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Synthesis and Base Strengths of Some (ω-Methoxyalkyl)silanes and -germanes

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In an attempt to determine to what extent an electron-rich substituent is affected by a group 4 metal atom when not directly bonded to that metal atom, we have synthesized three series of compounds of the type $MH_3(CH_2)_nOCH_3$ in which M = C, Si, and Ge and n = 1–6. A comparison of their base strengths (proton affinities) as measured by the shift in the infrared OH stretching frequency of methanol upon complexation with the ethers shows that some factor(s) other than inductive effects significantly influences the electron-donating ability of oxygen in the silicon and germanium hydrides when n = 1 and 2. At n = 3–6, however, the basicities of these ethers converge toward those of the carbon analogs. The silicon and germanium compounds not previously known have been characterized by infrared, proton magnetic resonance, and mass spectra, vapor pressure data, and melting points.

Introduction

It is well documented that certain properties of organometallic compounds which contain a group 4 metal atom directly bonded to a potential electron donor are often anomalous compared to those of the carbon analogs.[1] Data from studies involving magnetic susceptibility,[2] dipole moments,[3] basicity,[4-6] bond lengths and bond angles,[7] and various kinds of spectra[8,9] have shown that many properties of organosilanes and -germanes are influenced by effects not evident in their carbon analogs. It has been suggested that these deviations are caused by an interaction which may be occurring between available vacant d orbitals on the group 4 metal atom (Si, Ge) and the lone pair of electrons on the directly bound donor atom (O, N, F).[10] The existence of a similar interaction between these atoms when they are not directly bound but separated by an intervening methylene group has also been suggested.[11] In the case of the SiH_3CH_2X compounds (X = halogen) the constancy of the dipole moments has been ascribed to the delocalization of electron density from the halogen to the silicon, an intramolecular interaction which decreases from Cl to Br to I.[3] There is little agreement, however, as to whether such anomalies in organosilicon hydrides cease when the donor substituent is beyond the β position; and too few data are available to assess the situation for organogermanium hydrides. We have, therefore, prepared a series of homologous (ω-methoxyalkyl)silanes and also (ω-methoxyalkyl)germanes in order to compare their properties to each other and to those of the appropriate carbon analogs in which no effects other than inductive are believed to occur.

The parameters chosen as indicative of possible donor–metal interaction were the base strengths of the $MH_3(CH_2)_nOCH_3$ compounds (M = C, Si, Ge; n = 0–6) and the PMR chemical shifts and coupling constants. Base strengths were determined by measuring the difference in the infrared spectra between the O–H stretching frequency of methanol when free and when hydrogen bonded to the group 4 ether. This shift has been shown to be directly related to the base strength of the ether[12] and presumably the electron availability on the Lewis base.

Experimental Section

Apparatus and Techniques. All synthetic work was carried out in a borosilicate glass vacuum system using standard vacuum techniques. Mass spectral data were obtained with a Du Pont Model 21-492 double-focusing spectrometer operating at 75 eV and 50 μA. PMR parameters were measured with a Varian Associates A-60A instrument whose probe temperature was 35°. Vapor-phase ir spectra were recorded using a 10-cm cell with KBr windows. Melting points were determined with a Stock magnetic plunger. Pressures were obtained using a mercury manometer which was read with the aid of a cathetometer. Temperatures beyond the range of the mercury thermometer were measured using an iron–constantan thermocouple with an ice-water reference junction.

Shifts in the stretching frequency between free and hydrogen-bonded O–H ($\Delta\nu$) were obtained with a Perkin-Elmer Model 421 grating spectrophotometer using linear scan (cm^{-1}). Typically, methanol and the ether of interest were condensed with either C_6H_{12} or CCl_4 as solvent to form a solution 0.02 M in MeOH and 0.2 M in ether. The resulting mixture was removed by means of a syringe through a serum cap and immediately injected into a 1-mm fixed-distance sodium chloride cell. A mixture containing only 0.2 M ether in the appropriate solvent was similarly placed in a matched cell for use as reference. A minimum of three spectra were recorded. No variation in $\Delta\nu$ was observed when the ether concentration was varied from 0.2 to 0.005 M while holding the methanol concentration at 0.02 M; similarly, the $\Delta\nu$ remained constant when the MeOH concentration was varied from 0.2 to 0.005 M with the ether concentration at 0.2 M.

