Formation of Halide Complexes of Methyl- and Inorganic Germaniun(IV) in Aqueous Hydrohalogenic Acid Solutions

Yoshiki Sohrin
Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611

(Received May 31, 1991)

The reaction of methyl- and inorganic germanium(IV) hydroxides ($(CH_3)_nGe(OH)_{4-n}$; $n=0, 1, 2$, or 3) with halide ions ($X^-=Cl^-$, Br^-, or I^-) to form halide complexes ($(CH_3)_nGeX_{4-n}$) in aqueous acidic solution has been investigated by liquid–liquid extraction, solid–liquid distribution (ion exchange), and ^1H NMR spectrometry. It has been found that methylgermanium moieties are hard Lewis acids similarly to inorganic germanium(IV), because the stability constant of the halide complexes decreases in the order $Cl^- > Br^- > I^-$. The stability constant for an X^- ion increases as the number of methyl groups attached to the germanium atom increases. The species of inorganic-, monomethyl-, and dimethylgermanium are nonionic and have a tetrahedral structure in HX solution, and OH^- ions attached to the germanium atom are stepwise substituted by X^- ions with an increase in HX activity. Trimethylgermanium alone forms a cation, when the activity of HX is not sufficiently high. These facts suggest that the transfer of a negative charge from methyl groups to the central germanium atom lowers the stability of the bond between the germanium atom (hard acid) and an OH^- ion (hard base).

Organogermanium(IV) compounds generally have a tetrahedral configuration and are expressed as R_nGeL_{4-n} ($n=1, 2, 3$, or 4), where R is a σ-bonded organic ligand and L is the other ligand bonding to the germanium atom via an atom other than carbon.[1,2] The germanium–carbon (Ge–C) bond is highly inert and stable to water or air, and methylgermanium species ($n \leqslant 3$) have been found in natural waters.[3] The aqueous solution chemistry of organogermanium, however, is only slightly known.

Inorganic germanium(IV) (Ge_i) is an extremely hard and strong Lewis acid. Ge_i of low concentration is thoroughly hydrolyzed and dissolved in water as $Ge(OH)_4$, which is sometimes mentioned as GeO_2. The hydroxide complex is transformed into the halide complex (GeX_4; X=Cl, Br, or I) in hydrohalogenic acid (HX) solution, which is extracted into nonpolar organic solvents.[4,5] Although it is reported that organogermanium compounds also dissolve in water as $R_nGe(OH)_{4-n}$ and form R_nGeX_{4-n} in HX solution,[6–8] there is no quantitative knowledge of the reaction.

While studies on the structure of germanium species in aqueous solution are also rare, it appears that the tetrahedral structure is common not only for the halide complexes but also for the hydroxide complexes. Raman spectra suggested that Ge_i is present as tetrahedral $[O_2Ge(OH)_2]^{2-}$ in nearly saturated aqueous KOH,[9] and that $(CH_3)_2Ge(OH)_2$ has a tetrahedral structure in water.[8]

In order to clarify the effect of methyl groups on the Lewis acid nature of the central germanium atom, a study on halide complexing of methyl- and inorganic germanium in HX solution by liquid–liquid extraction was undertaken. In the present paper, the data of liquid–liquid extraction have been analyzed based on the information on the charge and structure of the germanium species, which is obtained from solid–liquid distribution (ion exchange) and NMR chemical shift of the methyl protons.

Experimental

Reagents. Standard solutions of monomethylgermanium (MeGe), dimethylgermanium (Me_2Ge), and trimethylgermanium (Me_3Ge) (1×10^{-2} M; 1 M=1 mol dm^{-3}) were prepared by alkaline hydrolysis of their chlorides (Alfa or Aldrich) as described previously.[10] (Caution: Although the toxicity of organogermanium compounds is thought to be low,[1] handling of these compounds should be carried out in a hood to avoid inhalation). A standard solution of 1×10^{-2} M Ge_i was prepared from germanium dioxide (Wako) according to Shimomura et al.[11] These standard solutions were stable over a year. Other chemicals were of analytical reagent grade. Distilled water was used throughout.

Resins. The resins used were a strong basic anion-exchange resin, Muromac MSA-1 (100—200 mesh, Cl^- form, Muromachikagakukogyo), a strong acidic cation-exchange resin, Muromac MSC-1 (100—200 mesh, Na^+ form, Muromachikagakukogyo), and a CHP20P resin (200—400 mesh, Mitsubishi Chemicals) that had no ion-exchange groups. These resins were macroreticular styrene–divinylbenzene copolymers. The anion-exchange resin was washed successively with distilled water, methanol, 1 M HCl, and 1 M NaOH, changed into Cl^- form by soaking the resin in ten times volume of 2 M HCl overnight, and washed with distilled water until the effluent was free from Cl^- ions. The cation-exchange resin was washed in the same way, and converted to H^+ form in 4 M HCl. The CHP20P resin was washed successively with methanol, 1 M NaOH, 1 M HCl, and methanol. These resins were dried to a constant weight in a vacuum drying oven and stored in a desiccator.

Procedure. Liquid–Liquid Extraction: An aliquot of aqueous solution containing various concentrations of HX and 5×10^{-5}—1×10^{-3} M of a germanium compound was shaken with an aliquot of CCl_4 for 30 min in a 30 ml centrifuge tube at 25 ± 0.1 °C, using a Taitec bio-shaker BR-30L. After phase separation, the germanium concentration in both the phases was determined with a Japan Jarrel Ash ICAP-500 inductively coupled argon plasma emission spectrometer. The precise procedure was described previously.[10]

When HI solution was used as the aqueous phase, following precautions were taken to make the solution free from I_3^-. The experiment was done under red light, and aqueous and organic solutions were deaerated with nitrogen. The I_3^- ions were removed from an HI stock solution just before its use by passing the solution through the column in which an I^- form anion-exchange resin was packed. In spite of the above precautions, it was shown by absorbance measurement at 351 nm that I_3^- ions were formed during the extraction experiment. For example, 7.0×10^{-5} M and 2.2×10^{-3} M of I_3^- were found in 0.725 M and 5.90 M HI solutions, respectively. Thus Me_3Ge alone that was extracted into the organic phase in the lowest acid concentration range was examined in the HI–CCl_4 system.

