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Article

Use of ^{73}Ge NMR Spectroscopy for the Study of Electronic Interactions

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The lack of understanding of the structural and electronic factors that affect the often difficult to observe germanium resonance has been a major deterrent to studies of bonding interactions at germanium. We utilized the symmetrical system GeR_4 to determine what structural factors inherent in the R group affect the shape and position of the ^{73}Ge resonance. The ^{73}Ge resonances of symmetrical tetrakis germanium compounds of the type GeR_4 (R = alkyl, aryl), GeX_4 (X = F, Cl, Br, I), $Ge(OR)_4$ (R = alkyl, methoxyalkyl, dimethylaminoalkyl), $Ge(NR_2)_4$ (R = alkyl), and $Ge(SR)_4$ (R = alkyl, dimethylaminoalkyl) were examined for evidence of intramolecular coordination. Although many of these compounds have sharp resonances due to idealized tetrahedral symmetry with relatively long relaxation times, others have broad or no observable resonances due to fast quadrupolar relaxation. We hypothesize that the perturbation of symmetry by even weak Lewis interactions or conformational changes causes broadening of the resonance before the interaction can become sufficiently strong to cause the significant low-frequency shift generally associated with hypercoordination in most nuclei. Intermolecular coordination to $GeCl_4$ is believed to be responsible for the low-frequency shifts in ^{73}Ge resonances and the associated changes in peak widths in mixtures with bases such as tributylphosphine oxide (TBPO) and triethylphosphine oxide (TEPO). Adduct formation with these bases is confirmed by broad ^{31}P resonances that are resolved into five peaks at −40 °C. The exchange-broadened resonances due to the 1:1 and 1:2 TEPO adducts are also observed at −40 °C in the ^{73}Ge spectrum. Thus, relatively strong bonding to the germanium in $GeCl_4$ results in both low-frequency shifts and broadening of the resonance. The broad ^{73}Ge resonances that occur in some compounds may be in part due to exchange as well as quadrupolar relaxation.

Introduction

The presumed inability to observe a germanium resonance and lack of understanding of the structural and electronic factors that affect that resonance have contributed significantly to the dearth of information about bonding interactions at germanium. For example, Lewis acid−base interactions, especially intramolecular hypercoordination, have been well studied for the group 14 elements silicon and tin, but only a few contributions on these interactions in organogermanes have been reported.[1] Unlike silicon and tin, which have spin 1/2 nuclei and are relatively easy to observe, ^{73}Ge has a spin quantum number of 9/2 and a large quadrupole moment. This quadrupole moment leads to very broad resonances, in many cases too broad to observe, due to very rapid quadrupolar relaxation in organogermanes with unsymmetrical electric fields surrounding the ^{73}Ge nucleus. Historically, ^{73}Ge has also been difficult to observe because of its low value of the magnetogyric ratio and consequent low-resonance frequency. At this low frequency, spectrometer artifacts also lead to “base-line roll”, making detection of a signal more difficult. Thus, the low-frequency shifts that so nicely characterize hypercoordination in silicon and tin have rarely been reported for organogermanes.[2]

Indeed, the majority of studies of potentially hypercoordinated organogermanes report no low-frequency shift in the ^{73}Ge resonance when it is observed.[3,4] A small low-frequency shift was reported for ethoxygermatrane relative to tetra-

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ethoxygermane; the two compounds differ in their half-height widths: 165 Hz for the germatrane relative to 30 Hz for the germane.[5] Some studies suggest that the broadening of the resonance rather than a low-frequency shift may be indicative of hypercoordination.[3]

An ideal substrate for the study of electronic interactions at germanium is the symmetrical organogermane that contains aryl or alkyl groups containing Lewis-basic sites. We prepared a number of such compounds and obtained their ^{73}Ge NMR spectra. We also examined the intermolecular coordination of bases that produce soluble adducts with $GeCl_4$. Finally, because these effects are studied in solution, we also investigated the effect of solvents on the ^{73}Ge resonance. Our results suggest that, contrary to previous studies, both the position and the width of the ^{73}Ge resonance provide a useful probe of electronic changes at germanium.

Results and Discussion

The ^{73}Ge resonances for all of the symmetrical germanes studied in this work as well as selected germanes reported in the literature are presented in Table 1.

Table 1. ^{73}Ge NMR Parameters of Selected Tetrakis Organogermanium Compounds GeZ_4[a]

