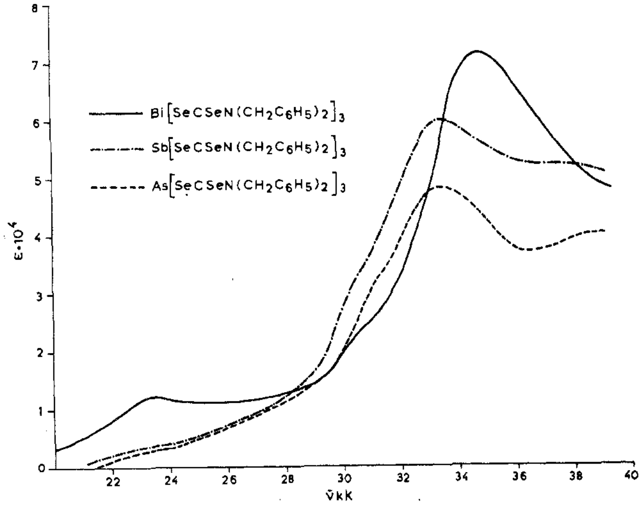

Figure 1. The absorption spectra of tris(dibenzyldiselenocarbamates) in chloroform.

of the bismuth compounds may be that the 6s lone pair electrons of the bismuth are more weakly bonded than the 5s and 4s lone pair electrons of the antimony and arsenic, respectively. Generally, the spectra of the prepared tdsc compounds, in both the visible and the ultraviolet regions, closely resemble those of the corresponding tdtc compounds except for a shift to lower frequencies. According to Cervone, *et al.*, this could be due to the smaller inter-electronic repulsions with selenium-containing ligands.[26]

Proton Nmr Spectra. The observed signals (Table II) in the pmr spectra appeared to be shifting to lower frequencies (smaller τ values) toward the signals of the corresponding protons of free amines. The shift differences are greater for those protons situated near the central atom and become smaller for those more distant. This is probably due to the deshielding effect which is less pronounced for the distant protons. The value of resonance frequencies is only slightly affected by the nature of the central metal atom and only a small shift to lower fields is observed as the electronegativity of the metal is decreased. But since the differences in the electronegativities of the central atoms are very small, it seems reasonable to accept the contribution of the back-donation effect as the cause of the observed shifting.

The proton signals of the studied tdsc compounds were observed to be shifted to lower magnetic fields relative to those of tdtc complexes. This difference could be correlated with the lower electron density around selenium atoms.

A very interesting feature of the nmr spectra of the studied compounds is that the resonance of methyl protons is shifted to lower magnetic fields going from As to Bi, but methylene protons have shown an inverse magnetic behavior and are shifted to higher magnetic fields going from As to Bi. While there is no simple way of theoretically explaining this phenomenon, perhaps the inverse effect can be correlated with the diamagnetic anisotropy contribution to methylene and methyl protons from the π-electron system in the $\mathrm{C}\overset{\cdots}{-}\mathrm{Se}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bonds. In some cases the methyl protons are possibly located in the paramagnetic region of the π current while the methylene protons are in the diamagnetic region. The proton signals of the coordinated diselenocarbamato groups in benzene solutions were observed to occur at higher fields than those observed in chloroform solutions (Table II). The benzene-induced solvent shifts are probably due to a benzene-solute interaction at the electron-deficient nitrogen atom of diselenocarbamato groups.

We have concluded here that on replacing sulfur by selenium in the studied carbamate complexes, there is little difference in the ionic character between the Se–M and S–M bonds and the molecular structure does not change significantly.

Registry No. $\mathrm{As[SeC(Se)N(C_2H_5)_2]_3}$, 41667-73-6; $\mathrm{Sb[SeC(Se)N(C_2H_5)_2]_3}$, 41667-74-7; $\mathrm{Bi[SeC(Se)N(C_2H_5)_2]_3}$, 25929-21-9; $\mathrm{As[SeC(Se)N(C_4H_9)_2]_3}$, 41667-76-9; $\mathrm{Sb[SeC(Se)N(C_4H_9)_2]_3}$, 41667-77-0; $\mathrm{Bi[SeC(Se)N(C_4H_9)_2]_3}$, 41667-78-1; $\mathrm{As[SeC(Se)N(CH_2C_6H_5)_2]_3}$, 41667-79-2; $\mathrm{Sb[SeC(Se)N(CH_2C_6H_5)_2]_3}$, 41667-80-5; $\mathrm{Bi[SeC(Se)N(CH_2C_6H_5)_2]_3}$, 41667-81-6.