Solid-Liquid Distribution: Nine ml of aqueous solution containing various concentrations of HCl and 0.50 g of a dried ion-exchange resin were placed in a 30 ml centrifuge tube. After the addition of 1 ml of a 1×10^{-2} M germanium standard solution, the tube was shaken gently for 24 h at 25±0.1 °C with the bio-shaker. The resin was separated by filtration, and shaken with 10 ml of 1 M NaOH for 24 h to elute the germanium compound. The germanium compound concentrations in the HCl solution and the eluate were determined with the ICAP-500. From these concentrations, the distribution coefficient

$$K_d = \text{Amount of germanium in resin (mol g}^{-1})/\text{Amount of germanium in HCl solution (mol ml}^{-1}) \qquad (1)$$

was calculated.

Since the CHP20P resin is hydrophobic, 0.50 g of the dried resin was first suspended in 5 ml of methanol. After the addition of 10 ml of distilled water, the resin was shaken with the methanol–water mixture for 30 min, and separated by filtration. The resin was shaken with distilled water, and finally with an HCl solution of which HCl concentration was the same as that in the distribution experiment. Then the resin was filtered and immediately used for the experiment. The subsequent procedure was similar to that for ion-exchange resins.

^{1}H NMR Spectra: ^{1}H NMR spectra were obtained in D_2O or $CDCl_3$ at 25±1 °C on a Varian VXR200 spectrometer with a Varian VXR4000 data station. Germanium compound concentrations were 10^{-1}—10^{-3} M. Chemical shifts were measured relative to the resonance of sodium 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid in D_2O and tetramethylsilane in $CDCl_3$.

Mean Activity of HX. The acid concentration in aqueous solution was measured by titration with an NaOH solution, using a Toa Electronics automatic titrator AUT-1 equipped with a glass electrode. The mean activity of HX ($a_\pm$), which was expressed on the molarity scale, was calculated from the measured concentration using a table described by Hamer and Wu[12] and the density data.[13] The initial and equilibrium concentrations of the acid agreed within 1% in solution containing more than 1 M of HX. For more dilute HX solution, however, the equilibrium concentration of the acid was lower than the initial concentration. This decrease was mainly caused by NaOH contained in the added germanium standard solution. Since the change in X^- ion concentration was negligible, the average of $a_\pm$ calculated from the initial and equilibrium concentrations of the acid was adopted as data. The error in $\log a_\pm$ brought about by the above treatment is possibly a maximum of 0.2 for 10^{-3} M HX solution.

Results and Discussion

Liquid-Liquid Extraction. The results of liquid-liquid extraction are illustrated in Fig. 1. The distribution ratio of a germanium compound (D) is plotted against $a_\pm$ on log–log scale. The D is defined as

$$D = C_{Ge,o}/C_{Ge} \qquad (2)$$

where $C_{Ge,o}$ and C_{Ge} mean the analytical molar

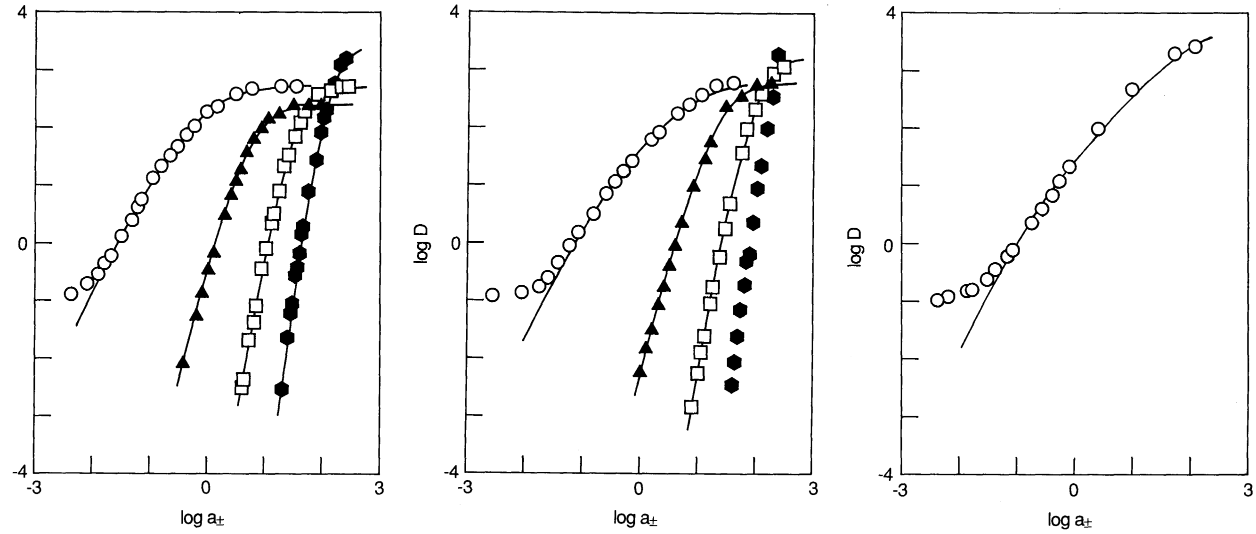

Fig. 1. Plots of log D vs. log $a_\pm$ for 5×10^{-5}—1×10^{-3} M germanium compounds. Solid curves are calculated using the partition constants (Table 1) and stepwise stability constants (Table 2). Only a portion of the experimental points are shown. (a, left) HCl–CCl_4 system; (b, center) HBr–CCl_4 system; (c, right) HI–CCl_4 system; ●, Ge_i; □, MeGe; ▲, Me_2Ge; ○, Me_3Ge.

concentration of the germanium compound in the organic phase and the aqueous phase, respectively. Cleavage of the Ge–C bonds did not occur under the experimental conditions. Distribution equilibrium was reached in a few minutes for all germanium compounds. The recovery was a minimum of 95%.