GeZ_4	^{73}Ge δ, ppm	$\Delta\nu_{1/2}$, Hz	solvent
Z = H			
H	$(-299)^{b}$	$(1)^{b}$	Bu_2O
Z = halogen			
Cl	$31^{b,c,d}(31)$	$2^{b,c,d}(14)$	toluene
Br	$-311^{b,c}$ (-306)	$2^{b,c}$ (13)	toluene
I	(-1104)	(18)	toluene
Z = R			
Et	18^{b} $(17)^{d}$	1^{b} $(2)^{d}$	$CDCl_3$
n-Pr	2^{b}	3^{b}	
n-Bu	$6\ (5)^{b,e,f,g}$	$5\ (15)^{b,e,f,g}$	$CDCl_3$
n-C_5H_{11}	6^{h}	10^{h}	
Ph	$-33\ (32)^{d}$	$6\ (6)^{d}$	DMSO
Z = OR			
Me	$(-38^{d,f}, -31)$	$(10,^{d,f}\ 29)$	$CDCl_3$, toluene
Et	$(-44^{i}, -42)$	$(30^{i}, 17)$	CD_3CN, toluene
n-Pr	$(-46)^{j,f}$	$(40)^{j,f}$	$CDCl_3$
i-Pr	$(-50)^{f}$	$(25)^{f}$	$CDCl_3$
n-Bu	$(-46^{f}, -42)$	$(40^{f}, 29)$	$CDCl_3$, toluene
i-Bu	$(-46^{f}, -49)$	$(30^{f}, 15)$	toluene
s-Bu	$(-48)^{f}$	$(45)^{f}$	$CDCl_3$
$CH_2CH_2CH(CH_3)_2$	(-41)	(51)	toluene
$CH_2CH{=}CH_2$	$(-44)^{f}$	$(32)^{f}$	$CDCl_3$
CH_2CF_3	$(-48)^{f}$	$(70)^{f}$	$CDCl_3$
CH_2CH_2CN	(-50)	(95)	toluene
$CH_2CH_2OCH_3$	(-51)	(68)	toluene
$(CH_2)_3OCH_3$	(-43)	(75)	toluene
$CH_2CH_2N(CH_3)_2$	(nro)	(nro)	toluene
$CH_2CH_2N(CH_2CH_3)_2$	(nro)	(nro)	toluene
$(CH_2)_3N(CH_3)_2$	(-45)	(103)	toluene
$(CH_2)_4N(CH_3)_2$	(-44)	(101)	toluene
Z = NR_2			
Me	$(49^{k}, 49)$	$(22^{k}, 27)$	C_6D_6, toluene
Z = SR			
Me	$(153)^{l}$		CH_2Cl_2
i-Pr	(138)	(37)	toluene
n-Bu	(120)	(39)	toluene
$CH_2CH_2N(CH_3)_2$	(141)	(79)	toluene

[a] Shifts referenced to tetramethylgermane; solution concentrations are 20 ± 5% (wt-wt, wt-vol); nro = no resonance observed. Literature values selected as representative among several reported. Values in parentheses were obtained in the solvent listed; values without parentheses were obtained neat; values without literature references were obtained in this study. Chemical shifts measured in this study have errors of approximately ±3 ppm, while half-height widths have relative uncertainties of approximately 8%. [b] Kaufmann, J.; Sahm, W.; Schwenk, A. *Z. Naturforsch., A: Phys. Sci.* **1971**, *26*, 1384−1389. [c] Kidd, R. G.; Spinney, H. G. *J. Am. Chem. Soc.* **1973**, *95*, 88−90. [d] Takeuchi, Y.; Harazono, T.; Kakimoto, N. *Inorg. Chem.* **1984**, *23*, 3835−3836. [e] Zicmane, I.; Liepins, E.; Lukevics, E.; Gar, T. K. *Zh. Obshch. Khim.* **1982**, *52*, 896−899. [f] Sekacis, I.; Liepins, E.; Zicmane, I.; Lukevics, E. *Zh. Obshch. Khim.* **1983**, *53*, 2064−2068. [g] Zitsmane, I. A.; Liepin'sh, E.E.; Lukevits, E.; Gar, T. K. *Zh. Obshch. Khim.* **1982**, *52*, 780−783. [h] Wilkins, A. L.; Watkinson, P., J.; Mackay, K. M. *J. Chem. Soc. A* **1987**, 2365−2372. [i] Kupce, E.; Ignatovitch, L. M.; Lukevics, E. *J. Organomet. Chem.* **1989**, *372*, 187−188. [j] Liepins, E.; Zicmane, I.; Lukevics, E. *J. Organomet. Chem.* **1986**, *306*, 327−335. [k] Kupce, E.; Upena, E.; Trusule, M.; Lukevics, E. *Kimijas Ser.* **1988**, *3*, 359−60. [l] Harris, R. K.; Kennedy, J. D.; McFarlane, W. Group IV-Silicon, Germanium, Tin, and Lead. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds; Academic Press: New York, 1978.

Tetraorganogermanes. Germane and its simple tetraalkyl derivatives clearly have tetrahedral symmetry (assuming conformationally flexible alkyl groups) and should have relatively long relaxation times. As is indicated in the table, these compounds have been reported to produce sharp resonances (in some cases with fine structure due to ^{73}Ge−^{1}H splitting) with half-height widths of less than 2 Hz. If electronegative groups such as alkoxy, alkylamino, or halo substitute for alkyl groups, thereby making the structure asymmetric, the electric field around the germanium loses its tetrahedral symmetry and the resonances are not observed. However, if the substitution involves a group with a fairly similar electronegativity, such as $R_3GeC_6H_5$, the resonance, though somewhat broader, can be observed (Schmidbaur et al. also comment on "surprisingly sharp" ^{73}Ge signals in aryl germanes $ArGeH_3$, Ar_2GeH_2, and Ar_3GeH).[6,7] Apparently, in these compounds the electron density has not been sufficiently perturbed to change the electric field gradient at the nucleus and the relaxation time remains long enough for observation of the resonance.