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[26] E. Cervone, F. Cammassei, M. Luciani, and C. Furlani, *J. Inorg. Nucl. Chem.*, 31, 1101 (1969).

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2-Bis(trifluoromethyl)phosphinopentaborane (9) and Its Nickel Tricarbonyl Complex

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Recent repetitions of the synthesis of $1\text{-}(CF_3)_2PB_5H_8$ [1] led to the isolation of the isomer $2\text{-}(CF_3)_2PB_5H_8$. This isomer was not noticed before, presumably because of its unexpectedly high volatility and its irreversible conversion to the 1 isomer.

Synthesis. The initial experiment leading to the discovery of $2\text{-}(CF_3)_2PB_5H_8$ was performed as described before,[1] but the poor quality of the available butyllithium led to low yields (for example, 5% of the 2 isomer and 10% of the 1 isomer), and impurities, probably including $C_4H_9P(CF_3)_2$ and $C_4H_9OP(CF_3)_2$, could not be eliminated. For better results, ethyllithium was employed, with the special advantage that the formation of LiB_5H_8 could be monitored by isolating the coproduced ethane. One fairly successful experiment was based upon the reaction of a 10-mg piece of bright lithium (freshly cut under dry methane) with C_2H_5Br (2 mmol) in ether[2] during 12 hr at −45° in a tube attached to the high-vacuum line. The formation of ethylene did not exceed 2%, *vs.* 100% in a parallel experiment at 25°.

For other experiments, a newly delivered commercial sample of LiC_2H_5 in benzene was filtered from the black precipitate, crystallized from the dark-brown solution, and redissolved in dry benzene to make a 0.7 *M* stock solution. Measured portions of this were freed of benzene in the high-vacuum line and redissolved in ether at −78°.

The best yield came from an experiment using 1.075 mmol of LiC_2H_5 with 1.312 mmol of B_5H_9, yielding 1.075 mmol of C_2H_6 during 2 hr at −50°; then 1.033 mmol of $(CF_3)_2PCl$, mixed in at −125°, reacted during a warm-up to −78° (12 hr). The ether and excess B_5H_9 were distilled off *in vacuo* at −45° and the phosphinopentaboranes were delivered during slow warming, finally to 50°. They were separated by repeated fractional condensation at −20 to −30°. The yield of $2\text{-}(CF_3)_2PB_5H_8$ was 0.158 mmol; of $1\text{-}(CF_3)_2PB_5H_8$, 0.331 mmol; total, 0.484 mmol or 45%.

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[1] A. B. Burg and H. Heinen, *Inorg. Chem.*, 7, 1021 (1968).

[2] T. V. Talalaeva and K. A. Kocheshkov, *J. Gen. Chem. USSR*, 23, 399 (1953).

It is quite probable that $(CF_3)_2PCl$ suffers base-catalyzed destruction, parallel to its conversion to phosphinopentaboranes. The earlier report of a 57% yield was based upon LiB_5H_8 with a 60% excess of $(CF_3)_2PCl$, none of which could be recovered.[1] On the basis of consumed $(CF_3)_2PCl$, therefore, the original yield was only 36%. Better results must depend upon laborious attempts to minimize the destructive side reaction.

Quest for the B-P-B Bridged Isomer. One experiment was planned for possible recognition of 2,3-μ-$(CF_3)_2PB_5H_8$, as the expected first product of the LiB_5H_8-$(CF_3)_2PCl$ reaction at low temperatures. The crude product, with ether and B_5H_9 removed at −60°, was poured *in vacuo* into an nmr tube which then was sealed off, all without warming the product above −60°. The ^{11}B nmr spectrum at −60° showed no sign of a third isomer; in particular, there was no signal in the region 40-45 ppm upfield of methyl borate, where B-P-B bridged boron had been seen for other phosphinopentaboranes.[1] The spectrum was just as expected for a mixture of the 1 and 2 isomers and did not change significantly on warming to 35°.

Isomerization Effects. The absence of isomerization during the warm-up to 35° implies a question about the manner of formation of the 1 isomer. If the B-P-B bridged isomer was the actual first product, it must have converted very rapidly to the 2 isomer. But it is well known that 1-2 isomerization of B_5H_9 derivatives is base catalyzed, and the strong base LiB_5H_8 always is present until its reaction with $(CF_3)_2PCl$ is complete. Accordingly, $2 \rightarrow 1$ isomerization could occur during the reaction, but not after the LiB_5H_8 has been used up. The consensus of a number of experiments would suggest that mixing the $(CF_3)_2PCl$ into the LiB_5H_8 solution at −78° gives a higher ratio of the 2 isomer to the 1 isomer, but the overall yields may be higher if the reaction is started at lower temperatures.

