trend indicated by the three available proton chemical shifts (see Table I) shows increasing σ-electron density on the metal with PF_3 substitution. The increase of the ^{55}Mn chemical shift with the number of PF_3 groups is in the expected direction; however, the linearity of the shift with substitution is surprising. The deviation of the chemical shift for $HMn(CO)_5$ reported here (2578 ppm) from the previous report[3] (2630 ppm) may be due in part to the lack of bulk susceptibility corrections for either measurement.

The line widths of the resonances observed are reported in Table I. These line widths appear to be insensitive to substitution for the first three PF_3 groups and then increase rapidly with the fourth and fifth substitutions. This unusual behavior prompted us to try a check of the relaxation mechanism to determine if factors other than the expected quadrupolar relaxation process were present. This was done by examining the temperature dependence of the line width of $HMn(CO)_5$ (the only compound available in sufficient quantity for the various measurements) between -10 and $+58°$. Viscosities (η) were measured[6] over the same temperature range for use in estimating the rotational correlation times (τ_c).[7] The line width of $HMn(CO)_5$ was found to be linearly dependent on the rotational correlation time, with zero intercept, indicating that quadrupolar relaxation is the predominant mechanism. Assuming that quadrupolar relaxation dominates for all of the compounds studied and that the viscosities do not vary significantly from compound to compound, we have estimated the rotational correlation times using maximum molecular radii estimated from empirical bond radii and van der Waals radii. These times are listed in Table I. From the correlation times and line widths, relative manganese nuclear quadrupole coupling constants for the entire series of compounds were calculated and are displayed in Table I and Figure 1. These quadrupole coupling constants vary with substitution in a much smoother way than the raw line-width data would suggest. Even so, we have been unable to discover any unique relative σ-donor and π-acceptor trends which would account for the apparent variation of quadrupole coupling constants.

In summary the ^{55}Mn nmr data for the series $HMn(CO)_{5-x}(PF_3)_x$ are consistent with the assumption that PF_3 is a better σ donor than CO. This result is consistent with Graham's force constant calculations[8] which indicate that, although PF_3 and CO are almost identical ligands in their bonding properties, PF_3 is a slightly better σ donor than CO. The relative π-acceptor properties cannot be distinguished with the present data.

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[6] The viscosity of $HMn(CO)_5$ in the range from -10 to 58° was found to obey the relation $\log \eta = (591/T) - 1.962$ with η in centipoise and T in degrees Kelvin.

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Evidence for Terminal Ethoxy Group Substitution in Ethoxydecaborane(14)

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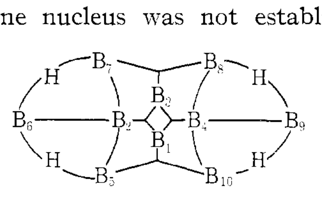
The preparation of ethoxydecaborane(14) from the reaction of iodine with a diethyl ether solution of decaborane was first reported by Hawthorne and Miller;[2] however, the position of C_2H_5O group substitution on the decaborane nucleus was not established. More recently, based on an interpretation of its 12.8-MHz ^{11}B nmr spectrum, it was suggested that the C_2H_5O group is located in a bridging (5,6-μ) position.[3] In view of the current interest in bridge substitution of boron hydrides, we have been prompted to reconsider the structure of this compound. To this end we prepared ethoxydecaborane and several of its deuterium-labeled derivatives and examined their 32.1-MHz ^{11}B nmr spectra. The results of this work are described below.



(B = B–H)

Experimental Section

Apparatus and Equipment.—All operations were carried out in an N_2-flushed glove bag or in standard vacuum line apparatus. Mass spectra were obtained using Varian Associates Model A-66 and CH-5 mass spectrometers. Electronic absorption spectra were obtained with a Cary 14 spectrophotometer. Boron-11 nmr spectra were obtained at 32.1 MHz on a Varian HA-100 spectrometer. Chemical shifts were measured relative to $B(OCH_3)_3$ (internal capillary) and are reported relative to $BF_3 \cdot O(C_2H_5)_2$. Boron-11 chemical shift values are given ±0.2 ppm. Spectra were calibrated using the integrator audiofrequency side bands. Spectra integrals were measured with a planimeter. Proton nmr spectra were obtained at 60-MHz using a Varian A-60A spectrometer. Proton chemical shifts were measured relative to internal $(CH_3)_4Si$.