It is also clear from the table that the simple tetraalkoxy-, tetra(dialkylamino)-, and tetrathioalkoxygermanes also have relatively sharp resonances. The same is true, of course, for the tetrahalogermanes. Of the compounds examined in this study, two—$Ge(O(CH_2)_2N(CH_3)_2)_4$ and $Ge(O(CH_2)_2N(CH_2CH_3)_2)_4$—did not show a detectable signal and both contain Lewis-basic sites at the end of the alkoxy chains. On the other hand, $Ge(O(CH_2)_3N(CH_3)_2)_4$, $Ge(O(CH_2)_4N(CH_3)_2)_4$, $Ge[O(CH_2)_2OCH_3]_4$, and $Ge[O(CH_2)_3OCH_3]_4$, which also contain terminal basic sites, give resonances with half-height widths of 103, 101, 68, and 75 Hz, respectively.

Quadrupolar relaxation is dominated by the effects of both the rotational correlation time and the electric field gradient

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at the nucleus;[8−10] however, since the correlation times are generally similar in nonviscous media, the electric field gradient is the more important factor.[11] The lack of a resonance for the dimethylaminoethoxygermane may be attributed to coordination of at least one of the dimethylamino nitrogens to the central germanium. This coordination distorts the geometry of the tetrakis compound, changes the electric field gradient at the nucleus, and allows rapid quadrupolar relaxation. This hypothesis receives support from molecular modeling using the Hartree−Fock approximation at the 3-21G level. Modeling showed a number of conformations with one nitrogen−germanium distance of 2.2 Å (less than the sum of the van der Waals radii) with energies lower than that for the extended, uncoordinated conformation.

The dimethylaminopropoxy derivative, on the other hand, exhibits a resonance, albeit somewhat broad ($\Delta\nu_{1/2} = 103$ Hz). Examination of CPK models shows that the extended conformation in the compound with the propyl bridge is less crowded than that of the ethyl derivative and, perhaps more importantly, that the dimethylamino nitrogen cannot approach as closely to the central atom. This observation is also supported by Hartree−Fock modeling, which shows only one conformation with a "coordinated" dimethylamino group among many that have N−Ge distances no less than 4.0 Å. The dimethylaminobutoxy derivative also exhibits a resonance indicative of a smaller distortion of the electric field due to a lower extent of hyperconjugation. The inability to observe a resonance for the diethylaminoethoxy derivative suggests that it is primarily the stereochemistry enforced by the ethyl bridge rather than steric hindrance at nitrogen that controls the coordination to germanium.

The compound $Ge[O(CH_2)_2OCH_3]_4$, the methoxy analog of $Ge[O(CH_2)_2N(CH_3)_2]_4$, has a ^{73}Ge resonance with a half-height width of 68 Hz, indicating that the methoxy analog interacts less strongly with the germanium. This is presumably related to the difference in basicity of the two terminal sites. For the compound $Ge[S(CH_2)_2N(CH_3)_2]_4$ the ^{73}Ge resonance has a half-height width of 79 Hz, indicating that substitution of sulfur for oxygen at the germanium likely decreases the Lewis acidity of the germanium, resulting in a smaller extent of coordination from the dimethylamino group. It is also apparent from CPK models that the larger sulfur atoms surrounding the germanium hinder approach of the dimethylamino group.

The possibility that the broad resonances are a result of intermolecular interactions rather than intramolecular coordination was eliminated by the observed absence of significant changes in line width upon dilution from 50% to 0.5%. The observation of intramolecular coordination in dimethylaminoethoxytin derivatives also lends credence to our hypothesis of intramolecular coordination in the dimethylaminoethoxygermane.[12] Of course, the tin analogs would be expected to have a greater extent of coordination because of the greater Lewis acidity of the tin center.

Table 2. ^{73}Ge/^{31}P NMR Spectra of 1:1 Germanium Tetrachloride Adducts with Phosphinobases in CH_2Cl_2[a]

	^{73}Ge NMR spectra	^{31}P NMR spectra	
base	RT, δ, ppm, $\nu_{1/2}$ Hz	RT, δ, ppm	−40 °C, δ, ppm
TEPO	−18, 200	73.3, 64.1	74.1, 75.1, 76.4, 78.6
TBPO	−3, 110	72.1, 69.2, 61.3	68.7, 69.7, 71.0, 73.6
TBP	31, 20	104	104

[a] ^{73}Ge shifts are relative to tetramethylgermane. ^{31}P shifts are relative to phosphoric acid. δ ^{73}Ge ($GeCl_4$) = 31 ppm, δ ^{31}P (TBPO) = 48.2 ppm, δ ^{31}P (TEPO) = 51.8 ppm.

