

were described in a recent paper.¹⁷

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Raman and Infrared Spectra of Cyanodifluorophosphine

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The Raman spectra of gaseous, liquid, and solid cyanodifluorophosphine and the infrared spectra of the gas and solid have been recorded. The nine fundamental vibrations have been assigned on the basis of the depolarization values, infrared band contours, and group frequencies. A normal-coordinate calculation was carried out. Extensive mixing was found between the PF₂ wag and PF₂ scissors but the other fundamentals appeared to be relatively "pure" motions. In the solid state, there appear to be two molecules per primitive cell. A large number of "hot bands" were observed on both the C≡N and P—C stretching modes.

Introduction

From an investigation of the microwave spectrum of cyanodifluorophosphine, Schwendeman and co-workers² found the PCN moiety to be nonlinear with an angle of $171.2 \pm 0.8^\circ$. These authors found and assigned transitions for the first and second excited vibrational state of about 125 cm^{-1} . They also observed rotational transitions arising from molecules in the first excited state of a second vibrational mode whose relative intensity indicated that the vibration was intermediate between those of the first and the second excited states of the lowest frequency fundamental.

Rudolph et al.³ reported the infrared spectrum above 200 cm^{-1} but they did not observe the two lowest frequency fundamentals in the expected region ($250\text{--}320 \text{ cm}^{-1}$). Additionally, these authors,³ although stating that it was possible that the two fundamentals might occur below 200 cm^{-1} , tentatively assigned the two PCN bending modes at 549 and 460.5 cm^{-1} which is too high in frequency for these normal motions compared to their values in related molecules.⁴ Also, the "hot bands" on the CN stretching mode indicated a very low frequency fundamental and the effect of the nonlinearity of the PCN moiety on the CN out-of-plane bending mode is questionable. Since no Raman data have been reported for this molecule, we have recorded the Raman spectra of gaseous, liquid, and solid F₂PCN. We have also obtained the far-infrared spectrum of the gas and solid and the results of our study are reported herein.

Experimental Section

All preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Difluorocyanophosphine was prepared as reported previously⁵ from PF₂I and AgCN (Columbia Organic Chemical Co.). Difluoriodophosphine was also prepared by a published procedure.⁶ The purification of PF₂CN was achieved by means of a low-temperature vacuum fractionation column⁷ and the purity was monitored by ³¹P NMR (XL-100, 40.5 MHz) and mass

spectroscopy (Perkin-Elmer RMU-6, 70 eV).³

Infrared spectra were obtained using a Digilab FTS-15 B Fourier transform interferometer.⁸ A germanium beamsplitter on a KBr substrate and a glow source covered the $3800\text{--}400\text{-cm}^{-1}$ region while a 12.5μ Mylar beamsplitter and a high-pressure Hg arc lamp source were used for the $400\text{--}80 \text{ cm}^{-1}$ region. Spectra of the gaseous phase were obtained using a 10-cm glass cell with KBr and high-density polyethylene windows for the mid-infrared and the far-infrared, respectively. Sample pressures were approximately 5 Torr for the mid-infrared and 100 Torr for the far-infrared spectra.

Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The FTS uses a He—Ne laser as a frequency reference of high stability. Calibration is achieved by adjusting a software parameter, the laser wavelength, to reproduce an observed vibrational transition of a suitable standard at its correct frequency. As a result, the accuracy of a measured frequency can be expected to be better than the available resolution throughout the spectrum. The spectra were run at an effective resolution of better than 0.5 cm^{-1} using a modified "boxcar" apodization function.

The Raman spectra were obtained with a Cary Model 82 Raman spectrophotometer equipped with a Spectra Physics Model 171 argon ion laser with excitation wavelength of 5145 \AA . The laser could provide approximately 2 W of power at the sample. Spectra of the gas phase were recorded using the Cary multipass accessory at sample pressures of ≈ 200 Torr. Spectra of the liquid at -15°C and the solid at -160°C were obtained using a method similar to that described by Miller and Harney⁹ with the sample sealed in a glass capillary. Polarization measurements were made using the standard Cary accessories. Frequencies measured for sharp, resolvable bands are expected to be accurate to at least $\pm 2 \text{ cm}^{-1}$.