Syntheses. The reference alkyl methyl ethers were synthesized by reaction of the appropriate 1-chloroalkane with $NaOCH_3$. Compounds of the $SiH_3(CH_2)_nOCH_3$ series in which n = 2, 4, and 6 and those of the series $GeH_3(CH_2)_nOCH_3$ in which n = 2, 3, 4, and 6 were prepared by the general reaction of $KSiH_3$ or $KGeH_3$ with the appropriate 1-haloalkyl methyl ether. Typically, 5 ml of hexamethylphosphotriamide (Fisher) in a 100-ml flask was degassed, refluxed under vacuum pumping for 10 min, and then cooled with an ice bath. The vessel was subsequently opened to the air, potassium (2.6 mg-atoms) was added, and the vessel was rapidly reevacuated. Silane or germane (2.7 mmol) was condensed into the flask and the solution was stirred in a bath just above 0° until all of the potassium had disappeared. The volatile products, which consisted of a condensable and noncondensable fraction at −196°, were discarded. The appropriate 1-haloalkyl methyl ether (2.5 mmol) was condensed onto the prepared $KSiH_3$ ($KGeH_3$), the solution was allowed to warm to room temperature, and after 15 min of stirring the volatile contents of the flask were removed. The ethers of interest were separated by trap-to-trap fractionation and purified by low-temperature distillation. The yield, distillation temperature, and characterization of each of the compounds prepared in this fashion are given below. The $(M - 1)^+$ ions characteristic of silanes were observed in each case in less than 10% abundance.

$SiH_3(CH_2)_2OCH_3$. The yield in HMPA was undetermined; however, a reaction in which $KSiH_3$ had been prepared in monoglyme at −78° and then combined with $Cl(CH_2)_2OCH_3$ without solvent present was 50% based upon the SiH_4 used in the reaction. Distillation temperature was −80°. The Dumas molecular weight found was 90.23 (calcd 90.20). Over the temperature range −46 to +10° the vapor pressure data fit the equation $\ln P = 3661.9/T(°\mathrm{K}) + 17.529$ which results in an extrapolated boiling point, ΔH_v, and Trouton constant of 62.9°, 7.276 kcal/mol, and 21.7 eu, respectively. Major peaks in the ir spectrum occur at 2984, 2923, 2895, 2853, 2825 (m), 2156 (s), 1373 (m), 1125 (s), and 936 cm^{-1} (vs). Mass spectral peaks in >10% relative abundance occur at *m/e* values of 28 (21%), 31 (25%), 45 (74%), 58 (13%), 59 (30%), 60 (12%), 61 (100%), and 62 (32%). The melting point is below −160°.

$SiH_3(CH_2)_4OCH_3$. (4-Methoxybutyl)silane was distilled at −56° as a tensimetrically pure compound (4.6 mm at 0°) in 20% yield based upon the starting $Br(CH_2)_4OCH_3$. Major peaks in the ir spectrum occur at 3000, 2944, 2911, 2867, 2840 (m), 2156 (s), 1132 (m–s), and 938 cm^{-1} (vs). Mass spectral peaks in >10% relative abundance occur at *m/e* values of 31 (11%), 41 (12%), 45 (100%), 55 (19%), 56 (39%), 58 (89%), 59 (26%), 61 (59%), 63 (32%), 75 (20%), 86 (11%), and 117 (17%). The melting point is −106.9°.

$SiH_3(CH_2)_6OCH_3$. (6-Methoxyhexyl)silane was distilled from a −31° trap as a tensimetrically pure compound (4.0 mm at 24.6°) in 18% yield based upon the starting chloride. Major peaks in the ir spectrum are found at 2931, 2863 (m), 2154 (s), 1130 (m), and 935 cm^{-1} (vs). Major mass spectral peaks occur at *m/e* values of 41 (12%), 45 (100%), 55 (19%), 56 (13%), 58 (67%), 59 (37%), 61 (27%), 63 (53%), 71 (12%), 72 (37%), 73 (11%), 82 (10%), 83 (22%), 85 (35%), 86 (68%), 99 (12%), and 114 (21%). The melting point is −66.7°.