Log D did not depend on the initial concentration of germanium compounds in the aqueous phase which varied between 5×10^{-5} and 1×10^{-3} M. This fact suggests that germanium species are monomeric in both the aqueous and organic phases. While the log D vs. log $a_\pm$ plot of Me_3Ge is sigmoid, the plateau in the lower log $a_\pm$ range does not appear for the other germanium compounds. Germanium compounds should exist as nonionic hydroxides ($(CH_3)_nGe(OH)_{4-n}$; hereafter n=0, 1, 2, or 3) in water.[4,7,8] When the formation and distribution of halide complexes ($(CH_3)_nGeX_{4-n}$) are negligible in the low log $a_\pm$ range, D is independent of log $a_\pm$ and equal to the partition constant of the hydroxide:

$$P_{OH} = [(CH_3)_nGe(OH)_{4-n}]_o/[(CH_3)_nGe(OH)_{4-n}], \tag{3}$$

where brackets signify the molar concentration. Log P_{OH} of Me_3Ge is −0.95. The formation of oligomers of Me_2Ge, MeGe, and Ge_i is unlikely in the low log $a_\pm$ range, because log D of these compounds is much lower than the log P_{OH} of Me_3Ge.

Log D increases with the increase in log $a_\pm$. This is caused by the formation and distribution of the germanium halide complex. Benoit and Clerc[4] investigated the liquid–liquid extraction of Ge_i in the HCl–CCl_4 system, and found that the analytical ratio of Ge:Cl in the organic phase was 1:4. When log $a_\pm$ is sufficiently high, log D does not depend on log $a_\pm$, which implies that $(CH_3)_nGeX_{4-n}$ is the dominant species in both the aqueous and organic phases. Then, D agrees with the partition constant of the halide complex:

$$P_x = [(CH_3)_nGeX_{4-n}]_o/[(CH_3)_nGeX_{4-n}]. \tag{4}$$

It is obvious from Fig. 1 that P_x is much higher than P_{OH} for each germanium compound.

The analysis of the data is carried out on the assumption that $(CH_3)_nGeX_{4-n}$ alone is extracted into the organic phase. With regard to Me_3Ge, the D corrected by subtracting P_{OH} from the apparent D is used for the analysis. The log D vs. log $a_\pm$ plot is linear in the low log $a_\pm$ range for all systems. The slope is almost 2 for Me_3Ge, 4 for Me_2Ge, 6 for MeGe, and 8 for Ge_i (Table 1). The extraction equilibrium, overall stability constant, and extraction constant can be expressed as

$$(CH_3)_nGe(OH)_{4-n} + (4-n)H^+ + (4-n)X^- \rightleftharpoons (CH_3)_nGeX_{4-n} + (4-n)H_2O, \tag{5}$$

$$(CH_3)_nGeX_{4-n} \rightleftharpoons (CH_3)_nGeX_{4-n,o}, \tag{6}$$

$$\beta^0 = ((CH_3)_nGeX_{4-n})(H_2O)^{4-n}/((CH_3)_nGe(OH)_{4-n})(H^+)^{4-n}(X^-)^{4-n}, \tag{7}$$

$$K_{ex}{}^0 = ((CH_3)_nGeX_{4-n})_o(H_2O)^{4-n}/((CH_3)_nGe(OH)_{4-n})(H^+)^{4-n}(X^-)^{4-n} \tag{8}$$
$$=\beta^0 P_x{}^0,$$

where parentheses represent the activity and superscript 0 denotes the thermodynamic constant. The following are also assumed: (i) the activity coefficients are unity for germanium species in both the aqueous and organic

Table 1. Extraction Constants, Partition Constants, and Overall Stability Constants for Halide Complexes of Methyl- and Inorganic Germanium at 25 °C

	log D vs. log $a_\pm$ Slope[a]	log $K_{ex}{}^0$[b]	log $P_x{}^0$	log β^0
		HCl[c]		
Ge_i	7.99±0.56[d] (5)[e]	−12.99±0.04	3.42±0.23[f]	−16.41±0.23
MeGe	5.94±0.27 (7)	−6.22±0.03	2.70±0.03 (4)	−8.92±0.04
Me_2Ge	3.77±0.01 (4)	−0.44±0.02	2.39±0.03 (5)	−2.83±0.04
Me_3Ge	1.93±0.03 (12)	3.03±0.01	2.73±0.01 (4)	0.30±0.01
		HBr		
Ge_i	7.98±0.72 (8)	−15.20±0.04	4.4[g]	−19.6
MeGe	5.42±0.17 (8)	−8.24±0.03	3.20±0.08[f]	−11.44±0.09
Me_2Ge	3.58±0.05 (9)	−2.31±0.04	2.78±0.03 (3)	−5.09±0.05
Me_3Ge	1.84±0.10 (8)	2.32±0.03	2.83±0.02 (3)	−0.51±0.04
		HI		
Me_3Ge	1.59±0.03 (6)	2.12±0.05	3.69±0.15[f]	−1.57±0.16

a) Calculated using points adopted from a linear portion in the low log $a_\pm$ range, where the variation in log D is about 2. b) Equation 10 was fitted to the same points which were used to calculate the slope. c) Ref. 10. d) Standard deviation. e) Number of points. f) Evaluated by the curve fitting. g) Estimated from Fig. 2.

phases; (ii) the activity of water is unity; (iii) the activities of H^+ and X^- ions are equal to $a_\pm$. Then,

$$D = ((CH_3)_nGeX_{4-n})_o/((CH_3)_nGe(OH)_{4-n}), \qquad (9)$$

$$\log D = 2(4-n)\log a_\pm + \log K_{ex}^0. \qquad (10)$$

The observed slopes can be rationalized by Eq. 10.