Pure 2-$(CF_3)_2PB_5H_8$ remained stable for at least 24 hr in a sealed tube at 25° without a catalyst, but 7% conversion to the 1 isomer occurred when the molecular weight of the vapor was determined (found, 232.5; calcd, 231.0), during 1 hr at 70° in the presence of mercury vapor. A 66-mg sample, left for 36 hr with a catalytic trace of hexamethylenetetramine at 25°, was found to be completely isomerized. As little as 0.1% presence of 2-$(CF_3)_2PB_5H_8$ could have been detected in the infrared spectrum of a top fraction but was absent. Thus, it seems that 1-$(CF_3)_2PB_5H_8$ is even more resistant to isomerization than 1-IB_5H_8.[3]

Volatility. The equilibrium vapor pressures of 2-$(CF_3)_2PB_5H_8$ are described by the equation $\log P = 6.312 + 1.75 \log T - 0.005T - 2486/T$ (observed examples: 4.5 mm at 18.9°, 6.0 mm at 23.2°, 9.8 mm at 32.1°, 16.3 mm at 41.0°, and 28.0 mm at 52.5°; calcd, 4.5, 5.9, 9.8, 16.4, and 28.0 mm), giving the normal boiling point as 147° and the Trouton constant as 21.0 eu. The 80% lower volatility of 1-$(CF_3)_2PB_5H_8$ is not easily understood on the basis of pyramid stacking, for the CF_3 groups would be expected to interfere with the van der Waals attraction of 1-P for the basal B_4 square of the next molecule.

Nmr Spectra. The magnetic resonance spectra for four different nuclei in 2-$(CF_3)_2PB_5H_8$ were recorded by the Varian HA-100 instrument in the HR mode, with chemical shifts measured by tube substitution. The proton spectrum (Figure 1) is consistent with a 2-pentaborane derivative, although the 1-BH and 4-BH signals are not so recognizable as the four major peaks for the 3,5-BH. The ^{11}B spectrum (Figure 2) also superposes the three basal BH signals, but the high resolution for 1-BH indicates minimal 1-$(CF_3)_2PB_5H_8$ impurity. The ^{31}P spectrum appeared as a ragged peak 36 ppm upfield of H_3PO_4, presumably representing a blurred quartet of septets. The ^{19}F spectrum was a clean (slightly broadened) doublet 48.6 ppm upfield of Cl_3CF ($J = 68$ cps). In one sample, 1-$(CF_3)_2PB_5H_8$ was seen as a 2% impurity: its well-separated doublet ($J = 70$ cps) was easily observed 1.0 ppm farther upfield. These fluorine spectra offer the best means of analysis of a mixture of both isomers.

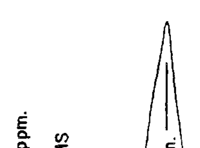

Figure 1. Proton nmr spectrum of 2-$(CF_3)_2PB_5H_8$. The most recognizable multiplet is the 1:1:1:1 quartet for the 3-BH and 5-BH units, with the second and third peaks raised by superposition with the 1-BH and 4-BH signals, which complicate the fourth peak. These 1-BH and 4-BH quartets have their fourth peaks buried under the major singlet for the BHB bridging protons, disturbing its symmetry.

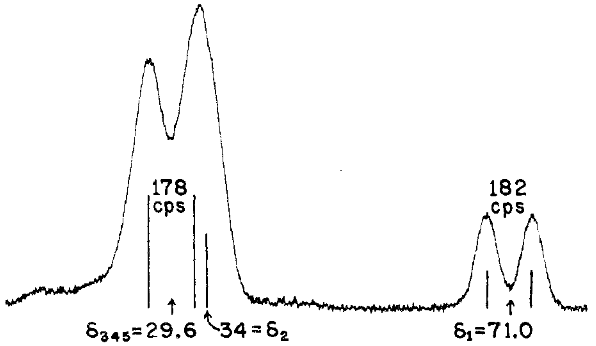

Figure 2. Boron nmr spectrum of 2-$(CF_3)_2PB_5H_8$, with δ values measured in parts per million upfield from methyl borate. The 178-cps coupling constant for the 3, 4, and 5 BH units is assumed from the proton spectrum. The 2-B signal is assumed to be a singlet, since B-P coupling usually is not resolved for such compounds. The small low-field signal represents not an impurity, but a 2-kc residual side band for 1-B.