$GeH_3(CH_2)_2OCH_3$. After a trap-to-trap fractionation at −78° the contents of this trap were condensed into a low-temperature still and distilled at −68° until all traces of MeOH were removed. Pure $GeH_3(CH_2)_2OCH_3$ was then obtained in 31% yield at −63°. The experimental Dumas molecular weight was 134.6 (calcd 134.6). Over the temperature range −32 to +24° the vapor pressure data fit the equation $\ln P = 4038.6/T(°\mathrm{K}) + 18.095$ which results in an extrapolated boiling point, ΔH_v, and Trouton constant of 79.1°, 8.025 kcal/mol, and 22.8 eu, respectively. Major peaks in the ir spectrum occur at 2975, 2942, 2812, 2886, 2842, 2814 (m), 2066 (s), 1381 (d, m), 1132 (s), 844, and 836 cm^{-1} (s). Major mass spectral peaks occur at *m/e* values of 45 (87%), 59 (48%), 60 (28%), 73 (16%), 74 (12%), 75 (20%), 77 (20%), 101 (28%), 103 (74%), 104 (26%), 105 (100%), 106 (35%), 107 (81%), 108 (18%), 109 (16%), 134 (11%), and 135 (10%). The melting point is −157.1°.

$GeH_3(CH_2)_3OCH_3$. Distillate collected up to −61° was discarded. In order to remove the last traces of MeOH the remaining still contents were placed over sodium in vacuo until gas evolution ceased; then they were returned to the still. The still temperature was maintained at −57° until three consecutive fractions had identical vapor pressures (8.1 mm at 0°). (3-Methoxypropyl)germane was obtained in 40% yield based upon the amount of GeH_4 consumed in the reaction. Over the temperature range −16 to +26° the vapor pressure data fit the equation $\ln P = 4567.6/T(°\mathrm{K}) + 18.818$ resulting in an extrapolated boiling point, ΔH_v, and Trouton constant of 101.7°, 9.076 kcal/mol, and 24.2 eu, respectively. Major peaks in the ir spectrum occur at 2978, 2920, 2856, 2821 (m), 2069 (vs), 1131 (s), and 836 cm^{-1} (vs). Major mass spectral peaks occur at *m/e* values of 41 (13%), 43 (12%), 45 (100%), 75 (10%), 77 (10%), 101 (14%), 103 (26%), 104 (15%), 105 (35%), 106 (18%), 107 (26%), 108 (17%), and 109 (11%). The melting point is −97.7°.

$GeH_3(CH_2)_4OCH_3$. Reaction products which distilled below −42° were discarded and the still was held constant at this temperature until three consecutive fractions had identical ir spectra and the same vapor pressure at 0° (2.0 mm). The yield was 70% based upon the $Br(CH_2)_4OCH_3$ used in the reaction. A mass spectrum of the germanium-containing ether showed no bromide contaminant was present. Major peaks in the mass spectrum occur at *m/e* values of 15 (50%), 27 (26%), 28 (17%), 29 (37%), 41 (19%), 45 (100%), 55 (21%), and 58 (17%). Major peaks in the ir spectrum are found at 2918, 2847, 2813 (m), 2057 (s), 1132 (s), and 835 cm^{-1} (vs). The melting point is −109.8°.

Table I. $\Delta\nu^a$ Values for $MH_3(CH_2)_nOCH_3$ Compounds

	Carbon Tetrachloride			Cyclohexane		
	M = C	M = Si	M = Ge	M = C	M = Si	M = Ge
$n = 0$	$(130)^b$	$(92)^d$	$(155)^c$			
$n = 1$	$136\ (142)^c$	$117\ (0)^d$	$118\ (126)^c$	120	100	100
$n = 2$	137	123	122	120	103	105
$n = 3$	138	132	131	120	114	115
$n = 4$		136	135		116	117
$n = 5$	138			121		
$n = 6$			137		120	120

[a] Values in cm^{-1}. The number appears to be unaffected by ether concentration in the range employed, 0.005–0.2 *M*, and thus it is assumed that the value reported is close to that at infinite dilution. [b] Reference 14. [c] Reference 13. [d] Reference 27; no band observed when $n = 1$.