Materials.—Diethyl ether and *n*-heptane were distilled from $LiAlH_4$. Iodine (Baker Chemicals), NaH (Metal Hydrides, Inc.), and NaD (Alfa Inorganics) were used without further purification. Perdeuteriodecaborane-d_{14} ($B_{10}D_{14}$) was obtained from the repeated exchange and equilibration of $B_{10}H_{14}$ in D_2O–dioxane and dioxane, respectively.[4] Complete exchange (estimated >90%) was verified by comparison of its ^{11}B nmr spectrum with $B_{10}D_{14}$ prepared from B_2D_6 (>96% D) pyrolysis.[5] The 1,2,3,4-decaborane-d_4 was prepared by a previously reported method[6] and was shown by ^{11}B nmr to be deuterium labeled exclusively in the 1,2,3,4 positions. Decaborane(14) ($B_{10}H_{14}$) and the deu-

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[1] National Science Foundation undergraduate research participant, summer 1968.

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terium-labeled samples were sublimed and stored under a dry N_2 atmosphere prior to use in an experiment.

Preparation of Ethoxydecaboranes.—Samples of $C_2H_5OB_{10}H_{13}$, $C_2H_5OB_{10}H_9D_4$, and $C_2H_5OB_{10}D_{13}$ were prepared from the reaction of iodine with diethyl ether solutions of $NaB_{10}H_{13}$, $NaB_{10}H_9D_4$, and $NaB_{10}D_{13}$, respectively.[2] Upon completion of a typical reaction, the reaction mixture was filtered and the filtrate was evaporated under vacuum until only a viscous oil remained. The oil was extracted with *n*-heptane. The heptane extract was allowed to stand over mercury for 5–10 min to decompose any unreacted iodine or iodinated products, the latter having been reported to form in the reaction.[7] The ^{11}B nmr spectrum of the heptane solution showed it to consist of a mixture of decaborane and ethoxydecaborane. Repeated passage of this mixture into a short-path-length U-tube distillation apparatus maintained at 0° resulted in removal of the decaborane and condensation of ethoxydecaborane in the 0° trap. The pure $C_2H_5OB_{10}H_{13}$ obtained and purified according to this procedure melts at 10° and exhibits an uv spectral absorption at 295 mμ.

Anal. Calcd for $C_2H_{18}B_{10}O$: C, 14.44; H, 10.90; B, 65.04; mol wt, 166.36. Found: C, 14.3; H, 11.0; B, 64.5; mol wt (vapor pressure lowering in pentane), 164.

The mass spectrum of $C_2H_5OB_{10}H_{13}$ exhibits a series of peak envelopes at *m/e* 10–168. The highest mass peak corresponds to the $C_2H_5O^{11}B_{10}H_{13}^+$ ion and is 14.5% (relative intensity) of the most intense peak at *m/e* 165. The two largest envelopes occur at *m/e* 126–138 and *m/e* 154–168, corresponding to $B_{10}H_xO^+$ and $B_{10}C_2H_xO$ ion fragments, respectively. No peaks were present above *m/e* 168 and no characteristic $B_{10}H_{14}$ parent peak envelope was present (*m/e* 106–124).

Ethoxydecaborane samples were transferred into nmr tubes *in vacuo* and diluted to 20–30% (by volume) solutions with $(CH_3)_4Si$.