When $\log a_\pm$ is sufficiently high,

$$\log D = \log P_x^0. \qquad (11)$$

Thus, β^0 can be estimated from the extraction data. The values of $\log K_{ex}^0$, $\log P_x^0$, and $\log \beta^0$ obtained by a linear least-squares method are listed on Table 1. The plateau in the higher $\log a_\pm$ range was not observed for Ge_i in the HCl and HBr systems, MeGe in the HBr system, and Me_3Ge in the HI system. Log P_x^0 of $GeCl_4$, CH_3GeBr_3, and $(CH_3)_3GeI$ is obtained as a parameter in the estimation of stepwise stability constants which is described later. This estimation can not be applied to $GeBr_4$, because the $\log P_x^0$ is very high. Figure 2 shows the relationship between $\log P_x^0$ and van der Waals volumes (V_w) of the germanium halide complexes that are calculated according to Bondi.[14] A fairly good correlation is observed among MeGe, Me_2Ge, and Me_3Ge, and the regression line is

$$\log P_x^0 = 0.100\ V_w - 3.18 \qquad (r = 0.890). \qquad (12)$$

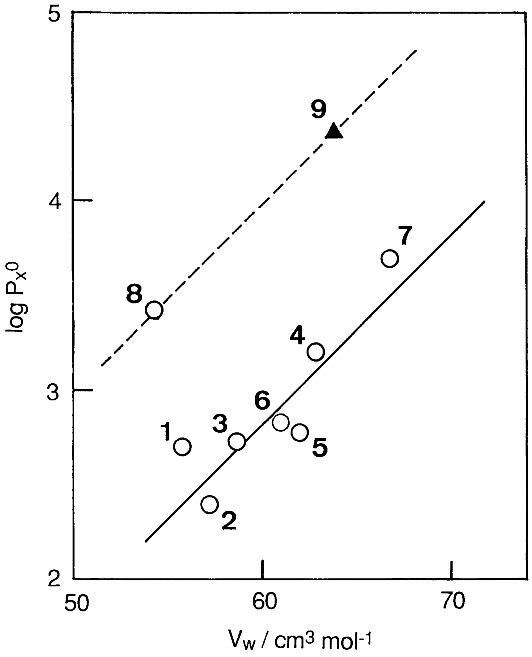

Fig. 2. Plots of $\log P_x^0$ vs. V_w for germanium halides. The solid line shows Eq. 12. ○, determined from the liquid–liquid extraction data; ▲, estimated; 1, CH_3GeCl_3; 2, $(CH_3)_2GeCl_2$; 3, $(CH_3)_3GeCl$; 4, CH_3GeBr_3; 5, $(CH_3)_2GeBr_2$; 6, $(CH_3)_3GeBr$; 7, $(CH_3)_3GeI$; 8, $GeCl_4$; 9, $GeBr_4$.

Log P_x^0 of $GeCl_4$ is higher than that expected from this correlation, which is attributable to that the molecule has no dipole moment and is highly soluble in CCl_4. Assuming that the same extent of departure from the regression line occurs for $GeBr_4$, the $\log P_x^0$ is evaluated to be 4.4. Although application of the regular solution theory[15] was tried, no improvement over the above estimation of $\log P_x^0$ was made because of increased number of unknown parameters.

Solid–Liquid Distribution. The dependence of $\log K_d$ on $\log a_\pm$ of HCl is realized in Fig. 3. The recovery of germanium compounds was poorer (minimum 80%) and the experimental error was larger than that in the liquid–liquid extraction.

Although distribution of Ge_i, MeGe and Me_2Ge to the ion-exchange resins is negligible in the low $\log a_\pm$ range, that to the CHP20P resin is significant. The value of $\log K_d$ for the CHP20P resin is enhanced in the order Ge_i<MeGe<Me_2Ge<Me_3Ge. These facts support that the germanium compounds are dissolved as the nonionic hydroxides in water. Log K_d for the CHP20P resin rises with increasing $\log a_\pm$, which is ascribed to the formation and distribution of the germanium chlorides.

Log K_d of Ge_i, MeGe, and Me_2Ge for the anion- and cation-exchange resins also increases with the increase in $\log a_\pm$, while the value of $\log K_d$ is lower than that for the CHP20P resin. It is probable that the distribution of these compounds is caused not by ionic interaction but by hydrophobic adsorption on the resin substrate. Hence, the dominant dissolved species of Ge_i, MeGe, and Me_2Ge are nonionic in HCl solution. The coordination number of the germanium atom in these compounds remains at four, and OH^- ions bonded to the germanium atom are stepwise substituted by Cl^- ions with increasing $\log a_\pm$.

It has been supposed that Ge_i forms anionic species, such as $[Ge(OH)_xCl_{5-x}]^-$ or $[Ge(OH)_xCl_{6-x}]^{2-}$, in HCl solution (>5 M; $\log a_\pm$>1.2).[4,16-18] Distribution of Ge_i to an anion-exchange resin was given as a piece of the evidence.[16] However, $\log K_d$ of Ge_i for the CHP20P resin is higher than that for the anion-exchange resin, and the distribution to the cation-exchange resin is significant above 6.5 M of HCl ($\log a_\pm$>1.6), as shown in Fig. 3. Although it was stated that electrophoresis of the Ge_i anion was observed in 6 M HCl ($\log a_\pm$=1.4),[17] the conclusion was based on the concentration difference of less than 5%, of which significance was doubtful from an analytical point of view. Everest and Harrison[18] claimed the presence of Ge_i anion in 6—9 M HCl solution saturated with Ge_i, because solubility of Ge_i and its adsorption on an anion-exchange resin had the maximum in this [HCl] range. They also reported that the solubility maximum did not occur in HBr solution and that no Ge_i bromo complexes were formed. In dilute Ge_i solution, however, the distribution to the anion-exchange resin shows no maximum in 6—9 M HCl (Fig. 3: 1.4—2.2 in $\log a_\pm$), and the nature of $\log D$ vs.