$GeH_3(CH_2)_6OCH_3$. Pure (6-methoxyhexyl)germane distilled at −12° and had a vapor pressure of 1.6 mm at 30°. The yield averaged 3% based upon the starting chloride. Major peaks in the ir spectrum, which was taken as a neat liquid between KBr plates, occur at 2976 (m), 2923, 2855 (s), 2057 (s), 1451 (m), 1120 (s), 878 (m), and 829 cm^{-1} (vs). Mass spectral peaks in >10% relative abundance occur at *m/e* values of 41 (13%), 45 (100%), 54 (14%), 55 (27%), 82 (28%), 105 (12%), and 118 (11%). The melting point is −72.9°.

$SiH_3(CH_2)_3OCH_3$. (3-Methoxypropyl)trichlorosilane was prepared by vigorously refluxing 0.05 mol of $CH_2{=}CHCH_2OCH_3$ with excess $HSiCl_3$ (0.07 mol) in the presence of $H_2PtCl_6 \cdot 6H_2O$ catalyst. The reaction was complete in 8.5 hr based upon the disappearance of the olefinic protons in the PMR spectrum. The excess $HSiCl_3$ was removed by distillation and a small amount of *n*-butyl ether was added to the reaction mixture. The vessel was attached to the vacuum line and evacuated, and the contents were reduced with $LiAlH_4$. Pure $SiH_3(CH_2)_3OCH_3$ distilled at −50° in 70% yield based upon the starting olefin. Major peaks in the ir spectrum occur at 2962, 2928, 2894, 2867, 2830 (m), 2150 (s), 1134 (s), and 938 cm^{-1} (vs). Major mass spectral peaks occur at *m/e* values of 31 (19%), 41 (12%), 42 (21%), 43 (14%), 44 (11%), 45 (99%), 55 (21%), 59 (25%), 60 (11%), 61 (100%), 62 (11%), 75 (12%), 75 (16%), 76 (12%), and 103 (18%). Over the temperature range −25 to +23° vapor pressure data fit the equation $\ln P = 4032.9/T(°\mathrm{K}) + 17.704$ yielding an extrapolated boiling point, ΔH_v, and Trouton constant of 91.2°, 8.013 kcal/mol, and 21.9 eu, respectively. The melting point is −88.2°.

$GeH_3CH_2OCH_3$. (Methoxymethyl)trichlorogermane was obtained by stirring equimolar quantities of $HGeCl_3$ and $ClCH_2OCH_3$ at room temperature. The condensation reaction which was monitored by PMR was complete in 0.5 hr. To the reaction vessel was added a small amount of *n*-butyl ether and the trichloride was reduced with $LiAlH_4$. The $GeH_3CH_2OCH_3$ in 85% yield was easily purified by low-temperature distillation between −85 and −68°. The Dumas molecular weight found was 120.6 (calcd 120.7). The ir and PMR spectra of this compound agreed well with those previously reported.[13]

Results

Base Strengths. Under the conditions used in these experiments addition of a Lewis acid such as methanol to an ether (Lewis base) results in complexation which can be detected in the infrared spectra by a sharp band due to the stretching of the free methanol O–H bond and a somewhat broader band due to the stretch of the hydrogen-bonded OH. The difference between the free and hydrogen-bonded stretching frequencies ($\Delta\nu$) is a measure of the strength of the hydrogen bond and is, therefore, related to the basicity of the ether. The free OH stretching frequency of methanol was found to be 3613 ± 2 cm^{-1} in CCl_4 and 3612 ± 2 cm^{-1} in C_6H_{12} regardless of the ether present. The $\Delta\nu$ value for diethyl ether in CCl_4 was 144

Table II. Proton Chemical Shifts for $MH_3(CH_2)_nOCH_3$ Compounds[a]