The intramolecular coordination postulated for the dimethylamino- and methoxyalkoxy derivatives is very likely dynamic (fluxional). However, the ^{73}Ge resonance could not be observed for the dimethylaminoethoxy derivative even at −80 °C. Hence, we attribute the broadening of many germanium resonances to the presence of relatively small interactions at the germanium nucleus, which sufficiently perturb the symmetry of the electric field to decrease the relaxation time significantly. A consequence of this hypothesis is that weak hypercoordination can broaden the resonance without providing enough electron density at the germanium to shift the resonance strongly to lower frequency. In other words, the *perturbation of symmetry causes broadening of the resonance before the interaction can become sufficiently strong to cause the low-frequency shift generally associated with hypercoordination in many nuclei*. In order to test this hypothesis, we studied intermolecular coordination, where perturbation of the electric field gradient should produce broad resonances that may or may not show lower frequency shifts, depending on the extent of the interaction, as well as the ^{73}Ge spectrum of an octahedral complex where the resonance should be sharp (because of O_h symmetry) and shifted to lower frequencies.

Intermolecular Coordination. Investigations of intermolecular coordination with solution NMR studies of the group 14 halides are frequently hindered by the insolubility of the complexes. Our attempts to study the interactions between $GeCl_4$ and bases such as pyridine, triethylamine, dipyridyl, dimethyl sulfoxide, and hexamethylphosphoramide resulted in formation of insoluble materials. With phosphines and phosphine oxides, however, the solutions obtained in most cases show a shift to lower frequency in the ^{73}Ge resonance and an increase in peak width. The ^{73}Ge chemical shifts observed for $GeCl_4$ with tributylphosphine (TBP), tributylphosphine oxide (TBPO), and triethylphosphine oxide (TEPO) in methylene chloride are 31, −3, and −18 ppm, respectively, for 1:1 mixtures with $GeCl_4$ (Table 2).

Relative to the chemical shift of $GeCl_4$ (29.4 ppm in CH_2Cl_2), these correspond to low-frequcncy shifts of 0, 32, and 37 ppm. The half-height width of the ^{73}Ge resonance is increased from 14 Hz for $GeCl_4$ to 110 Hz in solutions with TBPO and to 200 Hz with TEPO in CH_2Cl_2.

The conductivities of the TEPO and TBPO mixtures in CH_2Cl_2 are low (6−30 μS/cm for a 4.3×10^{-3} M solution),

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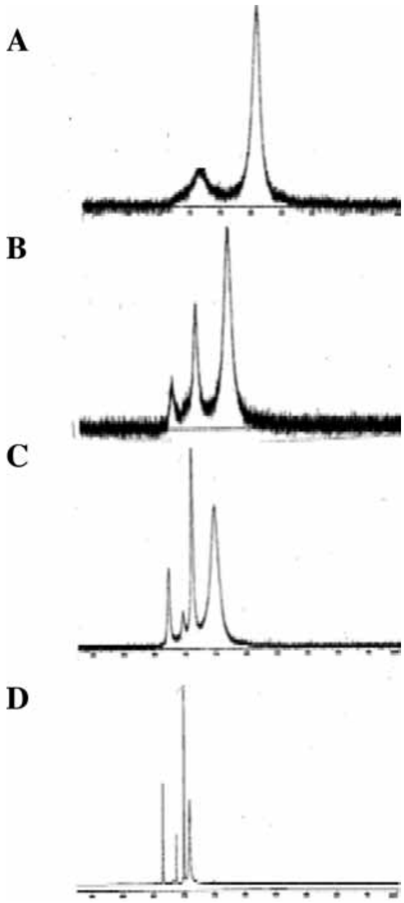

Figure 1. ^{31}P NMR Spectra of $GeCl_4$−TEPO adduct at (A) 25, (B) 10, (C) 0, and (D) −40 °C. Mole ratio of $GeCl_4$ to TEPO = 1:1, ca. 10% in CH_2Cl_2.

whereas the conductivities of the mixtures with TBP are considerably higher in CH_2Cl_2 (160−200 μS/cm for a 4.3 $\times$ 10^{-3} M solution) and can be compared to the conductivity of 70 μS/cm for the ionic liquid trihexyltetradecylphosphonium chloride at the same concentration. Formation of an electrolyte with TBP, probably $GeCl_3(TBP)^+Cl^-$, similar to those reported for $SiCl_4$,[13] is also supported by the high-frequency ^{31}P shift of 104 ppm (the ^{31}P shift of TBP in CH_2Cl_2 is −31.6 ppm). This shift is consistent with the presence of a deshielded phosphorus in the ion $Cl_3Ge{-}PBu_3^+$. The ^{31}P shift of the octahedral adduct formed between $SnCl_4$ and TBP is reported as 14.3 ppm; the ^{31}P shift of the $GeCl_4$ adduct could be expected to be in the same general area.[14]

The ^{31}P spectra of TEPO and TBPO in 1:0.5, 1:1, and 1:2 mol ratio mixtures ($GeCl_4$ to base) at room temperature contain two broad peaks in the region 65−80 ppm. As the ratio of base to $GeCl_4$ is increased, the higher frequency peak increases in intensity relative to the other. As the temperature is decreased for mixtures with TEPO, both peaks split into two peaks at about 0 °C (Figure 1).