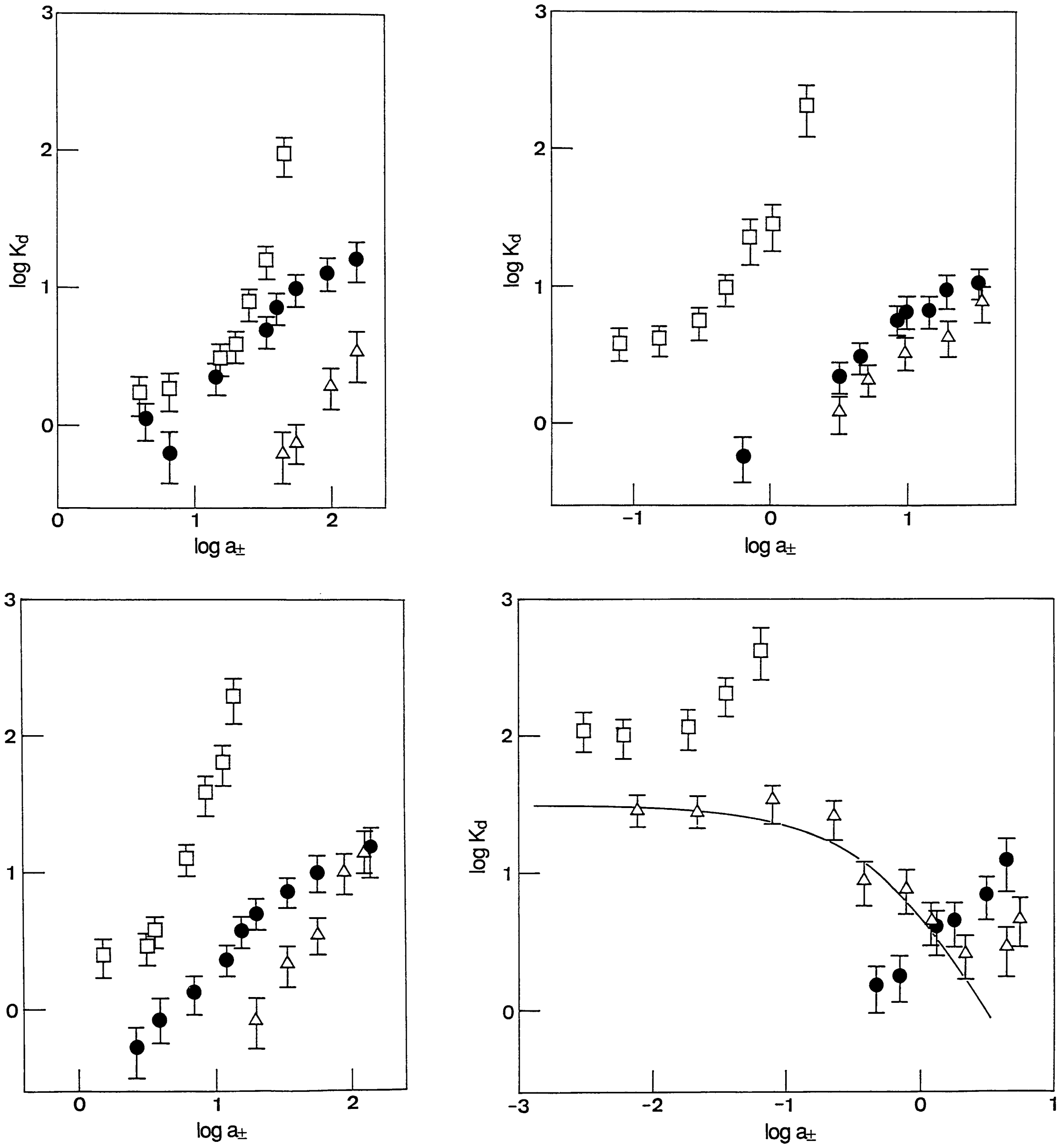

Fig. 3. Plots of log K_d vs. log $a_\pm$ for 1×10^{-3} M germanium compounds in HCl solution. Vertical bars show the 1 standard deviation. The solid curve is calculated from Eq. 20. (a, top left) Ge$_i$; (b, bottom left) MeGe; (c, top right) Me$_2$Ge; (d, bottom right) Me$_3$Ge; ●, anion-exchange resin; △, cation-exchange resin; □, CHP20P resin.

log $a\pm$ plots for Ge$_i$ in the HCl and HBr systems is identical (Fig. 1). Benoit and Clerc[4] gave the solvent extraction data in evidence of the Ge$_i$ anion. They extracted $GeCl_4$ from aqueous phases which contained a constant total molality of HCl–$HClO_4$ or HCl–LiCl into an organic phase of CCl_4, to investigate the dependence of log D on log(Cl^-) or log(H^+). When the total molality was 12.0 mol kg^{-1} (log $a\pm$=2.32), d log D/d log(Cl^-)=−0.2 and d log D/d log(H^+)=0.7 were found, and the Ge$_i$ species was thought to be $[GeCl_4(OH)(H_2O)]^-$. However, the activity coefficients of Cl^- and H^+ ions are likely to vary with the change in the solute composition, when the total molality is high. Figure 1 shows that d log D/d log $a\pm$ is 1.90 for 12.0 mol kg^{-1} HCl, which can not be explained on the presence of $[GeCl_4(OH)(H_2O)]^-$. The previously reported evidence of the Ge$_i$ anion is controvertible as described above. Consequently, it is presumed that Ge$_i$ does not form anionic species and retains a tetrahedral configuration in HX solution similarly to Me$_2$Ge and MeGe.

A remarkable difference of cation-exchange behavior for Me$_3$Ge from that for the other germanium compounds appears in Fig. 3. Me$_3$Ge is highly adsorbed by the cation-exchange resin in the low log $a\pm$ range, whereas it is not adsorbed by the anion-exchange resin. This indicates that Me$_3$Ge forms a cation in HCl solution.

