These evidences seem to suggest that the complexes of the type $[\mathrm{Co(PhP(OC_2H_5)_2)_4X}]\mathrm{BPh_4}$ ($\mathrm{X^-} = \mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{N_3^-}$, $\mathrm{NCS^-}$) are five-coordinate and they appear to be the first compounds of cobalt(II) with the donor atom set $\mathrm{P_4X}$ in which the phosphine ligands are monodentate.

The solution data have been obtained by dissolving the complexes in the presence of an excess of free ligand to force the dissociative process to the left

$$[\mathrm{CoL_4X}]^+ \longleftrightarrow [\mathrm{CoL_3X}]^+ + \mathrm{L} \qquad (1)$$

($\mathrm{L} = \mathrm{PhP(OC_2H_5)_2}$). Evidence for the existence of such equilibrium has been also obtained from the study of the electronic spectra in 1,2-dichloroethane or nitrobenzene in the visible region. When free ligand is not present the absorption spectrum, as for example the spectrum of $[\mathrm{Co(PhP(OC_2H_5)_2)_4I}]\mathrm{BPh_4}$ (Figure 1), shows a multiple band that, on the basis of the similarity with other four-coordinated phosphine cobalt(II) complexes, has been tentatively attributed to the $[\mathrm{Co(PhP(OC_2H_5)_2)_3X}]^+$ species. Since Beer's law is obeyed in the range 10^{-4} to 5×10^{-3} *M* both in polar and nonpolar organic solvents it is probable that in these conditions the equilibrium 1 lies completely to the right. Addition of free $\mathrm{PhP(OC_2H_5)_2}$ to the solution causes the spectrum in the range 5000–22,000 cm^{-1} to change. When there is approximately a 50-fold molar excess of phosphine with respect to complex, further addition of ligand has no effect upon the spectrum which now closely resembles that of the complex in its solid state (Figure 2). The spectral data reported in Table II and Figure 2 relate to solutions containing nearly a 100-fold molar excess of the phosphine. The similarity of both the electronic spectra and the magnetic moments in solution and in solid suggests that, under such conditions, the coordination and probably also the geometrical structure around the cobalt atom could be the same.

A comparison of the electronic spectra of the complexes reported here with those of the already known compounds[4] $[\mathrm{Co(QP)X}]\mathrm{BPh_4}$ which have a trigonal-bipyramidal structure and those of $[\mathrm{Co(AP)_2X}]\mathrm{ClO_4}$ complexes[11] (AP = diphenyl(*o*-diphenylarsinophenyl)-phosphine) for which Dyer and Meek proposed a square-pyramidal structure shows rough similarities. Studies are in progress to correlate the position of the band maxima in the 5000–22,000 cm^{-1} region to the d–d transitions and to find a relationship between electronic spectra and geometrical structure.

However, further useful information can be obtained from the infrared absorption spectra of the solids which are reported in Table III.

$[\mathrm{Co(PhP(OC_2H_5)_2)_4NCS}]\mathrm{BPh_4}$ and $[\mathrm{Co(PhP(OC_2H_5)_2)_3(NCS)_2}]$ have a strong peak at 2060 and 2066 cm^{-1}, respectively, assigned to the CN stretching vibrations of NCS terminal groups bonded to the metal atom through the nitrogen.[13] The presence of only one band in the second complex indicates that the two thiocyanato groups are trans.

The absence of bands in the 2150–2180-cm^{-1} region indicates[13] the absence of bridging NCS groups and therefore the complexes can be considered to be five-coordinate. The lower CN stretching frequencies of the second and third compounds reported in Table III, compared with the ν(CN) frequencies of the last two thiocyanato complexes, are probably due to the fact that π interactions from the metal to the phosphine ligands in the case of alkyl or aryl tertiary phosphines or diphosphines are weaker than in the case of phenyldiethoxyphosphine.

TABLE III

INFRARED DATA FOR SOME COBALT(II) COMPLEXES IN SOLID

Compound	ν(CN), cm^{-1}	$\nu(\mathrm{N_3})$, cm^{-1}
$[\mathrm{Co(PhP(OC_2H_5)_2)_4N_3}]\mathrm{BPh_4}$		2062
$[\mathrm{Co(PhP(OC_2H_5)_2)_4NCS}]\mathrm{BPh_4}$	2060	
$[\mathrm{Co(PhP(OC_2H_5)_2)_3(NCS)_2}]^a$	2066	
$[\mathrm{Co(Ph_2P(CH_2)_2PPh_2)_2NCS}]\mathrm{ClO_4}^b$	2083	
$[\mathrm{Co(PR_3)_3(NCS)_2}]^c$	2080	

[a] In 1,2-dichloroethane solution with $[\mathrm{PhP(OC_2H_5)_2}] = 0.1$ *M*, ν(CN) is 2064 cm^{-1}. [b] From ref 1. [c] From ref 2. $\mathrm{PR_3}$ is alkyl or aryl phosphine.