Infrared Spectra. For comparison, the infrared spectra of the two isomers were recorded to 1-cm^{-1} accuracy by a well-calibrated Beckman IR7 instrument with NaCl and CsI optics. The frequencies (cm^{-1}) of the peaks are listed as follows, with relative intensities in parentheses. The question marks indicate peaks too complex for accurate measurement of frequency. It is noticed that the more symmetrical 1 isomer shows fewer peaks, as expected.

1-$(CF_3)_2PB_5H_8$: 2626 (6.7), 1865 (2.5), 1470 (2.5), 1434 (2.8), 1395? (1.7), 1292? (0.4), 1189 (28), 1153 (40), 1141 (42), 1105 (22), 1060 (0.2), 1033? (0.2), 993? (0.1), 903? (2.3), 883 (2.9), 805 (0.3), 741 (0.6), 678 (2.7), 558 (0.6), 458 (4.5), 435 (1.1).

2-$(CF_3)_2PB_5H_8$: 2627 (14), 2618 (12), 1930? (0.1), 1882 (0.3), 1842 (1.3), 1500? (0.5), 1455 (2.3), 1403 (8), 1319 (0.4), 1288 (0.7), 1190 (48), 1158 (53), 1136 (54), 1109 (25), 1038 (1.6), 976 (0.5), 923 (3.4), 888 (4.6), 847 (1.3), 747

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

(1.2), 697 (1.0), 670 (3.4), 612 (1.7), 570 (1.4), 545 (0.5), 498? (0.4), 453 (7), 419 (1.4).

Nickel Carbonyl Complex. The question whether 2-$(CF_3)_2PB_5H_8$ could form a ligand-$Ni(CO)_3$ complex without isomerization to the known 1-$(CF_3)_2PB_5H_8Ni(CO)_3$[4] was answered affirmatively by an experiment employing 0.250 mmol of nearly pure 2-$(CF_3)_2PB_5H_8$ with 0.2 ml of $Ni(CO)_4$ left together for 1 hr at 0°. The evolution of CO (0.250 mmol) began rapidly and was soon complete. The reaction occurred in a vertical tube, to the top of which was sealed an inverted nmr tube. A side arm connected the system through a horizontal ground joint to the high-vacuum line, permitting rotation for pouring the product into the nmr tube. The sealed-off nmr tube was used for four-element nmr spectra, again recorded by the Varian HA-100 instrument. Minor formation of a low-density dark brown precipitate (at the 35° probe temperature) did not interfere with the results.

The proton nmr spectrum appeared much like Figure 1, except that the major quartet was centered at 2.04 ppm downfield of TMS ($J = 174$ cps), while the asymmetric BHB peak maximized at +2.52. This obviously is different from 1-$(CF_3)_2PB_5H_8Ni(CO)_3$, for which the corresponding numbers are -2.74 ($J = 169$ cps) and +1.95 ppm.[4] The ^{19}F spectrum was a doublet at 57.0 ppm upfield of Cl_3CF ($J = 73$ cps), sharing a peak with the doublet for 1-$(CF_3)_2PB_5H_8Ni(CO)_3$ (57.8 ppm, $J = 75$ cps),[4] present as a 10% impurity. Thus, the isomeric impurity confirmed the 0.8-ppm difference of chemical shift. The ^{31}P spectrum again was only poorly recorded but could be seen as a ragged peak 15 ppm downfield of H_3PO_4. The signal:noise ratio was no greater than 3, but six repetitions of the scan left no doubt of a genuine signal.

The ^{11}B spectrum for 2-$(CF_3)_2PB_5H_8Ni(CO)_3$ was almost the same as Figure 2, but with subtly different parameters: δ_{345} 29 ± 0.5 ppm ($J = 175$ cps); δ_2 32.1 ppm; δ_1 70.0 ppm ($J = 178$ cps). Unlike the 1-isomer complex, 2-$(CF_3)_2PB_5H_8Ni(CO)_3$ failed to show B–P coupling, perhaps partly on account of superposition with the doublets belonging to the three other basal boron atoms.

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Registry No. 1-$(CF_3)_2PB_5H_8$, 19570-53-7; 2-$(CF_3)_2PB_5H_8$, 41699-88-1; 2-$(CF_3)_2PB_5H_8Ni(CO)_3$, 41699-89-2; B_5H_9, 19624-22-7; $(CF_3)_2PCl$, 650-52-2.

(4) A. B. Burg and I. B. Mishra, *J. Organometal Chem.*, **24**, C33 (1970).

