2H_8$	5.8	5.8[b]	9.8	15.9		
$1,7\text{-}(CH_3S)_2\text{-}1,7\text{-}B_{10}C_2H_{10}$	5.8	9.7	9.7	11.6		−73.7
$9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3S)_2\text{-}1,7\text{-}B_{10}C_2H_8$	5.4	6.2[b]	10.0	16.0		

Compd	$\delta(^{11}B)$[a]				$\delta(^1H)$[a]	$\delta(^{13}C)$[a]
	B(9,12)	B(8,10)	B(4,5,7,11)	B(3,6)		
$1,2\text{-}B_{10}C_2H_{12}$	3.1	9.6	13.9	[c]	−4.40	−56.2
$9\text{-}Br\text{-}1,2\text{-}B_{10}C_2H_{11}$	0.2[b] B(9)	8.5	13.3	[c]	−4.61	−55.7
	2.3 B(12)		14.2			−48.8
$9,12\text{-}Br_2\text{-}1,2\text{-}B_{10}C_2H_{10}$	−0.1[b]	8.0	13.6	15.9	−4.78	−48.5
$8,9,12\text{-}Br_3\text{-}1,2\text{-}B_{10}C_2H_9$	−0.2[b]	5.2[b] B(8)	13.0	[c]	−5.04	−47.9
		8.3 B(10)	15.2	19.5 B(6)		

[a] Chemical shifts in ppm. [b] Substituted position. [c] This resonance overlaps with the B(4,5,7,11) resonance(s) so that an accurate measurement of the chemical shift cannot be made.

$[X\text{-}C_6H_4\text{-}N_2HB_{10}H_9]^-$ derivatives,[4] a shielding effect was also observed for the boron resonance antipodal (on the opposite side of the cage) to the substituted atom in the polyhedron.

We wish to report observations which suggest that a long-range shielding effect, perhaps similar to that operant in the other borane derivatives mentioned above, occurs within the icosahedral $B_{10}C_2H_{12}$ and $B_{10}H_{10}CHP$ carboranes and the $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co$ metallocarboranes.

Experimental Section

^{11}B and ^1H nmr spectra were obtained at 70.6 and 220 MHz, respectively, with a Varian Associates HR-200 spectrometer. A Fourier transform pulsed nmr spectrometer described previously[5] was used to obtain ^{13}C and ^{31}P nmr spectra at 15.1 and 24.3 MHz, respectively. The ^{11}B nmr chemical shifts were measured relative to an external $BF_3\cdot O(C_2H_5)_2$ reference, ^1H nmr chemical shifts relative to an internal TMS reference, ^{31}P nmr chemical shifts relative to an external 85% H_3PO_4 reference, and ^{13}C nmr chemical shifts relative to the internal acetone solvent resonance. ^{13}C nmr chemical shifts are reported in ppm *downfield* from an internal TMS reference using the conversion

$$\delta_{TMS} = \delta_{(CH_3)_2CO} - 30.43 \text{ ppm}$$

All spectra were recorded in acetone or acetone-d_6 solution with the following estimated accuracies: ^1H, ±0.03 ppm; ^{11}B, ±0.2 ppm; ^{13}C, ±0.5 ppm; ^{31}P, ±0.5 ppm. *Positive* values for the nmr chemical shifts imply resonances which appear *upfield* from the reference.

Literature methods were used to prepare $9\text{-}Br\text{-}1,2\text{-}B_{10}C_2H_{11}$, $9,12\text{-}Br_2\text{-}1,2\text{-}B_{10}C_2H_{10}$, $8,9,12\text{-}Br_3\text{-}1,2\text{-}B_{10}C_2H_9$, $9\text{-}Br\text{-}1,7\text{-}B_{10}C_2H_{11}$, and $9,10\text{-}Br_2\text{-}1,7\text{-}B_{10}C_2H_{10}$.[6] Reaction of $1,7\text{-}B_{10}C_2H_{12}$ with Cl_2 in carbon tetrachloride in the presence of aluminum chloride afforded $9,10\text{-}Cl_2\text{-}1,7\text{-}B_{10}C_2H_{10}$, mp 225–228° (evacuated sealed capillary). Treatment of $9,10\text{-}Br_2\text{-}1,7\text{-}Li_2\text{-}1,7\text{-}B_{10}C_2H_8$ with sulfur and methyl iodide afforded $9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3S)_2\text{-}1,7\text{-}B_{10}C_2H_8$, mp 93–95°.[7] The halogenated carboranes were converted into the cobalt metalloboranes by a published procedure.[8] Analytical data for the new compounds prepared for this study are presented in Table I.