Assignment of the higher frequency peaks at 76.4 and 78.6 ppm to geometric isomers of an octahedral complex is consistent with the increase in intensity of those peaks at higher ratios of base to $GeCl_4$ and assignment of the $SnCl_4(TBPO)_2$ trans isomer at 68.8 ppm.[15] The peaks at lower frequencies can be attributed to geometric isomers in a 5-coordinate complex. The broader peak at 74.1 ppm can tentatively be attributed to exchange of free base with the more labile axial trigonal bipyramidal isomer. It is likely that the peak at 76.4 ppm can be assigned to the equatorial isomer. The increase in intensity of the higher frequency peaks attributed to the octahedral isomers relative to the lower frequency peaks suggests that the 1:2 stoichiometry is thermodynamically favored relative to the 1:1 adduct. The 1:1 adducts appear to undergo exchange with either free base or other adducts more rapidly than the 1:2 adducts. The same behavior is observed for the adduct of $GeCl_4$ with TBPO.

Examination of the room-temperature ^{73}Ge spectra of the TEPO adduct shows a resonance at 10 ppm ($\Delta\nu_{1/2}$ = 90 Hz) at a 1:0.5 mol ratio (acid to base) that moves to −40 ppm and broadens to 400 Hz at a 1:2 mol ratio and cannot be observed at a 1:4 mol ratio. At −40 °C, a mole ratio of 1:2.5 produces ^{73}Ge resonances at −20 ($\Delta\nu_{1/2}$ = 270 Hz) and −360 ppm ($\Delta\nu_{1/2}$ = 100 Hz) and at a 1:4 mol ratio these resonance change in intensity with the higher frequency peak decreasing in intensity and shifting to −100 ppm ($\Delta\nu_{1/2}$ = 200 Hz) while the lower frequency peak increases in intensity and shifts only slightly to −370 ppm ($\Delta\nu_{1/2}$ = 120 Hz) (Figure 2).

The change in relative intensities as the ratio of base to acid increases as well as the position of the resonances indicates that these can be attributed to the 1:1 and 1:2 adducts, respectively. The width of the peak at −370 ppm is smaller than that of the higher frequency peak, suggesting that either the symmetry of the 1:2 adduct(s) is greater or that exchange is slower. The latter explanation is more likely given the sharper ^{31}P peaks for the 1:2 adducts and the change in chemical shift of the higher frequency peak as the ratio of TEPO to $GeCl_4$ is increased. The two resonances did not change significantly at −80 °C.

We conclude, therefore, that intermolecular coordination also results in both a low-frequency shift and broadening of the ^{73}Ge resonance, at least with a tetrahedral Lewis acid. When the bonding interaction is weak there is a small or no low-frequency shift in the ^{73}Ge resonance but broadening still occurs (see below for the contribution of solvent effects). For example, with acetonitrile, THF, and acetone the ^{73}Ge chemical shifts and half-height widths of $GeCl_4$ are 29.6 ($\Delta\nu_{1/2}$ = 4 Hz), 25.5 ($\Delta\nu_{1/2}$ = 25 Hz), and 22.0 ppm ($\Delta\nu_{1/2}$ = 230 Hz), respectively.

We also examined a complex of high symmetry. The ^{73}Ge shift in the octahedral hexa(thiocyanato) complex $Ge(SCN)_6^{2-}$ was obtained as −420 ppm, which is 332 ppm upfield from the tetracoordinate cyanate, $Ge(NCO)_4$ (−88.3 ppm).[16] Of course, the octahedral symmetry of this complex produces relatively slow quadrupolar relaxation which allows the low-frequency shift to be observed. The shift of the tin analog $Sn(NCS)_6^{2-}$ of −842 ppm can be compared with the

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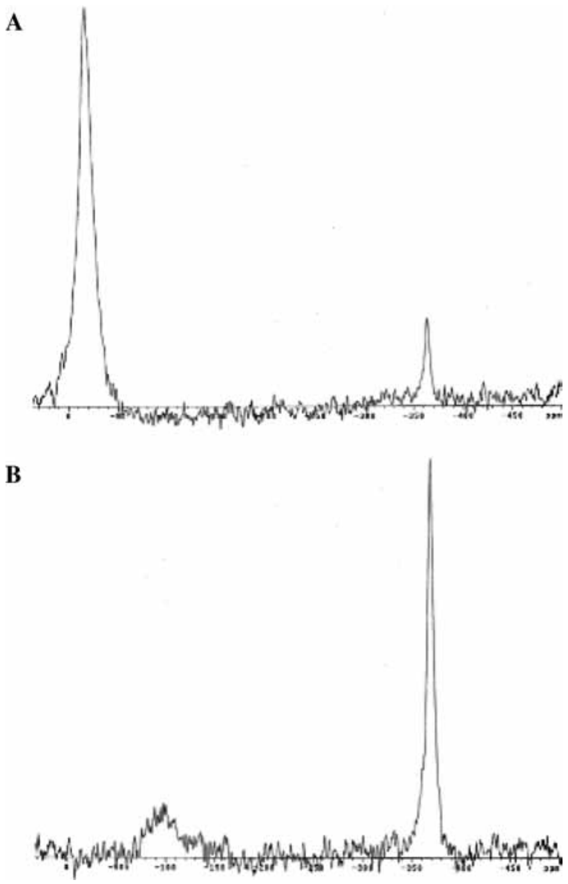