Results and Discussion

The composition of the $C_2H_5OB_{10}H_{13}$ prepared in this study and its identity with the $C_2H_5OB_{10}H_{13}$ reported by Hawthorne and Miller[2] were established on the basis of elemental analysis, uv, ^{11}B nmr, ^1H nmr, and mass spectral data. Ethoxydecaborane exhibited an uv absorption at 295 mμ, in agreement with the previously reported[2] value of 295 mμ. The ^{11}B nmr spectrum (see discussion below) yielded spectral integrals consistent with those expected for a B_{10} hydride. The ^1H nmr spectrum exhibited a 1:3:3:1 quartet (δ −3.94 ppm, J = 7.2 cps; relative area 2.0) and a 1:2:1 triplet (δ −1.27 ppm, J = 7.2 cps; relative area 3.04), assignable to C_2H_5O group protons, and a series of broad poorly resolved peaks in the base line of the spectrum, due to protons on boron. No diethyl ether resonance peaks, at δ −3.36 and −1.16 ppm,[8] were observed. The mass spectrum of $C_2H_5OB_{10}H_{13}$ exhibits peaks from *m/e* 10–168, which can be assigned to $^{10}B^+$–$^{11}B_{10}H_{13}OC_2H_5^+$ ion fragments, respectively. The absence of peaks above *m/e* 168 precludes the existence of measurable quantities of iodinated decaboranes or decaborane derivatives containing more than one C_2H_5O group. The notable absence of a peak envelope in the *m/e* 106–124 region and the fact that the molecular weight, determined by vapor pressure lowering in pentane, is close to the theoretically expected value argue against the presence of significant quantities of $B_{10}H_{14}$ or other species of molecular weight lower than that of $B_{10}H_{13}OC_2H_5$.

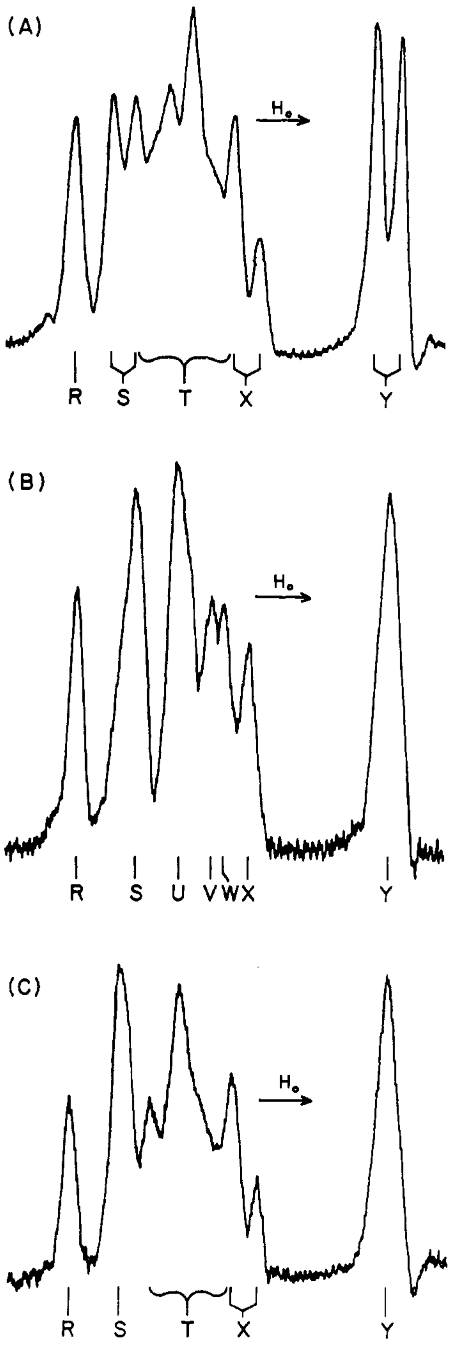

Figure 1.—The ^{11}B nmr spectra of $C_2H_5OB_{10}H_{13}$ (A), $C_2H_5OB_{10}D_{13}$ (B), and $C_2H_5OB_{10}H_9D_4$ (C).