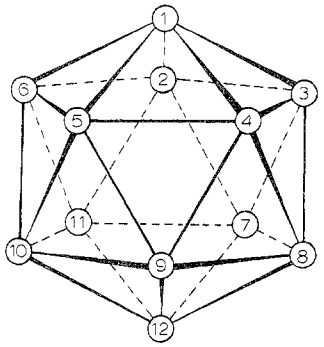

Figure 1. Icosahedral numbering system.

Results and Discussion

We have reported previously that in the 70.6-MHz ^{11}B nmr spectrum of $9,10\text{-}Br_2\text{-}1,7\text{-}B_{10}C_2H_{10}$ the B(2,3) resonance which arises from boron nuclei at the 2,3 position of the icosahedral cage (see Figure 1) (*i.e.*, those borons antipodal to the point of halogen substitution) is shielded by 4.8 ppm relative to the B(2,3) resonance in the parent $1,7\text{-}B_{10}C_2H_{12}$ derivative, while the proximate B(4,6,8,11) and B(5,12) resonances are deshielded by only 0.5 and 0.6 ppm, respectively.[9] Very similar features are observed in the spectrum of $9,10\text{-}Cl_2\text{-}1,7\text{-}B_{10}C_2H_{10}$ indicating that this antipodal shielding may be a general effect of halogen substitution (see

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(9) L. J. Todd, *Pure Appl. Chem.*, 30, 587 (1972).

Table III. ^1H and ^{13}C Nmr Chemical Shifts for Some Brominated Metallocarboranes

Compd	$\delta(^1H)^a$	$\delta(^{13}C)^a$
$[(CH_3)_4N^+][(1,2\text{-}B_9C_2H_{11})_2Co^-]$	−3.94	−51.5
$[(CH_3)_4N^+][(9\text{-}Br\text{-}1,2\text{-}B_9C_2H_{10})_2Co^-]$	−4.08	−50.0
	−4.03	−46.6
$[(CH_3)_4N^+][(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co^-]$	−4.16	−45.9

[a] Chemical shifts in ppm.

the neutral carboranes. In the dibromo derivative ($n = 2$) both carbons are antipodal to a bromine substituent, and they are shielded by 5.6 ppm relative to the parent metallocarborane. In the monobrominated derivative ($n = 1$) the nonequivalent carbon resonances are shielded by 1.5 and 4.9 ppm.

Aluminum chloride catalyzed bromination of $1,2\text{-}B_{10}H_{10}$CHP gives a $1,2\text{-}B_{10}H_8Br_2$CHP derivative.[13] The symmetry

Table IV. Nmr Data for Some Phosphacarborane Derivatives

Compd	$\delta(^{11}B)^a$ B(9,12)	B(8,10)	B(4,5,7,11)	B(3,6)	$\delta(^1H)^a$	$\delta(^{13}C)^a$	$\delta(^{31}P)^a$
$1,2\text{-}B_{10}H_{10}$CHP	−9.3 −2.4	0.85	6.7	10.8	−4.15 (15[b])	−68.4 (210[c])	56.3 (60[d])
$1,2\text{-}B_{10}H_8Br_2$CHP	−7.5[e] −4.2[e]	−0.14	7.3	12.2	−4.43 (15[b])	−60.9	120.0 (63[d])

[a] Chemical shifts in ppm. [b] $^2J_{^{31}P^1H}$ in Hz. [c] $J_{^{13}C^1H}$ in Hz. [d] $J_{^{13}C^{31}P}$ in Hz. [e] Substituted position.