Vibrational Spectrum and Assignment

Using the molecular structure and dipole moment components determined in a microwave study of cyanodifluorophosphine by Lee et al.,² the molecule is seen to exhibit C_s symmetry and should have nine infrared and Raman active fundamentals, distributed as six a' and three a'' . Infrared spectra of the sample in the gaseous phase should exhibit A/C

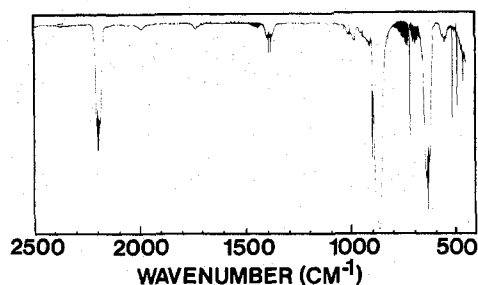


Figure 1. Mid-infrared spectrum of gaseous cyanodifluorophosphine.

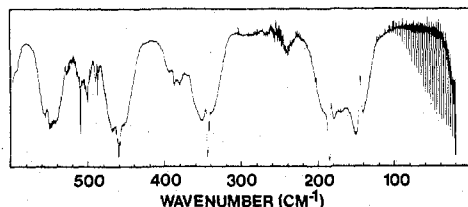


Figure 2. Far-infrared spectrum of gaseous cyanodifluorophosphine. The regions near 230 and 500 cm^{-1} show a much lower signal to noise ratio due to the energy limiting characteristic of the Mylar beam-splitter.

hybrid band contours for the a' modes, while the a'' modes should be pure B-type bands. The mid-infrared spectrum of PF_2CN has been examined previously by Rudolph et al.,³ who suggested a vibrational assignment using the results for PF_2Cl ¹⁰ as a guide. However, since their results were only partial and tentative, a more complete vibrational investigation was undertaken.

The mid-infrared spectrum of gaseous cyanodifluorophosphine is shown in Figure 1. The sample proved to be quite difficult to work with and it was not possible to eliminate the appearance of decomposition products in the spectrum. Two major impurities, HCN and PF_3 , were easily identified and peaks due to them are so marked in Table I, which lists observed vibrational frequencies for PF_2CN . Using the "spectral subtraction" routines on the FTS-15B and the results of separate experiments, it was possible to identify certain other bands which are clearly the result of one or more additional impurities whose composition remains unknown. Probable decomposition pathways include disproportionation and hydrolysis, PF_3 being a product of the first and HCN a product of the latter, although no experiments were undertaken to determine this conclusively.

Several fundamentals can be assigned on the basis of the mid-infrared spectrum alone. The band system near 2200 cm^{-1} is clearly ν_1 , the $\text{C}\equiv\text{N}$ stretch. A discussion of the complexity of this and several other bands will be deferred until a later section. The intense band system near 870 cm^{-1} encompasses both ν_2 and ν_7 , the P-F stretches, and the strong band system near 630 cm^{-1} is easily attributed to ν_3 , the P-C stretching fundamental.

An investigation of the far-infrared spectrum of gaseous PF_2CN , shown in Figure 2, places the P-C \equiv N bending fundamentals, ν_6 (in-plane) and ν_9 (out-of-plane), at 185 and 145 cm^{-1} , respectively. This is the region where such fundamentals would be expected from work on the similar molecule $(\text{CH}_3)_2\text{PCN}$,¹¹ and the observed band contours make it a simple matter to distinguish between the two modes. This leaves the two a' deformations, the PF_2 wag and scissors, and the a'' PF_2 twisting vibration yet to be assigned. It was the location and description of these modes which proved to be the most troublesome of the entire problem, and, in view of the applicability of these results to other molecules containing the $-\text{PF}_2$ moiety, a fairly detailed description of our arguments is warranted.

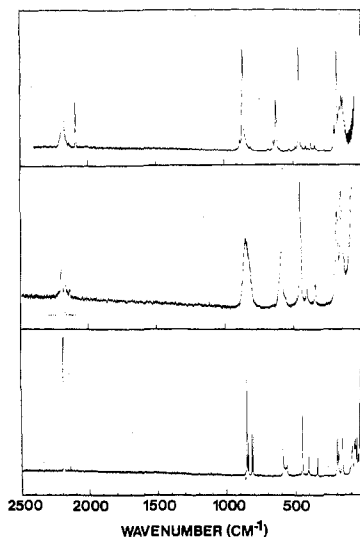


Figure 3. Raman spectra of cyanodifluorophosphine in three phases: upper trace, gaseous; middle trace, liquid; lower trace, solid.