	MH_3	MCH_2	H_2CO	OCH_3
		M = Carbon		
$n = 0$	(6.79)[b]			(6.79)[b]
$n = 1$	8.88	6.68		6.78
$n = 2$	9.12	8.45	6.76	6.79
$n = 3$	9.10		6.71	6.77
$n = 5$	9.10		6.71	6.77
		M = Silicon		
$n = 0$	(5.48)[c]			(6.59)[c]
$n = 1$	6.46 (6.46)[d]	6.72 (6.67)[d]		6.75 (6.73)[d]
$n = 2$	6.55	8.91	6.57	6.78
$n = 3$	6.46	9.23	6.72	6.77
$n = 4$	6.48	9.16	6.72	6.78
$n = 6$	6.48	9.25	6.72	6.78
		M = Germanium		
$n = 0$	(4.88)[e]			(6.51)[e]
$n = 1$	(6.42)[f]	(6.42)[f]		(6.77)[f]
$n = 2$	6.54	8.66	6.56	6.77
$n = 3$	6.53	8.96	6.73	6.79
$n = 4$	6.53	9.00	6.70	6.77
$n = 6$	6.55	8.98	6.72	6.79

[a] τ values relative to TMS. Values extrapolated to infinite dilution in cyclohexane. [b] Values from ref 27. [c] Reference 28. [d] Reference 15. [e] Reference 29. [f] Reference 13. Also reported in benzene: $\tau(OCH_3)$ 6.89, $\tau(GeH_3)$ 6.39, $\tau(CH_2O)$ 6.54.

Table III. Observed Coupling Constants (Hz) for $MH_3(CH_2)_nOCH_3$ Compounds

	$J_{H-H'}$-(MH_3-CH_2)	$J_{H-H'}$-(CH_2-CH_2O)	$J_{^{13}C-H}$-(OCH_3)	$J_{^{29}Si-H}$-(SiH_3)
		M = Carbon		
$n = 1$	7.1		139.5	
$n = 2$	6.6	6.4	139.5	
$n = 3$	*a*	6.3	140.0	
$n = 5$	*a*	6.2	140.0	
		M = Silicon		
$n = 1$[b]	3.5		140.3	199.1
$n = 2$	3.9	7.5	140.2	195.8
$n = 3$	3.9	6.1	140.4	194.6[c]
$n = 4$	3.8	6.2	140.0	193.1
$n = 6$	3.9	6.4	140.1	193.1
		M = Germanium		
$n = 1$	(3.1)[d]		140.5	
$n = 2$	3.5	7.5	139.9	
$n = 3$	3.5	6.3	141.6[c]	
$n = 4$	3.4	6.4	140.7	
$n = 6$	3.4	*a*	139.7	

[a] Accurate values could not be obtained due to either overlapping peaks or virtual coupling distortions. [b] Literature values (Hz):[15] $J_{H-H'} = 2.55$, $J_{^{29}Si-H} = 203.3$, and $J_{^{13}C-H} = 141.0$. [c] Upfield satellite obscured. [d] In benzene; ref 13.

cm^{-1} (lit.[14] 144 and 145 cm^{-1}) and in C_6H_{12} was 124 cm^{-1}. Table I summarizes the values of $\Delta\nu$ for the series of hydrides $MH_3(CH_2)_nOCH_3$ in which M = C, Si, Ge and n = 0–6; the reproducibility of the data recorded in this investigation is ±2 cm^{-1}. The ratio of $\Delta\nu_{CCl_4}/\Delta\nu_{C_6H_{12}}$ from the table remains remarkably constant within each series as well as among the three series (1.16 ± 0.03).

PMR. Table II presents the chemical shifts at infinite dilution for the major protons of the $MH_3(CH_2)_nOCH_3$ compounds. Except for the expected deviations caused by virtual coupling of the methylene groups in the longer alkyl chains, the spectra are first order. Table III records the $J_{^{13}C-H}(OCH_3)$, $J_{^{29}Si-H}(SiH_3)$, and selected $J_{H-H'}$ values as determined in this investigation. Coupling constants are measured to ±0.2 Hz.

Discussion

Syntheses. (Methoxymethyl)silane[15] and -germane[13] have been prepared previously in low or moderate yields. In the latter case dimethoxymethane (bp 44.2°) is a side product which is not easily separated from the main product, $GeH_3CH_2OCH_3$ (bp 44.4°). Condensation of $ClCH_2OCH_3$ and $HGeCl_3$[16] followed by reduction of the trichloride as reported here, however, circumvents this problem and gives an 85% yield of the Ge-containing ether which is easily purified. In contrast to the room-temperature reaction with $ClCH_2OCH_3$, no reaction could be obtained between $HGeCl_3$ and $Cl(CH_2)_nOCH_3$ in which n = 2, 4, or 6, even when they are heated to 100°.

