different kinds of carbonyl groups, which gives promise for its use in coordination chemistry. Another important advantage of the method is that super acid can protonate and, therefore, solubilize many neutrally charged compounds which are so insoluble in ordinary solvents that observation by nmr is virtually impossible. For example, Pt^{II}(gly)$_2$,[8] which is sparingly soluble in such solvents as chloroform, water, and dimethyl sulfoxide, dissolves readily in super acid, yielding a broad carbonyl region nmr pattern centered at 13.48 ppm.

It appears that this technique is limited to kinetically inert compounds, because EDTA chelates of Mg^{2+}, Ca^{2+}, and Pb^{2+} yield no discernible resonance in the 11–14-ppm range, probably because of their complete dissociation in super acid.

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Manganese Nuclear Magnetic Resonance of the Phosphorus Trifluoride Derivatives of Manganese Pentacarbonyl Hydride

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We have studied the ^{55}Mn nuclear resonances for the series of compounds $HMn(CO)_{5-x}(PF_3)_x$, $x = 0$–5, previously reported by Miles and Clark.[1] Resonances were obtained for the pure liquids in 5-mm evacuated nmr tubes using a Varian broad-line nmr spectrometer with a fixed-frequency 10-MHz radiofrequency unit. Magnetic field calibrations were obtained with an Alpha proton nmr magnetometer and a Hewlett-Packard 5246L frequency counter. Only a single manganese resonance was observed for each composition even though geometric isomers are present. For the intermediate compositions $x = 1$–4, more than one isomer is seen by ^{19}F and ^{1}H nmr (as separate resonances) and by infrared spectroscopy.[2] It is estimated that minor isomers can constitute 15–20% of each composition. This suggests that the isomers for the intermediate species have chemical shifts which differ by less than the line widths (200 ppm). No unusual line-width behavior was observed which could be attributed to the presence of isomers. This agrees with the observation of only a single broad resonance for a mixture of *cis*- and *trans*-$CH_3COMn(CO)_4(P[C_6H_5]_3)$.[3] In addition, there was no fine structure nor line-width trends that could be attributed to manganese–phosphorus coupling.

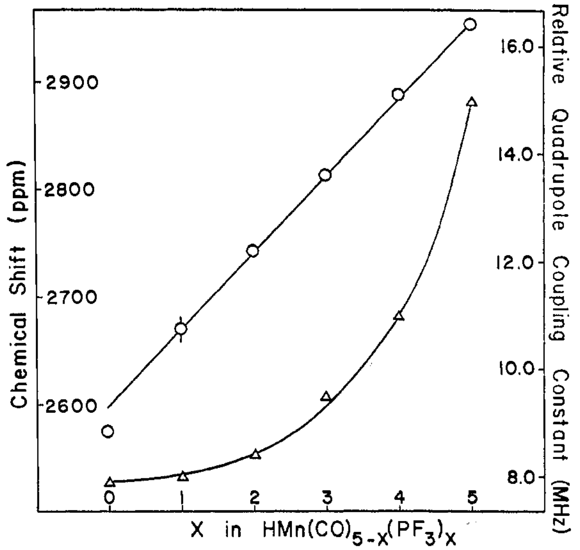

Figure 1.—The ^{55}Mn chemical shift (O) within the series $HMn(CO)_{5-x}(PF_3)_x$ and the relative quadrupole coupling constants (Δ) for the same series. The error bar of the chemical shift is shown for $HMn(CO)_4(PF_3)$ and is the same for the other members of the series.

The chemical shifts observed for this series of compounds, shown in Table I and Figure 1, are larger upfield (diamagnetic) shifts than previously observed for manganese.[3] This is to be expected, however, because substitution of PF_3 for CO also causes blue shifts in the optical spectra[4] of most $M(CO)_x(PF_3)_y$ systems. The blue shift has actually been observed by comparing the spectra of five of the manganese–hydride species. These increased electronic splittings attenuate the orbital mixing that leads to paramagnetic shifts such as those observed for cobalt(III) complexes.[5] It is also possible that diamagnetic susceptibility effects are important for these complexes which have very little paramagnetism. The trend of the diamagnetic contributions should be in the same direction as the paramagnetic terms in this series because the

TABLE I

NMR DATA FOR $HMn(CO)_{5-x}(PF_3)_x$

x	σ(^{55}Mn),[a,b] ppm	Line width,[c] G	Rotational correlation time,[d] τ_0, nsec	e^2qQ/h,[d] MHz	σ(H),[e] ppm
0	2578	2.28	0.22	7.9	38.7
1	2673	2.35	0.22	8.0	39.9
2	2742	2.21	0.19	8.4	41.8
3	2813	2.35	0.16	9.5	...
4	2888	3.20	0.16	11.0	...
5	2953	5.93	0.16	15.0	...

[a] Relative to saturated aqueous $LiMnO_4$ without bulk susceptibility corrections. [b] Estimated error ±10 ppm. [c] Derivative peak to valley line widths at 30°; estimated error ±0.05 G. [d] Estimated as described in text. [e] Absolute.

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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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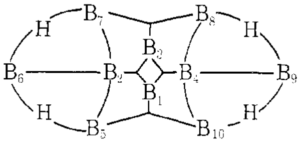
The preparation of ethoxydecaborane(14) from the reaction of iodine with a diethyl ether solution of decaborane was first reported by Hawthorne and Miller;[2] however, the position of C_2H_5O group substitution on the decaborane nucleus was not established. More recently, based on an interpretation of 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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