In PF_3 , a molecule of C_{3v} symmetry, the corresponding vibrational modes are the a_1 and e deformations occurring near 487 and 344 cm^{-1} , respectively.¹² Substitution of another group for one of the fluorine atoms can give a molecule which has C_s symmetry, like PF_2CN . The a_1 vibration becomes an a' , the PF_2 wagging vibration, and the e mode degeneracy is removed, becoming an a' scissoring vibration and an a'' twisting vibration. If the mass and electronegativity of the substituent, $-\text{C}\equiv\text{N}$ in this case, is not too different from fluorine, one would expect the wagging mode near 480 cm^{-1} and the twist and scissors near 340 cm^{-1} . It should be noted that, although the twisting vibration can be identified by its Raman depolarization ratio, there is no way to distinguish the wag and the scissors on the basis of the vibrational spectra alone. The observation of a band near 358 cm^{-1} of HPF_2 by Rudolph and Parry¹³ implies that this must be the PF_2 scissoring mode, as the other deformational modes for this molecule are primarily hydrogen motions and, as such, much higher in frequency. Thus, 360 cm^{-1} can be taken as an upper limit to the PF_2 scissoring fundamental, since replacement of the hydrogen with a heavier substituent would be expected to lower the vibrational frequency.

In the far-infrared spectrum of PF_2CN , ν_4 and ν_5 , the wag and scissors, are seen at 460 and 345 cm^{-1} , respectively, but there is no apparent B-type band to associate with ν_8 , the twisting vibration. The Raman spectra of PF_2CN in the gaseous, liquid, and solid phases, shown in Figure 3, reveal the missing twist as a weak, depolarized band at 412 cm^{-1} in the liquid which shifts to 415 cm^{-1} upon solidification. An extremely weak band seen at 412 cm^{-1} in the Raman spectrum of gaseous PF_2CN is probably not due to ν_8 , since it seemed to be polarized and is more likely a difference band or impurity peak. These results imply that ν_8 is so weak in the gaseous-phase spectrum as to be unobservable.

The doublets observed for several fundamentals in the Raman spectrum of the solid are attributed to factor group splitting by the presence of two molecules per unit cell occupying different lattice sites. For such a crystal one would expect six optical librations and three optical translations to be observable in the spectrum of the solid. We have observed nine bands in the very low frequency region of the Raman spectrum of solid PF_2CN which show the temperature-dependent frequency shift typical of lattice modes and have made a tentative assignment accordingly. There is a possibility that one or more of the higher bands in this group are the result of a two-phonon process at the Brillouin zone edge, and a

Table I. Observed Vibrational Frequencies (cm^{-1}), Assignments, and PED for the Gas Phase for Cyanodifluorophosphine

IR gas	Band types	Rel intens	Raman gas	Depol	Rel intens	Raman liq	Depol	Rel intens	Raman solid	Rel intens	Calcd	Assignment and PED for gas phase
3340	R	vw										
3294	P	vw										
2805	C	vvw										ν_1 of HCN, present as an impurity
2518	R											$\nu_2 + \nu_3$ of HCN impurity
2502	Q	vw										Unidentified impurity
2486												
2200	R											
2195.5	Q		2195.5			2192	p	vvs	2198	vvs	2195.5	ν_1 94% $\text{C}\equiv\text{N}$ str
2193.0	Q		2193.0									$\nu_1 + \nu_9 - \nu_9'$
2190.5	Q		2190.5									$\nu_1 + 2\nu_9 - 2\nu_9'$
2188.5	Q	s	2188.5	p	vvs							$\nu_1 + 3\nu_9 - 3\nu_9'$
2186.0	Q		2186.0									$\nu_1 + 4\nu_9 - 4\nu_9'$
2183.5	Q		2183.5									$\nu_1 + 5\nu_9 - 5\nu_9'$
2181.5	Q		2181.5									$\nu_1 + 6\nu_9 - 6\nu_9'$
2179.5	Q											$\nu_1 + 7\nu_9 - 7\nu_9'$
2177.5	Q											$\nu_1 + 8\nu_9 - 8\nu_9'$
												ν_2 of HCN impurity
1726		vw	2095		m							$2\nu_2$ or $\nu_2 + \nu_7$
1412	B-type, center	vw										$2\nu_3$ of HCN impurity
1386	R											Unidentified impurity
1383	Q											
1374	Q	w										
1366	Q											
1004	R											Unidentified impurity
996	Q	vw										
992	Q											
978	P											
944	R											
936	Q											
930	Q	vw										
920	P											
906	R	w										
892	Q	vvs	892	sh, p	w							
874	R											
869	Q	vvs	869	p	s	858	brd, p	m			869.1	ν_1 of PF_3 , present as impurity
864	P											ν_2 86% P-F sym str 7% PF_2 wag
866	R	vvs	(863)	sh, dp?	w	(840)	sh, dp?	w			861.0	ν_7 96% P-F asym str
857	P	vvs	(854)									
726	R	w										
712	Q											
694	P	w										
648	sh	m	648	p	w							ν_3 of HCN impurity
												$\nu_4 + \nu_6$