Table II). In $9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3)_2\text{-}1,7\text{-}B_{10}C_2H_8$ and $9,10\text{-}Br_2\text{-}1,7\text{-}(CH_3S)_2\text{-}1,7\text{-}B_{10}C_2H_8$ the bromine substituents produce antipodal shieldings of 4.2 and 4.4 ppm, respectively, which suggests that a similar long-range shielding effect exists in carborane derivatives in which substituents other than hydrogen are attached to the carbon atoms. In the ^{11}B nmr spectrum of $9\text{-}Br\text{-}1,7\text{-}B_{10}C_2H_{11}$, the B(2) and B(3) resonances are found to be magnetically nonequivalent with one nucleus in this previously degenerate set shielded by 4.4 ppm while the other is shielded by 1.0 ppm. These results suggest that bromine substitution on an icosahedral carborane cage produces a substantial perturbation of the shielding of the antipodal necleus, *i.e.*, the nucleus diametrically opposite to the point of substitution.[10]

To test this hypothesis we have examined the ^{13}C nmr spectra of the series of brominated *o*-carborane derivatives $9\text{-}Br\text{-}1,2\text{-}B_{10}C_2H_{11}$, $9,12\text{-}Br_2\text{-}1,2\text{-}B_{10}C_2H_{10}$, and $8,9,12\text{-}Br_3\text{-}1,2\text{-}B_{10}C_2H_9$ (see Table II). In $9\text{-}Br\text{-}1,2\text{-}B_{10}C_2H_{11}$ in which only one carbon nucleus is antipodal to the bromine substituent, the carbon resonances are magnetically nonequivalent with one resonance shielded by 7.4 ppm and the other by 0.5 ppm relative to the unsubstituted $1,2\text{-}B_{10}C_2H_{12}$ derivative. In $9,12\text{-}Br_2\text{-}1,2\text{-}B_{10}C_2H_{10}$ in which both carbons are antipodal to a bromine substituent, the carbon resonances are equivalent and they are shielded by 7.7 ppm relative to $1,2\text{-}B_{10}C_2H_{12}$. In $8,9,12\text{-}Br_3\text{-}1,2\text{-}B_{10}C_2H_9$ the third bromine at B(8) is not antipodal to either carbon atom and it has little effect upon the ^{13}C nmr chemical shift. The B(8) position is, however, antipodal to one of the boron nuclei in the B(3,6) set. In the parent $1,2\text{-}B_{10}C_2H_{12}$ carborane the B(3,6) resonance appears at highest field in the ^{11}B nmr spectrum.[11] The antipodal shielding effect should strongly influence one of these positions, *viz.* B(6), and accordingly in the ^{11}B nmr spectrum of this tribromo derivative, a doublet of unit area appears at high field approximately 4 ppm upfield of the B(3) resonance. As in the $1,7\text{-}B_{10}C_2H_{12}$ derivatives, proximate unsubstituted positions appear to be affected to a lesser extent.

The ^{13}C nmr spectra of a series of brominated polyhedral metallocarboranes of the type $[Br_n\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11-n}]_2Co^-$ have been studied to determine whether antipodal shielding effects can be observed in these complexes.[12] The results presented in Table III parallel the trends seen previously for

(10) Another group has recently reported similar results: S. Hermanek, J. Plesek, and B. Stibr, Abstracts, Second International Meeting on Boron Chemistry, Leeds, England, March 1974, No. 38.

(11) A. R. Siedle, G. M. Bodner, A. R. Garber, and L. J. Todd, to be submitted for publication.

of $1,2\text{-}B_{10}H_{10}$CHP is such that only two boron atoms B(9) and B(12) are unique and these nuclei give rise to doublet resonances each of unit area at lowest field in the ^{11}B nmr spectrum (see Table IV). In the ^{11}B nmr spectrum of the dibromo derivative the two low-field resonances of unit area are each singlets. This suggests that the points of substitution in $B_{10}H_8Br_2$CHP are B(9) and B(12). As in $1,2\text{-}B_{10}C_2H_{12}$ the positions of attack by electrophilic reagents are those most distant from the heteroatoms.[13] The ^1H, ^{13}C, and ^{31}P nmr chemical shifts for these two phosphacarboranes are given in Table IV. It can be seen that in $9,12\text{-}Br_2\text{-}1,2\text{-}B_{10}H_8$CHP both the carbon and phosphorus nuclei are shielded by the antipodal bromine substitution.