On substitution of one neutral ligand in the complex $[\mathrm{Co(PhP(OC_2H_5)_2)_4NCS}]\mathrm{BPh_4}$ by thiocyanate to give $[\mathrm{Co(PhP(OC_2H_5)_2)_3(NCS)_2}]$, the CN stretching frequency does not change very much (from 2060 to 2066 cm^{-1}). This may indicate that the electronic density on the central metal atom is roughly the same in both cases.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO 80302

1-(Chlorosilyl)pentaborane(9)[1]

BY THOMAS C. GEISLER AND ARLAN D. NORMAN*

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Previously, we reported the preparation and properties of 2- and μ-(halosilyl)pentaboranes(9).[2] Recently, our studies have been extended to include 1-silylpentaboranes. In this connection, we have prepared and characterized $1\text{-}(\mathrm{ClSiH_2})\mathrm{B_5H_8}$. These results are shown below. In addition, vapor tension *vs.* temperature data for $1\text{-}\mathrm{SiH_3B_5H_8}$ are reported which serve to complete the description of its physical properties.[3]

Experimental Section

Apparatus and Techniques.—All work was carried out in a standard high-vacuum system.[4,5] Vapor pressure *vs.* temperature data were obtained using an all-glass immersible tensimeter which had been predried with $\mathrm{SiH_3Br}$ for a period of 12 hr. Samples were frozen to −196° between pressure measurements to minimize decomposition. Melting points were obtained by the Stock method. Infrared spectra were obtained with Beckman IR-12 and Perkin-Elmer Model 337 spectrometers on gaseous samples in a 10-cm cell fitted with KBr windows. Proton nuclear magnetic resonance spectra were recorded at 60.0 MHz

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using a Varian Associates A-60A spectrometer with standard low-temperature accessories. Proton chemical shifts are reported relative to internal $(CH_3)_4Si$. The $^1H-\{^{11}B\}$ decoupling was accomplished using standard "noise" decoupling techniques. Boron-11 chemical shifts were measured relative to external $B(OCH_3)_3$ [δ −18.1 ppm from $BF_3 \cdot O(C_2H_5)_2$]. Chemical shifts are reported relative to $BF_3 \cdot O(C_2H_5)_2$. Mass spectra were obtained on a Varian MAT CH-7 spectrometer.

Materials.—Boron trichloride (Matheson Co.) was purified by fractional condensation prior to use.

Gas-phase pyrolysis of 2-$SiH_3B_5H_8$,[6] followed by high-vacuum column distillation, resulted in a high yield of 1-$SiH_3B_5H_8$ which was identified by ^1H nmr, ^{11}B nmr, and mass spectral data.[3] The vapor pressure *vs.* temperature data for 1-$SiH_3B_5H_8$, which were not reported earlier,[3] are given in Table I. The data conform to

TABLE I

VAPOR PRESSURE *vs.* TEMPERATURE DATA FOR 1-$SiH_3B_5H_8$

Temp, °C	P, mm		Temp, °C	P, mm	
	Obsd	Calcd		Obsd	Calcd
0.0	6.4	6.5	34.7	44.5	44.5
6.7	10.1	9.8	41.4	61.4	61.5
13.3	14.2	14.4	48.9	86.8	86.8
20.4	21.6	21.3	−0.1[a]	6.3	6.5
27.4	31.1	30.8			

[a] Pressure observed while decreasing temperature.

the equation $\log P = (-2042.2/T) + 8.2249$. The extrapolated boiling point is 105.7°, the molar heat of vaporization is 9.26 kcal, and Trouton's constant is 24.5 cal mol^{-1} deg^{-1}.

Synthesis of 1-($ClSiH_2$)B_5H_8.—Boron trichloride (0.30 mmol) and 1-$SiH_3B_5H_8$ (1.47 mmol) were condensed into a 25-ml Pyrex tube at −196°. The reactants were allowed to warm to room temperature and react for 30 min with occasional shaking. Volatile products were removed and passed through a −95° trap and into a −196° trap. No hydrogen was detected and nothing remained in the reaction tube. Condensing in the −196° trap was B_2H_6 which contained small amounts of B_2H_5Cl and $BHCl_2$ (0.16 mmol total; confirmed by ir spectrum[7,8]). The materials in the −95° trap were separated by high-vacuum column distillation and found to consist of 1-$SiH_3B_5H_8$ (0.58 mmol) and 1-($ClSiH_2$)B_5H_8 (0.84 mmol). No other volatile products were detected. The 1-($ClSiH_2$)B_5H_8 melts at −41.30 ± 0.01°. Vapor pressures of 0.5 mm at 0° and 1.6 mm at 20° were observed. Limited thermal stability prevented further vapor pressure *vs.* temperature data. A sharp cutoff in its mass spectrum was observed at *m/e* 132 (calcd for $^{37}Cl^{30}Si^{11}B_5H_{10}$, 132). The infrared spectrum (cm^{-1}; 2 mm pressure) showed 2615 (s), 2165 (vs), 1855 (w), 1495 (w, b), 1410 (w, b), 1060 (w), 960 (sh), 955 (m), 950 (sh), 885 (m), 835 (s), 675 (w), and 530 (m). The ^{11}B nmr spectrum exhibits resonances at δ 12.4 ppm (doublet, J = 168 Hz; area 3.95) and δ 58.0 ppm (singlet; area 1.00).