Evidence for terminal C_2H_5O group substitution of $C_2H_5OB_{10}H_{13}$ and its deuterium-labeled derivatives was obtained from the ^{11}B nmr spectra. The spectrum of $C_2H_5OB_{10}H_{13}$ (Figure 1A) consists of a low-field *singlet* R (δ −21.8 ppm), a doublet S (δ −12.7 ppm, J = 138 ± cps), a group of overlapping doublet resonances T, a doublet **X** (δ 11.1 ppm, J = 160 ± 3 cps), and a high-field doublet Y (δ 38.6 ppm, J = 153 ± 3 cps). The relative areas of the resonances R:S:(T + X):Y are 1.0:2.05:4.95:1.96, in agreement with the ratio of 1.0:2.0:5.0:2.0 expected for a B_{10} hydride. A small peak on the low-field side of R appeared in several

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spectra after the samples had been at room temperature for extended periods of time. In each of these cases, small, additional peaks attributable to C_2H_5O groups were also present in the ^1H nmr spectrum. However, the mass spectra of the samples were not significantly different from those of initially prepared ethoxydecaboranes. It is possible that these resonances indicate the presence of a second isomer of ethoxydecaborane. Since the quantity of this second material was not great enough to affect markedly the spectral integrals or the appearance of the spectra, it was not considered further in the analysis.

The spectrum of totally deuterated ethoxydecaborane ($C_2H_5OB_{10}D_{13}$) shown in Figure 1B consists of singlet resonances (relative intensities in parentheses) R (1.00), S (2.18), U, V, W, X ($U + V + W + X = 4.82$), and Y (2.17). Comparison of the latter spectrum with that of $C_2H_5OB_{10}H_{13}$ (Figure 1A) indicates clearly that S, X, and Y have undergone doublet to singlet collapse upon deuterium labeling and that T is composed of three resonances (U, V, and W); however, the one-boron singlet R (δ −21.8 ppm) remains unchanged. The presence of a one-boron singlet (R) in the spectrum of ethoxydecaborane is incompatable with bridge (μ) C_2H_5O group substitution, since a bridge-substituted molecule would be expected to have one terminal hydrogen on each boron. Therefore, one must conclude that the C_2H_5O group occupies a terminal position on the decaborane nucleus.

The position of terminal C_2H_5O group substitution is suggested on the basis of a comparison of the ^{11}B nmr spectrum of basal deuterated ethoxydecaborane (1,2,3,4-$C_2H_5OB_{10}H_9D_4$) with those of $C_2H_5OB_{10}H_{13}$ and $C_2H_5OB_{10}D_{13}$ and by comparison of the ethoxydecaborane spectra with the spectra reported for the other terminally substituted decaboranes. The spectrum of $C_2H_5OB_{10}H_9D_4$ shown in Figure 1C consists of singlets (relative areas in parentheses) R (1.00), S (2.16), and Y (2.20) and overlapping resonances T and X ($T + X = 4.84$), in which peaks corresponding to four borons, S and Y, have undergone doublet to singlet collapse. These data rule out basal (B-1,2,3,4) C_2H_5O group substitution and allow, by comparison of the spectra with that of $B_{10}H_{14}$, resonances S and Y to be assigned to 1,3- and 2,4-boron atoms, respectively.[9,10] Substitution in the 6 position should give rise to resonance peaks of relative areas 1.0:2.0:2.0:1.0, due to boron atoms B-6, B-5,7, B-8,10, and B-9, while 5 substitution might yield six peaks, each of area 1.0. Also, alleged 6 substitution in other substituted decaboranes systems, *e.g.*, $ClB_{10}H_{13}$,[11] $B_{10}H_{13}OB_{10}H_{13}$,[11] $C_2H_5B_{10}H_{13}$,[12] $(C_6H_5)_2PB_{10}H_{13}$,[13,14] and $(CH_3)_3SiOB_{10}H_{13}$,[15] results in splitting of the 2,4 doublet, whereas 5 substitution does not. Since ethoxydecaborane exhibits peaks R, U, V, W, and X in a ratio which is inconsistent for a 6-substituted system (Figure 1B) and the high-field doublet Y shows no splitting (Figures 1A and 1C), we conclude that ethoxydecaborane is probably terminally substituted in the 5 position.

Although resonance R can be assigned to a terminally bonded boron and S and Y can be assigned to borons 1, 2, 3, and 4, our evidence does not allow unambiguous assignment of the remaining peaks. Final assignment awaits a complete study of specifically labeled ethoxydecaborane derivatives.

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