In contrast to the observed shielding of polyhedral ^{11}B, ^{13}C, and ^{31}P nmr resonances, the introduction of halogen substituents leads to a gradual deshielding of exopolyhedral C–H ^1H nmr resonances. Similar effects have been observed by Stanko, *et al.*,[14] for a wide variety of halogenated carboranes. While the deshielding of the ^1H nmr resonance may be indicative of the inductive effect of an electronegative bromine substituent transmitted through the predominantly σ C–H bond, it is worth noting that the shielding of polyhedral nuclei need not imply an increased electron density at the antipodal nucleus. The dominant factor in ^{11}B, ^{13}C, and ^{31}P nmr chemical shifts will be the paramagnetic screening tensor[15] which is proportional to changes in the average excitation energy and the p-orbital occupation anisotropy, as well as electron density. The first two terms, which are particularly nebulous for these systems, can make very important contributions to the paramagnetic screening tensor. While Burg[16] has proposed an explanation for the trans effect in substituted pentaboranes, a rigorous explanation of the mechanism of this effect in icosahedral derivatives must await a clearer understanding of those factors which give rise to the nmr chemical shifts within electron-deficient polyhedral cages.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-33267X.

(12) ^{11}B nmr spectra for $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co^-$ and $[9,12\text{-}Br_2\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9]_2Co^-$ have been reported elsewhere: A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Organometal. Chem.*, 33, 137 (1971).

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(14) V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, *Zh. Strukt. Khim.*, 11, 542 (1970). The ^1H nmr chemical shift values reported by these workers differ from some of our data due to solvent effects.

(15) J. A. Pople, *Mol. Phys.*, 7, 301 (1963).

(16) A. B. Burg, *J. Amer. Chem. Soc.*, 90, 1407 (1968).

Registry No. 1,7-$B_{10}C_2H_{12}$, 16986-24-6; 9-Br-1,7-$B_{10}C_2H_{11}$, 17819-81-7; 9,10-Br_2-1,7-$B_{10}C_2H_{10}$, 17032-20-1; 9,10-Cl_2-1,7-$B_{10}C_2H_{10}$, 17702-39-5; 1,7-$(CH_3)_2$-1,7-$B_{10}C_2H_{10}$, 17499-00-2; 9,10-Br_2-1,7-$(CH_3)_2$-1,7-$B_{10}C_2H_8$, 51935-97-8; 1,7-$(CH_3S)_2$-1,7-$B_{10}C_2H_{10}$, 51935-98-9; 9,10-Br_2-1,7-$(CH_3S)_2$-1,7-$B_{10}C_2H_8$, 52003-52-8; 1,2-$B_{10}C_2H_{12}$, 16872-09-6; 9-Br-1,2-$B_{10}C_2H_{11}$, 17141-89-8; 9,12-Br_2-1,2-$B_{10}C_2H_{10}$, 17702-36-2; 8,9,12-Br_3-1,2-$B_{10}C_2H_9$, 20313-40-0; $[(CH_3)_4N^+][(1,2\text{-}B_9C_2H_{11})_2Co^-]$, 12305-41-8; $[(CH_3)_4N^+][(9\text{-Br-}1,2\text{-}B_9C_2H_{10})_2Co^-]$, 52003-54-0; $[(CH_3)_4N^+][(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2\text{-}Co^-]$, 51936-00-6; 1,2-$B_{10}H_{10}CHP$, 30112-97-1; 9,12-$Br_2$-1,2-$B_{10}H_8CHP$, 51936-01-7; ^{11}B, 14798-13-1; ^{13}C, 14762-74-4; P, 7723-14-0.

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Phosphoranes. I. Tris(trifluoromethyl)bis(dimethylamino)phosphorane, $(CF_3)_3P[N(CH_3)_2]_2$, and Related Chlorodimethylaminotrifluoromethylphosphoranes