^{1}H NMR Spectra. Methyl protons of each germanium compound gave a singlet resonance line in D_2O

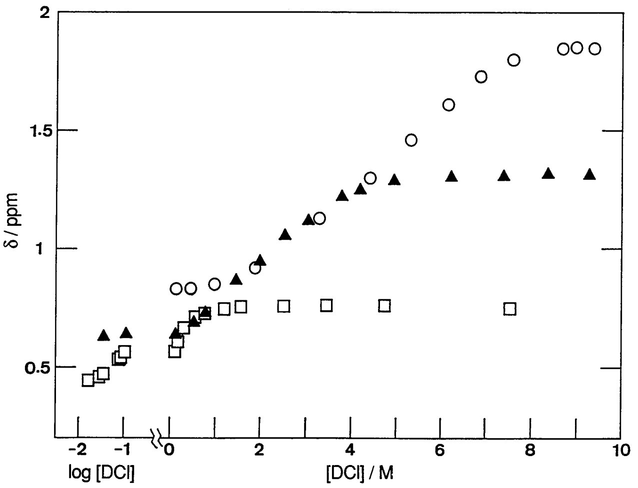

Fig. 4. Chemical shift of the methyl protons of 10^{-3}—10^{-1} M germanium compounds in D_2O as a function of [DCl]. ○, MeGe; ▲, Me_2Ge; □, Me_3Ge.

and $CDCl_3$ except one case that is mentioned later. The chemical shift of the methyl protons in D_2O is plotted against [DCl] in Fig. 4. The chemical shifts remain constant in the low [DCl] range, increase with the increase in [DCl], and reach to maximums. The maximums are the same as the chemical shifts for germanium chlorides in $CDCl_3$, which are 1.68 ppm for CH_3GeCl_3, 1.23 ppm for $(CH_3)_2GeCl_2$, and 0.72 ppm for $(CH_3)_3GeCl$. This supports that the dissolved species of methylgermanium in D_2O containing sufficiently high concentration of DCl are the chloride complexes with a tetrahedral configuration. The slight difference between the chemical shifts in D_2O and $CDCl_3$ is attributable to solvent effect.

The chemical shift of methyl protons for $(CH_3)_3GeOH$ was 0.44 ppm in D_2O and 0.42 ppm in $CDCl_3$, and that for $(CH_3)_3GeCl$ was 0.76 ppm in D_2O and 0.72 ppm in $CDCl_3$. The chemical shift was 1.22 ppm for $(CH_3)_3COH$, 1.60 ppm for $(CH_3)_3CCl$, 0.16 ppm for $(CH_3)_3SiOH$, and 0.42 ppm for $(CH_3)_3SiCl$ in $CDCl_3$. The absolute values of the chemical shift and the chemical shift changes caused by replacement of an OH^- ion bonded to the central atom by a Cl^- ion are similar among these compounds. Since the central carbon and silicon atoms in these compounds are sp^3 hybridized, it is assumed that the germanium atom of $(CH_3)_3GeOH$ and $(CH_3)_3GeCl$ is also sp^3 hybridized in both $CDCl_3$ and D_2O. With regard to the Me_3Ge cation that is suggested by the ion-exchange experiment, an sp^3d hybrid orbital is another possibility. A trimethyltin cation, $[(CH_3)_3Sn(H_2O)_2]^+$ has a bipyramidal sp^3d configuration, of which carbon atoms form a planar triangle.[19] It is difficult to presume the structure of Me_3Ge cation from the present data.

The chemical shift difference between the hydroxide and chloride complexes for Me_2Ge (0.67 ppm) and MeGe (1.02 ppm) in D_2O is twice and three times as great as that for Me_3Ge (0.32 ppm), respectively. This implies that the central germanium atoms of Me_2Ge and MeGe are also sp^3 hybridized, and that the effect of ligand exchange on the chemical shift is an additive property. Since the chemical shift increases monotonously, the formation of chloro complex anions in the intermediate [DCl] range is very unlikely.

When $(CH_3)_3GeOH$ was extracted from aqueous solution into $CDCl_3$, two singlet lines were found at 0.42 and 0.36 ppm in the organic phase. The peak area ratio was dependent on $C_{Me_3Ge,o}$, and the latter peak became large with increasing $C_{Me_3Ge,o}$. These peaks are assigned to $(CH_3)_3GeOH$ and $(CH_3)_3GeOGe(CH_3)_3$, respectively. The dimerization is written as

$$2(CH_3)_3GeOH_{,o} \rightleftharpoons (CH_3)_3GeOGe(CH_3)_{3,o} + H_2O. \qquad (13)$$

Since the reaction does not proceed at an appreciable rate after separation of the aqueous and organic phases, the two lines are observed separately. The equilibrium constant for the reaction (13) is estimated at 13 from $C_{Me_3Ge,o}$ and the peak area ratio. This value indicates that the dimer comprises only 2.5% of 10^{-3} M of Me_3Ge in $CDCl_3$ which is equilibrated with water, and that the dimerization is negligible in the analysis of the liquid–liquid extraction data. When Me_2Ge and MeGe were extracted from aqueous solution into $CDCl_3$, no methyl resonance lines other than those for $(CH_3)_2GeCl_2$ and CH_3GeCl_3 were found. Although the formation of Me_2Ge oligomers in CCl_4 has been reported,[20] it is also negligible in the liquid–liquid extraction.

Stepwise Stability Constants. Based on the above discussion, the germanium species in HX solution are presumed as follows. The species of Ge_i, MeGe, and Me_2Ge have a tetrahedral structure and are nonionic. Hydroxide ions attached to the central germanium atom are stepwise substituted by X^- ions with the increase in $\log a_\pm$. Me_3Ge forms a cation when the $\log a_\pm$ is not sufficiently high. Now, stepwise stability constants for these species are estimated from the liquid–liquid extraction data.