With the exception of $SiH_3(CH_2)_3OCH_3$ the remaining $MH_3(CH_2)_nOCH_3$ (M = Si, Ge) compounds were synthesized by the reaction of $KSiH_3$ or $KGeH_3$ with the appropriate 1-haloalkyl methyl ether.[17] Yields of the germyl compounds were much improved when KOH was used in lieu of potassium in the preparation of $KGeH_3$ and when HMPA[18] was used as solvent instead of monoglyme. In general 1-bromoalkyl methyl ethers gave higher yields than the corresponding chloro ethers.

(3-Methoxypropyl)silane was conveniently prepared by hydrosilylation[19] of $CH_2{=}CHCH_2OCH_3$ with $HSiCl_3$ followed by reduction of the trichloride. Attempts to prepare (3-methoxypropyl)germane by an analogous reaction led to a viscous, tacky material which PMR indicated could have been initially the condensation product $Cl_3GeCH_2CH{=}CH_2$. Neither cooling the allyl methyl ether to −78° nor adding H^+ to the $HGeCl_3$ to prevent the formation of $GeCl_2$, followed by slow addition of one reagent to the other, resulted in any insertion product. Attempted hydrosilylation of vinyl methyl ether with $HSiCl_3$ gave an olive green or brown solution which also appeared to polymerize.

All of the silicon and germanium hydrides prepared appear to be slightly air sensitive, with the lower members of each series being more sensitive than those of higher molecular weight. Under vacuum no signs of decomposition were seen once the ethers were pure. The thermal stability of $SiH_3(CH_2)_3OCH_3$ was such that keeping it at 90° for 3 months in a sealed, evacuated tube produced no changes in its ir or PMR spectra. Although organosilicon hydrides having a substituent on the β carbon tend to be reactive or unstable, eliminating ethylene, both $SiH_3(CH_2)_2OCH_3$ and its Ge analog were stable for days at room temperature.

Base Strengths. Within the $MH_3(CH_2)_nOCH_3$ series in Table I for which M = C only inductive effects are assumed to be operative. As the more electron-releasing ethyl group is substituted for a methyl, the value of $\Delta\nu$ increases; however, further elongation of the carbon chain results in little change in base strength. This trend is consistent with the reported inductive effects found in other alkyl compounds.[20]

In the silicon and germanium analogs the $\Delta\nu$ values, and therefore the basicities, are markedly less than those of the carbon ethers when n = 0, 1, or 2. Huheey[21] has reported the group electronegativities of the methyl and silyl groups are nearly equal (2.27 vs. 2.21 in Pauling units) and indicated that both groups are slightly electron releasing when attached to a carbon atom. It would appear from the $\Delta\nu$ values, then, that the inductive effects of the silyl group in the case of $SiH_3(CH_2)_nOCH_3$ compounds in which n = 0, 1, and 2 are being overridden by some other factor(s). If electron density on the oxygen atom were being donated to the group 4 metal atom (i.e., M = Si or Ge), a decrease in the ability of the ether to act as a Lewis base compared to the analogous compound in which M = C would be expected.

In contrast to the constant values for the higher molecular weight carbon ethers, the frequency shifts for the Si and Ge series in Table I increase substantially from n = 2 to n = 3.

From $n = 3$ to $n = 6$ the increase in $\Delta\nu$ is more gradual and the values converge toward those of the carbon ethers. Depending upon the strength of any metal–donor interaction within a homologous series, one might expect such increases in base strength as the number of intervening methylene groups further separates the interacting atoms and finally effectively isolates them. If at some value of n, however, the chain length had allowed pseudo ring formation with M and O atoms again proximate, a trend of decreasing $\Delta\nu$ values would have been expected. Apparently increasing entropy requirements make ring formation, such as that found in the dialkenylzinc compounds,[22] less and less likely for the compounds in Table I.

The $\Delta\nu$ reported for GeH_3OCH_3 is inconsistent with the other data in Table I and no explanation is apparent for this unusually high value. The frequency shifts obtained in this investigation for the remaining germanium hydrides, however, are identical within experimental error to those of the Si analogs. This trend would suggest that the factor(s) operating to affect the base strengths of the $SiH_3(CH_2)_nOCH_3$ compounds is equally effective in the germanium ethers when $n = 1–6$.