Table II. Symmetry Coordinates Used in the Normal-Coordinate Analysis

Species (C_3)	Symmetry coordinates ^a	Description
a'	$S_1 = s$	C≡N stretch
	$S_2 = t_{13} + t_{14}$	PF ₂ sym str
	$S_3 = r_{12}$	P-C str
	$S_4 = \alpha_{314}$	PF ₂ scissors
	$S_5 = \beta_{312} + \beta_{412}$	PF ₂ wag
	$S_6 = \pi_{125}$	P-C≡N in-plane bend
a''	$S_7 = t_{13} - t_{14}$	PF ₂ asym str
	$S_8 = \beta_{312} - \beta_{412}$	PF ₂ twist
	$S_9 = \sigma_{125}$	P-C≡N out-of-plane bend

^a Not normalized, refer to Figure 4 for notation.

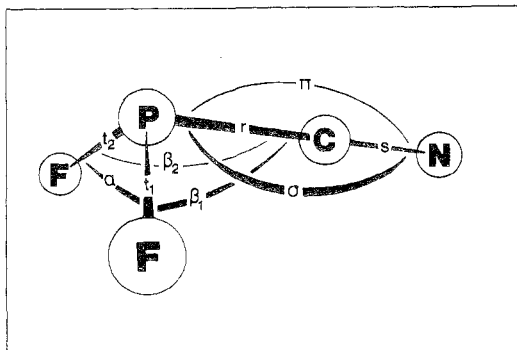


Figure 4. Perspective of cyanodifluorophosphine showing definitions for normal-coordinate analysis (refer to Table II).

positive assignment is not possible especially since the crystalline structure of this molecule is not known.

Normal-Coordinate Analysis

The molecular structure constants for PF₂CN were taken from ref 2 with one exception. The authors reported a nonlinear PCN angle of $171.2 \pm 0.8^\circ$ with the CN group tilted away from the fluorine atoms. While we believe this result is correct, the far-infrared and Raman spectra did not seem to indicate that the out-of-plane PCN bending fundamental is very different in form than the in-plane mode. That is to say, the vibration is still essentially a bending mode and not a torsional vibration. For this reason, the PCN linkage was assumed to be linear, and the two vibrations were treated as linear angle bends. The other structural constants used were $r_{PF} = 1.566 \text{ \AA}$, $r_{PC} = 1.815 \text{ \AA}$, $r_{CN} = 1.157 \text{ \AA}$, $\angle FPF = 99.2^\circ$, and $\angle FPC = 96.9^\circ$. Nine internal coordinates were defined as the basis set for the equations of motion and were used to construct the symmetry coordinates listed in Table II (refer to Figure 4). After choosing the seven principal valence force field constants, we were constrained to only two interaction constants to keep the number of force constants less than $3N - 6$. One of these, F_{rr} , was necessary to properly order the two P-F stretches. The choice of the other interaction constant was dependent on the assignment. At first we attempted a calculation with the PF₂ scissors assigned at 460 cm^{-1} and the wag assigned at 345 cm^{-1} and, using the $F_{\beta\beta}$ interaction, were able to reproduce the observed frequencies within an average error of 0.5 cm^{-1} or 2%. The potential energy distribution (PED) for this force field (treatment B) was quite "clean" with only the wag and the PCN in-plane bend mixing to any significant degree, but even then, each of these modes was at least 60% pure. This seemed acceptable until we were forced to assign the scissors and wag oppositely for the reasons given in the previous section. Using this final assignment, $F_{\beta\beta}$ was dropped and the interaction constant, $F_{\alpha\beta}$, included. The observed frequencies were again reproduced with this new force field (treatment A), to within an average error of 0.1 cm^{-1} or 0.02%. However, the PED for this force field, given in Table