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Hydrosulfides of Group I and Group II Metals

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A recent report by Petzel[2] prompts us to report the work going on in our laboratories on the reaction of the alkali and alkaline earth metals with hydrogen sulfide in liquid ammonia as well as the general studies on the systematic chemistry of the alkali and alkaline earth hydrosulfides and sulfides. Although the formation of the alkali and alkaline earth metal sulfides and polysulfides from the elements in liquid ammonia has been extensively studied,[3-6] the reaction system $M\text{-}H_2S$ in liquid ammonia (where M = group I or II metals) has drawn detailed attention only recently. Nelson and Lagowski[7] have suggested that the equilibrium of hydrogen sulfide in liquid ammonia to give the solvated hydrosulfide ion accounts for the formation of potassium hydrosulfide even when an excess of the metal is present in the solution. In the alkaline earth series Petzel has described good preparative methods for the sulfides starting from the reaction of hydrogen sulfide with the alkaline earth metal in liquid ammonia. Since the anhydrous hydrosulfides of the alkaline earth series have not been previously reported, our syntheses of these compounds help to resolve the seeming conflict between the observations of Lagowski and Petzel.

Experimental Section

Rubidium and cesium (99.99%, Alfa Inorganics) were separated under hard vacuum into smaller quantities (50–500 mg) in break-seal Pyrex ampoules before further use. Calcium, strontium, and barium were vacuum distilled by the method of Moyer, *et al.*[8] Hydrogen sulfide (Matheson Co.) was distilled through two traps at −80° and one at −112° and was collected at −196°. Ammonia (Matheson Co.) was degassed under vacuum at −196° and dried over sodium at −64°.

Method I. In a controlled-atmosphere glove box, the metal was dissolved in 200 ml of anhydrous ammonia in a Pyrex vessel refrigerated at −77°. Hydrogen sulfide was bubbled through the solution until the blue color discharged. The white precipitate was filtered from the solution and washed with three 150-ml portions of liquid ammonia. The product was vacuum-dried in the entry lock to the box prior to further examination.

Method II. The vessel for these reactions was designed in the shape of an "H" and was attached to a standard vacuum line. The metal was deposited in one leg; a measured amount of hydrogen sulfide was frozen into the other at −196°. Anhydrous ammonia was then condensed at −196° into both legs until about 5 ml of solution could be formed on allowing the vessel to warm to −48°. One solution was added to the other by tipping the vessel. The solutions were periodically stirred by using a glass encapsulated metal stirrer activated with a hand magnet. The hydrogen generated was collected by freezing the solutions at −196° and removing the gas with a Toepler pump. The reactions were complete when no further H_2 evolved. The stable products were removed from the vacuum line under an atmosphere of ammonia, after prior vaporization of the solvent. The unstable calcium and strontium products were degassed at −45° to remove the solvent ammonia and then warmed to room temperature with collection of the evolved gases. Hydrogen sulfide was separated from the gaseous mixture using Ascarite at −23°. Gases were analyzed using an Associated Electrical Industries MS 10 mass spectrometer.

Product handling was done in a nitrogen-flushed glove bag. All solids were characterized using Debye–Scherrer X-ray powder diffraction techniques. Thermal analyses were performed on the Du Pont 990 thermal analyzer system at typical scan times of 2–10° min^{-1} in the 0.4-mV/in. response range in a stream of pure argon.

Sulfur analyses of barium hydrosulfide hydrolyses products were determined by gravimetric methods as barium sulfate.

Results and Discussion

In work initiated some years ago[9] white precipitates were

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(1) Address correspondence to this author at the University of Connecticut.

(2) T. Petzel, *Z. Anorg. Allg. Chem.*, **396**, 173 (1973).

(3) "Gmelin's Handbuch der anorganischen Chemie," Verlag Chemie, Berlin.

(4) "Handbook of Preparative Inorganic Chemistry," Vol. 1, G. Brauer, Ed., 2nd ed, Academic Press, New York, N. Y., 1963.

(5) G. Watt, *Chem. Rev.*, **46**, 289 (1950).

(6) J. J. Lagowski and G. A. Moczygemba in "The Chemistry of Nonaqueous Solvents," Vol. II, J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1967, p 354.

(7) J. T. Nelson and J. J. Lagowski, *Inorg. Chem.*, **6**, 862 (1967).

(8) R. O. Moyer, Jr., C. Stanitski, J. Tanaka, M. I. Kay, and R. Kleinberg, *J. Solid State Chem.*, **3**, 541 (1971).