Figure 2. ^{73}Ge resonances at −40 °C for (A) 1:2.5 ($\delta = -19$ ppm, $\Delta\nu_{1/2} = 270$ Hz; $\delta = -365$ ppm, $\Delta\nu_{1/2} = 100$ Hz) and (B) 1:4 ($\delta = -100$ ppm, $\Delta\nu_{1/2} = 200$ Hz; $\delta = -370$ ppm, $\Delta\nu_{1/2} = 120$ Hz) mole ratios of $GeCl_4$ to TEPO.

value of −743 ppm predicted from the shift of $Ge(SCN)_6{}^{2-}$ using the equation[17]

$$\delta^{119}\mathrm{Sn} = 1.56 \quad \delta^{73}\mathrm{Ge} - 87.4 \qquad (1)$$

Solvent Effects. The dependence of the ^{73}Ge peak position and peak width on intermolecular coordination provided the occasion for exploration of the effects of solvent. The ^{73}Ge chemical shift of five compounds (p-$EtOPhGeMe_3$, $ClCH_2GeMe_3$, $Ge(Bu)_4$, Ph_2GeMe_2, and $GeCl_4$) showed very little dependence (±5 ppm) on solvent when examined in a total of nine solvents, but a significant effect on the peak width was observed. Multiple regression analysis of the half-height widths with various solvent parameters including viscosity, dielectric constant, dipole moment, polarizability, diamagnetic susceptibility, Hildebrand solubility parameter ($J^{1/2}/cm^{3/2}$), and donor number reveals a significant dependence only on viscosity, consistent with the effect of viscosity on the correlation time.

Conclusion

The differences among the ^{73}Ge NMR spectra of symmetrically substituted germanes, some nonsymmetrically substituted germanes, and adducts of various bases with $GeCl_4$ leads to the conclusion that where the quadrupolar relaxation is slow the ^{73}Ge resonance is observed to be shifted to low frequency upon coordination with basic sites. In cases where the germanium encounters weak hypercoordination the resonance broadens but the nucleus may not experience sufficient electron density to shift the resonance strongly to low frequency. In other words, in these cases, the perturbation of symmetry causes broadening of the resonance before the interaction can become sufficiently strong to cause the low-frequency shift generally associated with hypercoordination in most nuclei. Consequently, the width of the ^{73}Ge resonance can be interpreted as an indication of a distortion of the electric field around germanium (or the presence of fluxional behavior) and the position of the resonance in many cases provides a qualitative indication of the extent of the donation of electron density.

We find that ^{73}Ge NMR spectroscopy is considerably more useful than was previously thought. Certainly, perfect tetrahedral symmetry of groups surrounding germanium is not necessary for observation of a germanium resonance, although compounds containing groups of widely differing electronegativities may give rise to unobservable resonances. The observation of exchange broadening of resonances suggests that exchange processes also contribute significantly to the ability to observe the resonance. However, the ability to observe resonances due to adducts of differing stoichiometries and relatively low symmetries at low temperatures speaks to the usefulness of the technique.

Experimental Section

Materials and Reagents. The reactions and operations were performed in closed systems purged with argon. Products were vacuum filtered in an argon-purged glovebag. Glassware was dried and stored in a 125 °C oven for at least 24 h prior to use. Commercial solvents and reagents were first dried with Drierite and subsequently stored over Linde 4A molecular sieves. Commercial n-butyllithium was purchased (Sigma Aldrich) as a 2.5 M solution in hexanes. Germanium tetrachloride and germanium tetrabromide were purchased from Gelest. Tetrahydrofuran (THF) was dried over molecular sieves and then distilled from calcium hydride under an argon atmosphere prior to use. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

NMR Spectra. ^{1}H (500 MHz), ^{13}C (125.6 MHz), and ^{73}Ge (17.43 MHz) NMR spectra of the products were recorded on a Varian INOVA 500 MHz spectrometer. ^{73}Ge spectra were obtained using a 10-mm low gamma broadband probe at 17.43 MHz, with the Carr−Purcell−Meiboom−Gill pulse sequence (d2 = 0.0001 s) to reduce baseline roll. This pulse sequence was found to give peak widths within ca. 5% of those obtained using the standard single-pulse sequence using a 90° pulse and an acquisition time of 0.1 s with proton decoupling during acquisition. Multiple runs on different samples of the same compound produced uncertainties in the chemical shifts of ca. 3 ppm and peak widths of ca. 8%.