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New trifluoromethyldialkylaminophosphoranes $(CF_3)_3P[N(CH_3)_2]_2$, $(CF_3)_3PCl[N(CH_3)_2]$, and $(CF_3)_2PCl_2[N(CH_3)_2]$ were obtained from the trifluoromethylchlorophosphoranes and dimethylamine. The latter compound was also prepared by addition of Cl_2 to $(CF_3)_2PN(CH_3)_2$. Nmr spectroscopic behavior at low temperatures of the two tris(trifluoromethyl)-phosphoranes is consistent with two and one axial CF_3 substituents in a trigonal-bipyramidal framework, respectively. Axial substitution of CF_3 groups appears to be characterized by unusually low $^2J_{PF}$ (~50 Hz) couplings to phosphorus. The lack of temperature dependence in the ^{19}F nmr spectrum of $(CF_3)_2PCl_2[N(CH_3)_2]$ and the large $^2J_{PF}$ coupling constant (156.9 Hz) in this compound suggest equatorial CF_3 substitution and the absence of positional averaging. It is suggested that the halogens occupy axial positions in preference to CF_3 even if the halogen has a lower formal electronegativity than CF_3. Acidic reagents such as methanol, methyl mercaptan, and H_2S displace CF_3H from $(CF_3)_3P[N(CH_3)_2]_2$ to form pentavalent, four-coordinate products in complicated reactions. Some reduction to phosphorus(III) occurs in the sulfur system perhaps through intermediate, unstable thiophosphoranes. Alkaline hydrolysis liberates 2 mol of CF_3H quantitatively in all cases but neutral and acidic hydrolyses which also liberate CF_3H are less straightforward as a result of secondary reactions in the medium. The new anion $CF_3PO_3H^-$ has been observed in acidic media. Nmr parameters for $CF_3P(E)[N(CH_3)_2]_2$ and $CF_3P(E)Cl[N(CH_3)_2]$ (E = O, S) are reported for the first time.

Introduction

Recent review articles demonstrate a continuing active interest in the location of substituents in the five-coordinate phosphorane framework.[1,2] Early studies by Muetterties and coworkers[3] suggested that, for a limited range of substituents, the axial position of the assumed trigonal-bipyramidal framework was preferentially occupied by the most electronegative group. Trifluoromethylfluorophosphoranes presented some ambiguities which were resolved by assigning the CF_3 substituent to either axial or equatorial positions[3] in different molecules suggesting that CF_3 could replace F in axial position in some cases in spite of its lower electronegativity. Recent calculations[2c,4] have suggested that back-bonding into the "d" orbitals of the phosphorus atom is more effective from equatorial than from axial positions and this difference may well be responsible for the observed positional preferences. Thus, on phosphorus, groups with strong back-bonding tendencies would favor location in equatorial positions and those with weak or nonexistent back-bonding requirements favor axial positioning. Each group therefore has a specific "apicophilic" character.[4] We have been engaged in a systematic study of the chemistry of trifluoromethylphosphoranes with the aim of providing some insight into the substitutional preference of substituent groups on phosphorus. We report herein some studies of dimethylaminophosphoranes containing CF_3 substituents.

Experimental Section

Materials, Apparatus, and Techniques. All manipulations were carried out using standard vacuum techniques in a system constructed with Pyrex glass with stopcorks lubricated with Apiezon N grease. Involatile materials which remained in the reaction vessels were handled in a nitrogen atmosphere while aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

Reactions were generally carried out in sealed Pyrex glass tubes of approximate volumes 10, 25, or 75 cm^3 depending on the scale of the reaction and the maximum calculated pressure expected. A reactor tube which allowed combination of reagents in gaseous form in spite of relatively low volatility (Figure 1) was used in most of the reactions.

Materials. Trifluoromethyliodophosphines and $(CF_3)_3P$ were prepared from the reaction of CF_3I (Columbia Organic Chemical Co.) with red phosphorus at 220° for 48 hr.[5] The remaining trifluoromethylphosphorus compounds required in this study were prepared from these phosphines according to indicated literature methods. Commercially available chemicals of "reagent" grade were used without further purification. Gaseous reagents were usually fractionated before use to remove any moisture or gross impurites.

Instrumental Techniques. Infrared spectra of gases were obtained using a 9-cm gas cell with potassium bromide windows. All spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Gaseous samples were introduced directly through a heated inlet, whereas liquids of low volatility were introduced *via* a heated capillary. Solid samples were introduced *via* the direct probe. All nmr spectra were recorded with either a Varian A56/60, a Varian HA 100, or a Bruker HFX-90 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine spectra at 56.4 MHz using the A56/60 instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz and fluorine spectra

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