For Ge_i, MeGe, and Me_2Ge, the stepwise reaction and stability constant are written as

$$(CH_3)_nGe(OH)_{i+1}X_{j-1} + H^+ + X^- \rightleftharpoons (CH_3)_nGe(OH)_iX_j + H_2O, \qquad (14)$$

$$K_j^0 = ((CH_3)_nGe(OH)_iX_j)(H_2O)/((CH_3)_nGe(OH)_{i+1}X_{j-1})(H^+)(X^-), \qquad (15)$$

where $n+i+j=4$. For Me_3Ge, the stepwise reaction and stability constant can be defined as

$$(CH_3)_3GeOH + H^+ \rightleftharpoons [(CH_3)_3Ge(H_2O)]^+ \qquad (16)$$

Table 2. Stepwise Stability Constants for Methyl- and Inorganic Germanium Species in HX Solution at 25 °C

	$n^{a)}$	$\log K_1^0$	$\log K_2^0$	$\log K_3^0$	$\log K_4^0$	$\log \beta^{0b)}$
			HCl			
Ge_i	21	$-3.02\pm0.29^{c)}$	-3.84 ± 0.31	-4.82 ± 0.51	-5.09 ± 0.56	-16.77 ± 0.87
MeGe	25	-2.31 ± 0.10	-2.95 ± 0.12	-3.81 ± 0.06	—	-9.07 ± 0.17
Me_2Ge	17	-0.71 ± 0.04	-2.15 ± 0.03	—	—	-2.86 ± 0.05
			HBr			
MeGe	22	-2.57 ± 0.10	-4.32 ± 0.21	-4.67 ± 0.23	—	-11.56 ± 0.33
Me_2Ge	16	-1.59 ± 0.06	-3.49 ± 0.04	—	—	-5.08 ± 0.07

	n	$\log K_{1p}^0$		$\log K_{1x}^0$	$\log \beta^0$
			HCl		
Me_3Ge	27	0.55 ± 0.04		-0.18 ± 0.03	0.37 ± 0.05
			HBr		
Me_3Ge	28	0.72 ± 0.04		-1.16 ± 0.02	-0.44 ± 0.04
			HI		
Me_3Ge	15	0.71 ± 0.09		-2.21 ± 0.18	-1.50 ± 0.20

a) Number of points. b) Calculated from the stepwise stability constants. c) Standard deviation.

$$K_{1p}{}^0 \doteq ([(CH_3)_3Ge(H_2O)]^+)/((CH_3)_3GeOH)(H^+) \quad (17)$$

$$[(CH_3)_3Ge(H_2O)]^+ + X^- \rightleftharpoons (CH_3)_3GeX + H_2O \quad (18)$$

$$K_{1x}{}^0 = ((CH_3)_3GeX)(H_2O)/([(CH_3)_3Ge(H_2O)]^+)(X^-) \quad (19)$$

The assumptions that were made in the evaluation of $K_{ex}{}^0$ are adopted in a non-linear least-squares computation, except that the activity of water is calculated from the acid concentration and osmotic coefficient,[12] because wide ranges of [HX] are concerned in the computation. Resulting values are listed on Table 2. Log $P_x{}^0$ of $GeCl_4$, CH_3GeBr_3 and $(CH_3)_3GeI$ is also determined as a parameter by the computation (Table 1). The computation is inapplicable to Ge_i in the HBr system, because the bending on the log D vs. log $a_\pm$ plot is not observed. The solid curves in Fig. 1 are calculated using the partition and stepwise stability constants.

Values of log β^0 listed on Table 2 are calculated from the stepwise stability constants, and in agreement with those on Table 1. Figure 5 shows the equilibrium composition of the germanium species in aqueous solution as a function of [HCl]. It is apparent from Figs. 4 and 5 that the [DCl] range where the variation in the chemical shift occurs is coincident with the [HCl] range where the composition of the germanium species changes. Moreover, the distribution of Me_3Ge to the cation-exchange resin is reproduced using the stepwise stability constants. When the Me_3Ge cation is the only species that is adsorbed by the cation-exchange resin,

$$\begin{aligned} K_d &= 10^{-3}[[(CH_3)_3Ge(H_2O)]^+]_r/ \\ &\quad \{[(CH_3)_3GeOH] + [[(CH_3)_3Ge(H_2O)]^+] + [(CH_3)_3GeCl]\} \\ &= 10^{-3}K_H{}^{Me_3Ge}[H^+]_r/\{1/K_{1P}{}^0 + a_\pm + K_{1X}{}^0(a_\pm)^2/(H_2O)\}, \end{aligned} \quad (20)$$

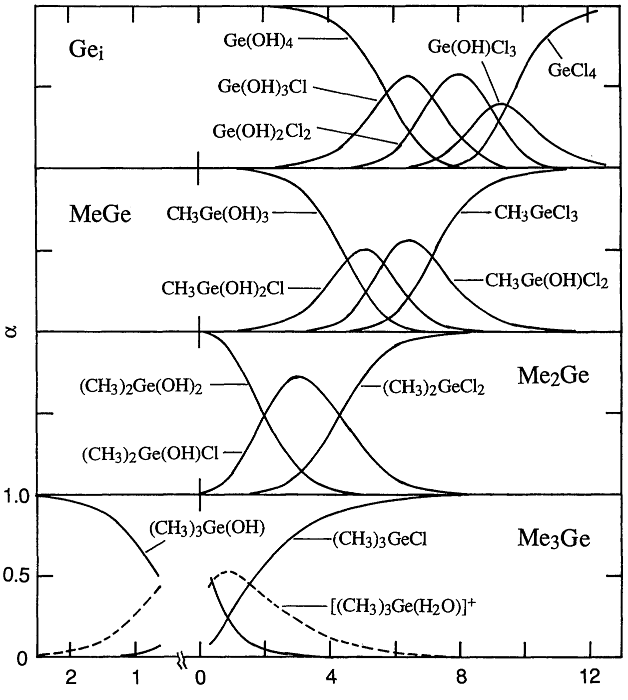

Fig. 5. Equilibrium composition of germanium species in aqueous solution as a function of [HCl].

where subscript r implies the concentration in the resin (mol g^{-1}) and

$$K_H{}^{Me_3Ge} = (H^+)[[(CH_3)_3Ge(H_2O)]^+]_r/[H^+]_r[[(CH_3)_3Ge(H_2O)]^+]. \quad (21)$$

Assuming that $K_H{}^{Me_3Ge}=1.7\times10^3$ and $[H]_r=5.0\times10^{-3}$, the solid curve in Fig. 3 is obtained. These results indicate the validity of the stepwise stability constants estimated here.