PMR. Except for the member of each series in which the oxygen is directly bound to the group 4 metal atom, i.e., SiH_3OCH_3 and GeH_3OCH_3, the $\tau(OCH_3)$ values appear unaffected by any changes in either M or n. This remarkable constancy could be attributed to the inability of inductive effects to travel efficiently through more than two bonds, or it may be due to the insensitivity of PMR to reflect the small changes in electron density which might be brought about by any back-donation from the oxygen to the metal atom.

Within the Si- and Ge-containing ethers $\tau(MH_3)$ and $\tau(MCH_2)$ are seen to increase from $n = 0$ to $n = 2$ and then to remain constant from $n = 3$ to $n = 6$. Since similar changes are recorded for the carbon ethers only, inductive effects may be necessary to explain these trends in the Si and Ge ethers. It is difficult to draw any conclusions from the values of $\tau(H_2CO)$ since no trend in these data is apparent when $n = 0–2$. It does appear, however, that the chemical shift of the H_2CO protons is independent of M at and beyond $n = 3$.

It has been shown[23] that the $^{13}C–H$ coupling constant is linearly related to the fraction of s character in the carbon hybrid orbital. Table III indicates that within experimental error all of the compounds of the $MH_3(CH_2)_nOCH_3$ series have identical $^{13}C–H(OCH_3)$ coupling constants. This would seem to imply that the hybridization of the carbon in the OCH_3 moiety is unaffected by M or n, and this trend parallels the constancy of the chemical shift of the OCH_3 protons. It has been reported[24] that the $^{29}Si–H$ coupling constants are also related to the degree of s character in the Si hybrid orbital, with higher J values being indicative of increased s character. For the alkylsilanes, $SiH_3(CH_2)_nCH_3$, in which no donor atom is present, the $^{29}Si–H$ coupling constants remain the same upon changing the length of the alkyl chain from hexyl ($J = 194$ Hz)[25] to methyl ($J = 194$ Hz).[26] The data in Table III, however, show that as n decreases from 3 to 1 in the silicon ethers, the coupling constants increase, indicating increasing s character in the Si orbitals as the Si and O atoms approach. This trend parallels that expected from increasing electron delocalization from O to Si as n becomes smaller.

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Registry No. $KSiH_3$, 13812-63-0; $KGeH_3$, 16693-26-8; $Cl(CH_2)_2OCH_3$, 627-42-9; $Br(CH_2)_4OCH_3$, 4457-67-4; $Cl(CH_2)_6OCH_3$, 22692-46-2; $H_2C{=}CHCH_2OCH_3$, 627-40-7; $HSiCl_3$, 10025-78-2; H_2PtCl_6, 16941-12-1; $LiAlH_4$, 16853-85-3; $HGeCl_3$, 1184-65-2; $ClCH_2OCH_3$, 107-30-2; H_3COCH_3, 115-10-6; $H_3CCH_2OCH_3$, 540-67-0; $H_3C(CH_2)_2OCH_3$, 557-17-5; $H_3C(CH_2)_3OCH_3$, 628-28-4; $H_3C(CH_2)_5OCH_3$, 4747-07-3; H_3SiOCH_3, 2171-96-2; $H_3SiCH_2OCH_3$, 5624-64-6; $H_3Si(CH_2)_2OCH_3$, 5624-62-4; $H_3Si(CH_2)_3OCH_3$, 5624-66-8; $H_3Si(CH_2)_4OCH_3$, 5624-61-3; $H_3Si(CH_2)_6OCH_3$, 5624-63-5; H_3GeOCH_3, 5910-93-0; $H_3GeCH_2OCH_3$, 16284-75-6; $H_3Ge(CH_2)_2OCH_3$, 54832-76-7; $H_3Ge(CH_2)_3OCH_3$, 54832-77-8; $H_3Ge(CH_2)_4OCH_3$, 54832-78-9; $H_3Ge(CH_2)_6OCH_3$, 54832-79-0; ^{13}C, 14762-74-4; ^{29}Si, 14304-87-1.

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