Molecular Modeling. Optimized geometries of selected molecules were calculated using the molecular modeling programs Gamess 2007 and Gaussian 98 revision A.9.[18] Calculation-type Hartree−Fock, basis set 3-21G was used. The optimized structures were viewed through WebMO Version 8.0 and MacMolPlt v5.6.1.[19]

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Synthesis of Tetrakis(alkoxy) and -Thiogermanium Compounds. All tetrakis(alkoxy) and -thiogermanium compounds were synthesized by addition of a solution of $GeCl_4$ in THF to a stirred solution of reactant and triethylamine in THF.

$Ge[O(CH_2)_2N(CH_3)_2]_4$. In the synthesis of $Ge[O(CH_2)_2N(CH_3)_2]_4$, $GeCl_4$ (10.0 g, 0.0466 mol) in THF (20 mL) was added dropwise to a stirred solution of 2-dimethylaminoethanol (19.25 g, 0.1866 mol) and triethylamine (20.77 g, 0.2052 mol) in THF (100 mL). The reaction mixtures were stirred at room temperature for several hours and then heated gently for several hours. Subsequently, the solution was cooled and stored in a refrigerator prior to suction filtration. The solvent was removed from the filtrate by reduced pressure distillation. ^1H NMR (500 MHz, $CDCl_3$): δ 3.45 (m, 8H, $-OCH_2$), 2.07 (m, 8H, $-CH_2$), 1.85, (s, 24H, $-NCH_3$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 60.7, 60.1, 45.1. ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ not observed. Anal. Calcd for $C_{16}H_{40}GeN_4O_4$: C, 45.21; H, 9.48. N, 13.18. Found: C, 44.01; H, 10.08; N, 12.59 (yield, 40%).

$Ge[O(CH_2)_2N(CH_2CH_3)_2]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.62 (t, 8H, $-OCH_2$), 2.38 (t, 8H, $-CH_2$), 2.33 (q, 16H, $-NCH_2$), 0.75 (t, 24H, $-CH_3$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 62.4 (s, $-OCH_2$), 54.5 (s, $-CH_2$), 46.9 (s, $-NCH_2$), 11.2 (s, $-CH_3$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ not observed. Anal. Calcd for $C_{24}H_{56}GeN_4O_4$: C, 53.63; H, 10.52. Found: C, 50.03; H, 10.49 (yield, 30%).

$Ge[O(CH_2)_3N(CH_3)_2]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 4.22 (m, 2H, $-OCH_2$), 2.68 (m, 8H, $-CH_2$), 2.52 (s, 24H, $-NCH_3$), 2.06 (m, 8H, $-CH_2$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 62.8 (s, $-OCH_2$), 55.3 (s, $-CH_2$), 44.6 (s, $-NCH_3$), 30.0 (s, $-CH_2$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ -45 (br s, $\Delta\nu_{1/2} = 103$ Hz). Anal. Calcd for $C_{20}H_{48}GeN_4O_4$: N, 11.64; C, 49.92; H, 10.05. Found: N, 11.42; C, 49.59; H, 10.36 (yield, 30%).

$Ge[O(CH_2)_4N(CH_3)_2]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.65 (m, 8H, $-OCH_2$), 2.06 (m, 8H, $-CH_2$), 2.00 (s, 24H, $-NCH_3$), 1.37 (m, 8H, $-CH_2$), 1.37 (m, 8H, $-CH_2$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 64.9 (s, $-OCH_2$), 59.1 (s, $-CH_2$), 45.0 (s, $-NCH_3$), 30.3 (s, $-CH_2$), 23.4 (s, $-CH_2$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ -44 (br s, $\Delta\nu_{1/2} = 101$ Hz). Anal. Calcd for $C_{24}H_{56}GeN_4O_4$: N, 10.43; C, 53.65; H, 10.50. Found: N, 9.84; C, 52.09; H, 11.16 (yield, 20%).

$Ge[O(CH_2)_2CN]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. In the preparation of $Ge[O(CH_2)_2CN]_4$, the reaction solution was cooled in an ice bath during addition of germane solution to the reactant 3-hydroxypropionitrile. After addition of germanium tetrachloride, the mixture was not heated during the reaction. The resulting product was suction filtered twice before the product was isolated by reduced pressure distillation. ^1H NMR (500 MHz, toluene-d_8): δ 4.06 (t, 8H, $-OCH_2$), 2.60 (t, 8H, $-CH_2$). ^{13}C NMR (125.6 MHz, toluene-d_8): δ 117.4 (s, CN), 60.5 (s, OCH_2), 21.2 (s, CH_2). ^{73}Ge NMR (17.43 MHz, toluene-d_8): δ -50 (br s, $\Delta\nu_{1/2} = 95$ Hz). Anal. Calcd for $C_{20}H_{16}N_4O_4Ge$: C, 40.80; H, 4.58. Found: C, 40.69; H, 5.09 (yield, 30%).