The ^1H nmr spectrum consists of three resonances: δ −2.66 (quartet, J = 168 Hz, area 4), 1.67 (broad singlet, area *ca.* 4), and −4.78 ppm (1:1:1:1 quartet at 34°, J = 10.4 Hz, area 2).

The decomposition of weighed samples of 1-($ClSiH_2$)B_5H_8 for elemental analysis was accomplished by hydrolysis for 12 hr at 95° with 2 ml of 2 *N* KOH, followed by the addition of 1 ml of 6 *N* HNO_3 and an additional 12 hr hydrolysis at 95°. Hydrolytic hydrogen was calculated according to the equation

$$ClSiH_2B_5H_8 + 17H_2O \longrightarrow SiO_2 + 5B(OH)_3 + HCl + 14H_2$$

Anal. Calcd: 27.8% Cl and 110 mmol/g of H_2. Found: 28.7% Cl and 110 mmol/g of H_2.

Results and Discussion

Boron trichlororide reacts smoothly with 1-$SiH_3B_5H_8$ to yield 1-($ClSiH_2$)B_5H_8 in essentially quantitative yield (>95%) according to

$$2BCl_3 + 6(1\text{-}SiH_3B_5H_8) \longrightarrow B_2H_6 + 6[1\text{-}(ClSiH_2)B_5H_8]$$

Halogenation occurs exclusively at the silicon atom. No evidence of reaction with the pentaborane cage or the Si–B bond is obtained. These observations parallel those of our earlier studies of analogous BCl_3–chlorination reactions of μ-and 2-$SiH_3B_5H_8$.[2] Within the limits of our experimental data no significant difference is observed in the ease of halogenation of the two isomeric, terminally bonded silylpentaboranes. The 2-$SiH_3B_5H_8$ and 1-$SiH_3B_5H_8$ react within 30 min between 0° and room temperature. However, the μ-$SiH_3B_5H_8$ is incompletely reacted after 4 hr at 45°. Thus our data allow only the conclusion that the rates of BCl_3 chlorination of the silylpentaborane isomers are $\mu < 1 \simeq 2$.

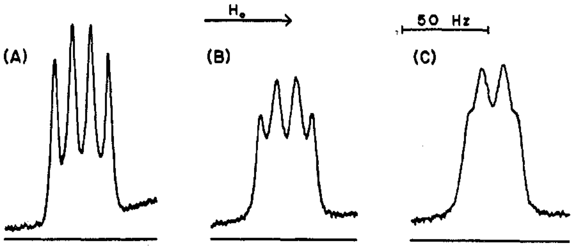

Figure 1.—The SiH_2 resonance in the ^1H nmr spectrum of 1-($ClSiH_2$)B_5H_8 at 34° (A), −71° (B), and −85° (C).

The spectral data obtained for 1-($ClSiH_2$)B_5H_8 provide for its unequivocal characterization. The mass spectrum exhibits a fragmentation pattern consistent with that observed for μ- and 2-(halosilyl) pentaboranes (9) and the presence of the weak molecular ion at *m/e* 132 confirms the molecular weight. The infrared spectrum shows characteristic Si–H, B–H (terminal), and B–H (bridge) stretching adsorptions at 2165, 2615, and 1855 cm^{-1}, respectively.[9–11] The resonances in the ^{11}B nmr spectrum at δ 12.4 (doublet, area 4) and 58.0 ppm (singlet, area 1) are attributed to the basal (B_{2-5}) and apical (B_1) boron atoms, respectively. The ^1H nmr resonances are assigned as δ −2.66 (terminal BH protons), 1.67 (bridging hydrogens), and −4.78 ppm (SiH_2 protons).

The SiH_2 resonance in the ^1H nmr spectrum is temperature dependent. The effect is similar but more striking to that observed earlier for μ- and 2-(halosilyl)-pentaboranes.[2] Representative SiH_2 resonances are shown in Figure 1. At ambient probe temperature (34 ± 1°) the resonance appears as a 1:1:1:1 quartet. The quartet structure arises from coupling to the apical boron atom, and from this quartet a ^2J(HSiB) coupling constant of 10.4 Hz is obtained. The quartet collapses to a sharp singlet $\nu_{1/2}$ = 2.8 Hz upon $^1H-\{^{11}B\}$ double resonance verifying the coupling assignment. Cooling the sample results in partial collapse of the quartet to an approximate doublet at −85°. Within experimental error, the chemical shift position of the resonance is invariant with temperature change. Owing to the marginal stability of the 1-($ClSiH_2$)B_5H_8, spectra were not obtained at temperatures greater than 34°. As discussed in our earlier report of μ- and 2-(halosilyl)pentaboranes,[2] it appears that this temperature dependence in the spectra may be attributed to electric quadrupolar relaxation effects.[12]

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