Table III. Internal Force Constants for F₂PCN^a

Force constant	Description	Value, ^b mdyn/Å	
		Treatment A	Treatment B
K_r	P-C str	3.04 ± 0.04	3.33 ± 0.03
K_t	C≡N str	17.39 ± 0.04	17.30 ± 0.04
K_s	P-F str	4.98 ± 0.02	4.98 ± 0.02
H_α	F-P-F bend	1.72 ± 0.03	2.13 ± 0.03
H_β	F-P-C bend	1.49 ± 0.02	1.20 ± 0.02
H_π	P-C≡N in-plane bend	0.11 ± 0.01	0.16 ± 0.01
H_σ	P-C≡N out-of-plane bend	0.15 ± 0.01	0.11 ± 0.01
F_{rr}	P-F str/P-F str	0.21 ± 0.02	0.21 ± 0.02
$F_{\beta\beta}$	F-P-C bend/F-P-C bend	0.0	-0.28 ± 0.02
$F_{\alpha\beta}$	F-P-F bend/F-P-C bend	0.30 ± 0.01	0.0

^a Valence force field constants. ^b All bending coordinates weighted by 1 Å.

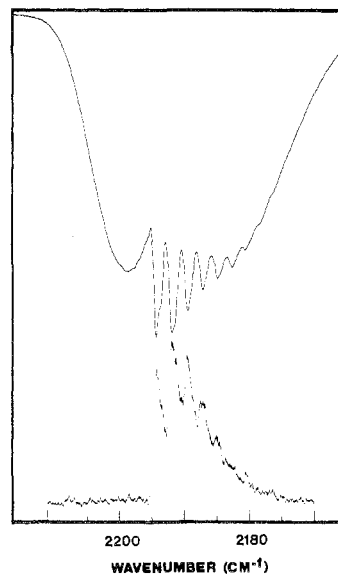


Figure 5. Spectra of gaseous cyanodifluorophosphine in the region of ν_1 , the C≡N stretch: upper trace, infrared; lower trace, Raman.

I, is not nearly so simple with the wag and scissors so badly mixed as to make a simplistic description of either of these modes impossible. In both cases Schachtschneider's perturbation program was used to adjust the force constants for a best fit to the observed frequencies and to test the constants for significance. Because of the importance of the JWJ matrix in the linear regression, the determinant of the matrix was tested after each iteration for singularity by comparing the product of the diagonal elements to the determinant, and these two quantities were found to be of similar magnitude. Several other interaction constants were tried besides $F_{\beta\beta}$ and $F_{\alpha\beta}$ but were found to be of little significance. The values of the internal force constants for both treatments A and B are given in Table III. An additional criticism of treatment B can be found in the value of H_α , the F-P-F bending force constant, where a value of 2.13 mdyn/\AA was found and is probably too large for a molecule of this kind. Otherwise, the values of the force constants are in reasonable agreement with those found for similar molecules.^{12,14}

Discussion

One of the most interesting features of the spectra of gaseous PF₂CN is the intense "hot" band series seen on the low-frequency side of the C≡N stretch. This region in the Raman and infrared is shown in Figure 5. The first "hot" band is almost as intense as the ground-state transition, and at least six additional lines are clearly distinguishable. Interestingly, no sum or difference bands of ν_1 with ν_6 or ν_9 are observed. The strong series of "hot" bands is repeated on the combination

band $\nu_8 + \nu_9$ seen near 550 cm^{-1} . If the other vibration involved in the "hot" band series is one of the PCN bending modes which are the lowest frequency fundamentals, a simple Boltzmann distribution does not account for the intensity of the observed series. For example, using ν_9 as the vibration which is excited, the population of the $v = 1$ level should be 48% of the ground state population and $v = 2$ less than 25%. It is possible, when the Boltzmann factor is on the order of unity, the intensity of such a $\nu_k + (\nu_1 - \nu_1)$ "hot" band is of the same order as that of the fundamental if the degree of coupling between the two vibrations is great enough.¹⁵ A similar effect has been observed for silacyclopentane by Durig and Willis.¹⁶

Although some evidence of the $2 \leftarrow 1$ transition of ν_9 was seen, the "hot" band transitions of ν_8 are apparently not very different in frequency from the $1 \leftarrow 0$ transition and are evident as a slight broadening of the main Q branch to the high-frequency side.

We have included the results of both normal-coordinate treatments to emphasize the danger of using normal-coordinate analysis to aid in the assignment of vibrational spectra. Both force fields reproduced the observed spectrum adequately, but we were forced to reject the assignment which gave the "cleaner" potential energy distribution in favor of one which we feel is more nearly correct.