$Ge[OCH_2CH_2CH(CH_3)_2]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. The reaction solution of $Ge[OCH_2CH_2CH(CH_3)_2]_4$ was cooled in an ice bath during addition of the germanium tetrachloride solution to the reactant. ^1H NMR (500 MHz, toluene-d_8): δ 3.83 (t, 8H, $-OCH_2$), 1.68 (m, 4H, $-CH$), 1.45 (q, 8H, $-CH_2$), 0.84 (d, 12H, $-CH_3$). ^{13}C NMR (125.6 MHz, toluene-d_8): δ 63.7 (s, $-OCH_2$), 41.7 (s, $-CH_2$), 24.5 (s, $-CH$), 22.5 (s, $-CH_3$). ^{73}Ge NMR (17.43 MHz, toluene-d_8): δ -41 (br s, $\Delta\nu_{1/2} = 51$ Hz). Anal. Calcd for $C_{20}H_{44}GeO_4$: C, 57.02; H, 10.55. Found: C, 55.53; H, 11.25 (yield, 30%).

$Ge[O(CH_2)_2OCH_3]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.93 (m, 8H, $-OCH_2$), 3.43 (m, 8H, $-CH_2$), 3.28 (s, 12H, $-OCH_3$). ^{13}C NMR ($CDCl_3$, 125.6 MHz): δ 73.6 (s, $-OCH_2$), 64.3 (s, $-CH_2$), 58.7 (s, $-OCH_3$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ -51 (br s, $\Delta\nu_{1/2} = 68$ Hz). Anal. Calcd for $C_{12}H_{28}GeO_8$: C, 38.65; H, 7.57. Found: C, 38.52; H, 8.26 (yield, 25%).

$Ge[O(CH_2)_3OCH_3]_4$. This tetrakis(alkoxy)germane was prepared as described for $Ge[O(CH_2)_2CN]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.87 (m, 8H, $-OCH_2$), 3.39 (m, 8H, $-CH_2$), 3.23 (s, 12H, $-OCH_3$), 1.78 (m, 8H, $-CH_2$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 68.8 (s, $-OCH_2$), 62.2 (s, $-CH_2$), 58.4 (s, $-OCH_3$), 32.7 (s, $-CH_2$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ -43 (br s, $\Delta\nu_{1/2} = 75$ Hz). Anal. Calcd for $C_{16}H_{36}GeO_8$: C, 44.79; H, 8.46. Found: C, 43.86; H, 9.04 (yield, 20%).

$Ge[S(CH_2)_3CH_3]_4$. This tetrakis(thio)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. The reaction mixture was heated during addition of germanium tetrachloride to reactants. ^1H NMR (500 MHz, toluene-d_8): δ 2.73 (t, 8H, $-SCH_2$), 1.60 (m, 8H, $-CH_2$), 1.37 (m, 8H, $-CH_2$), 0.86 (t, 12H, $-CH_3$). ^{13}C NMR (125.6 MHz, toluene-d_8): δ 34.2 (s, $-S\mathit{C}H_2$), 29.2 (s, $-\mathit{C}H_2$), 21.6 (s, $-\mathit{C}H_2$), 13.5 (s, $-\mathit{C}H_3$). ^{73}Ge NMR (17.43 MHz, toluene-d_8): δ 138 (br s, $\Delta\nu_{1/2} = 37$ Hz). Anal. Calcd for $C_{16}H_{36}GeS_4$: C, 44.76; H, 8.45. Found: C, 45.34; H, 9.08 (yield, 30%).

$Ge[SCH(CH_3)_2]_4$. This tetrakis(thio)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.41 (septet, 4H, $-SC\mathit{H}$), 1.38 (d, 24H, $-CH_3$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 36.3 (s, $-S\mathit{C}H$), 27.0 (s, $-\mathit{C}H_3$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ 120 (br s, $\Delta\nu_{1/2} = 39$ Hz). Anal. Calcd for $C_{12}H_{28}GeS_4$: C, 38.62; H, 7.56. Found: C, 39.31; H, 8.26 (yield, 50%).

$Ge[S(CH_2)_2N(CH_3)_2]_4$. This tetrakis(thio)germane was prepared as described for $Ge[O(CH_2)_2N(CH_3)_2]_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 2.73 (m, 8H, $-CH_2$), 2.40 (m, 8H, $-CH_2$), 2.10 (s, 24H, $-C\mathit{H}_3$). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 60.5 (s, $-S\mathit{C}H_2$), 45.0 (s, $-\mathit{C}H_3$), 26.9 (s, $-\mathit{C}H_3$). ^{73}Ge NMR (17.43 MHz, $CDCl_3$): δ 141 (br s, $\Delta\nu_{1/2} = 79$ Hz). Anal. Calcd for $C_{16}H_{40}GeN_4S_4$: N, 11.45; C, 39.27; H, 8.24. Found: N, 11.13; C, 38.10; H, 8.62 (yield, 20%).

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