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Small Metallocarboranes of Tin and Lead

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The polyhedral cage compounds $\text{SnC}_2\text{B}_4\text{H}_6$, $\text{PbC}_2\text{B}_4\text{H}_6$, $\text{Sn}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$, and $\text{Pb}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ have been prepared by reactions of SnCl_2 and PbBr_2 with the $\text{C}_2\text{B}_4\text{H}_7^-$ and $\text{C},\text{C}'-(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ ions in tetrahydrofuran. From their ^{11}B and ^1H NMR, IR, and mass spectra, these species were characterized as pentagonal-bipyramidal systems with the metal atom occupying an apex location and presumably directing an unshared electron pair outward from the polyhedron. The corresponding reactions employing GeI_2 gave highly unstable germacarboranes which were not isolated. Reactions of the $\text{C}_2\text{B}_3\text{H}_7^{2-}$ ion with SnCl_2 , PbBr_2 , and GeI_2 gave neutral 2,4- $\text{C}_2\text{B}_3\text{H}_7$, but no isolable heterocarborane products. The gas-phase reaction of $\text{Sn}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ gave 1,2,3- $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{CoSn}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$, a cage system containing tin and cobalt in the same polyhedron.

Introduction

Polyhedral carboranes containing an atom of germanium, tin, or lead (but not silicon) as an integral member of the cage have been known since Rudolph and co-workers¹ prepared $\text{MC}_2\text{B}_9\text{H}_{11}$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$) and Todd et al.² synthesized $\text{CH}_3\text{GeCB}_{10}\text{H}_{11}$. More recent work has produced $(\text{CO})_5\text{M-GeCB}_{10}\text{H}_{11}^-$ species³ in which an $\text{M}(\text{CO})_5$ ligand ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) is σ bonded to a germacarborane cage, as well as the germaphospha- and germaarsacarboranes⁴ $\text{GePCB}_9\text{H}_{10}$ and $\text{GeAsCB}_9\text{H}_{10}$. In addition, the 11-vertex *nido*-metallocarboranes $(\text{CH}_3)_2\text{GeB}_{10}\text{H}_{12}$ and $(\text{CH}_3)_2\text{SnB}_{10}\text{H}_{12}$ have been reported by Loffredo and Norman.⁵ Except for the latter two 11-atom cages, all of the above species are 12-vertex systems analogous to the prototype icosahedral carborane, $\text{C}_2\text{B}_{10}\text{H}_{12}$.

Other than bridged species such as $\mu\text{-(CH}_3)_3\text{MC}_2\text{B}_4\text{H}_7$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$)⁶ and $\mu\text{-(CH}_3)_3\text{M}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$ ($\text{M} = \text{Si}, \text{Ge}$)⁷ in which the metal is joined to the cage via a B-M-B three-center bond but is not fully a part of the cage framework, no examples of sub-icosahedral carboranes containing group 4 heteroatoms have been reported.⁸ Indeed, the only small

carboranes containing main-group heteroatoms of any type are the $\text{CH}_3\text{MC}_2\text{B}_4\text{H}_6$ species ($\text{M} = \text{Ga}, \text{In}$).⁹ During earlier studies in this laboratory,⁶ we explored the possibility that the group 4 bridged compounds $\mu\text{-GeH}_3\text{C}_2\text{B}_4\text{H}_7$, $\mu\text{-(CH}_3)_3\text{SnC}_2\text{B}_4\text{H}_7$, and $\mu\text{-(CH}_3)_3\text{PbC}_2\text{B}_4\text{H}_7$ and/or various silicon analogues of these could be converted to closed polyhedral heterocarboranes of the formula $\text{MC}_2\text{B}_4\text{H}_6$. These efforts were encouraged by the finding¹⁰ that the bridged species $\mu\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)Fe}(\text{CO})_2\text{C}_2\text{B}_4\text{H}_7$ is indeed converted to the *closo*-metallocarboranes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^{II}\text{C}_2\text{B}_4\text{H}_7$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^{III}\text{C}_2\text{B}_4\text{H}_6$ by ultraviolet irradiation; however, no such cage closure has been achieved with the group 4 compounds.

Since, on the other hand, the insertion of transition metal ions into small metallocarboranes such as $\text{C}_2\text{B}_4\text{H}_8$, $\text{C}_2\text{B}_3\text{H}_5$, and $\text{C}_2\text{B}_5\text{H}_7$ has generated a versatile and rich chemistry,¹¹ it appeared likely that this latter work could usefully be extended to some of the main-group elements. In this paper we describe the synthesis of some lower homologues of the $\text{MC}_2\text{B}_{n-2}\text{H}_n$ series as well as a novel cage system which incorporates both main-group and transition metals.