Effect of Methyl Groups on the Lewis Acid Nature of the Central Atom. Log β^0 for a methylgermanium moiety decreases in the order $Cl^- > Br^- > I^-$ (Tables 1 and 2). This indicates that the methylgermanium moieties are hard Lewis acids similarly to Ge_i.[8] Log β^0 for an X^- ion increases as the number of methyl groups attached to the germanium atom increases. The same tendency appears in the stepwise stability constants for an equivalent coordination site (Table 2). For chloride complexes, $\log K_4{}^0 = -5.09$ for Ge_i, $\log K_3{}^0 = -3.81$ for MeGe, $\log K_2{}^0 = -2.15$ for Me_2Ge, and $\log K_{1p}{}^0 K_{1x}{}^0 = 0.37$ for Me_3Ge. Thus an OH^- ion bound to a germanium atom is easily replaced by an X^- ion, when methyl groups are attached to the germanium atom. This feature is clearly shown in Fig. 5. The [HCl] range where the species composition changes shifts to a lower concentration range with the increase in the number of methyl groups.

Since the charge and structure of germanium compounds do not alter in the present reaction, solvent effects are not serious. The tetrahedral configuration around the central germanium atom implies that the steric strain between the ligands bonded to the germanium atom is hardly affected by the size of the ligands investigated in this paper. Consequently, the dominant factor is an inductive effect. The transfer of a negative charge from a soft base CH_3^- to the central germanium atom increases the electron density on the germanium atom, and weakens the ionic interaction between the germanium atom and a hard base, such as an OH^- ion.[21]

The inductive effect is most pronounced for Me_3Ge. The acidity of the central germanium atom of Me_3Ge is remarkably reduced by methylation. The Me_3Ge moiety can not cause hydrolysis in dilute HX solution, and forms a hydrated cation. Such a hydrated cation is not formed by Ge_i, MeGe, and Me_2Ge in HCl and HBr solutions. However, since $\log P_{1x}{}^0$ of Me_3Ge decreases in the order $Cl^- > Br^- > I^-$, the Me_3Ge moiety is still a hard acid. Hence, the electron donation from methyl groups that reduces the bond stability between the germanium atom and a hard base does not result in stabilization of the bond between the germanium atom and a soft base, such as an I^- ion.

Cassol et al.[22] reported a similar effect by methylation on complex formation between methyltin(IV) cations, which are also hard, but are weaker Lewis acids, and F^- or Cl^- ions. According to their data, the number of methyl groups bonded to the tin atom hardly affects the tendency to bind Cl^- in equivalent coordination places: as an example, $\log K_3 = -0.25$ for CH_3Sn^{3+}, $\log K_2 = -0.23$ for $(CH_3)_2Sn^{2+}$, and $\log K_1 = -0.17$ for $(CH_3)_3Sn^+$. The tendency to bind F^-, however, decreases with the increase in the number of the methyl groups: $\log K_3 = 4.12$ for CH_3Sn^{3+}, $\log K_2 = 2.87$ for $(CH_3)_2Sn^{2+}$, and $\log K_1 = 2.27$ for $(CH_3)_3Sn^+$. The structure of methyltin cations is different from that of methylgermanium compounds: The dimethyltin cation has an octahedral configuration containing linear C–Sn–C and the trimethyltin cation has a bipyramidal configuration.[19] Accordingly, the inductive effect of methyl groups on the tin atom is similar to that on the germanium atom despite the distinction of hybridization.

Quite a different effect has been reported on a methylmercury(II) cation, of which the central atom has a d^{10} electronic configuration similarly to germanium(IV) and tin(IV) atoms. Since the halide complex stability constant of Hg^{2+} and CH_3Hg^+ decreases in the order $I^- > Br^- > Cl^- > F^-$,[19,23] these cations are soft acids. In this case, methylation reduces stability of the bond between the mercury atom and a soft base. For example, the stability constants of iodides are $\log K_1 = 12.87$, $\log K_2 = 10.95$ for Hg^{2+}, and $\log K_1 = 8.60$ for CH_3Hg^+, whereas those of fluorides are $\log K_1 = 1.03$ for Hg^{2+}, and $\log K_1 = 1.50$ for CH_3Hg^+.[19,23] An explicit and extensive explanation of the effect by methylation on the Lewis acid nature of the various atoms has not been given yet.

The author wishes to thank Professor Masakazu Matsui, Dr. Sorin Kihara, and Dr. Eiichiro Nakayama for helpful discussions.

References

1) B. J. Aylett, "Organometallic Compounds," 4th ed, Chapman and Hall, London (1979), Vol. 1, Part 2, Chap. 3.

2) R. C. Poller, in "Comprehensive Organic Chemistry," ed by D. N. Jones, Pergamon Press, Oxford (1979), Vol. 3, pp. 1061—1073.

3) B. L. Lewis, M. O. Andreae, and P. N. Froelich, *Mar. Chem.*, **27**, 179 (1989).

4) R. L. Benoit and P. Clerc, *J. Phys. Chem.*, **65**, 676 (1961).

5) S. Siekierski and R. Olszer, *J. Inorg. Nucl. Chem.*, **25**, 1351 (1963).

6) C. A. Kraus and E. A. Flood, *J. Am. Chem. Soc.*, **54**, 1635 (1932).

7) E. G. Rochow and A. L. Allred, *J. Am. Chem. Soc.*, **77**, 4489 (1955).

8) R. S. Tobias and S. Hutcheson, *J. Organomet. Chem.*, **6**, 535 (1966).

9) G. E. Walrafen, *J. Chem. Phys.*, **42**, 485 (1965).

10) Y. Sohrin, *Anal. Chem.*, **63**, 811 (1991).

11) S. Shimomura, H. Sakurai, H. Morita, Y. Mino, and M. Inoue, *Anal. Chim. Acta*, **91**, 421 (1977).

12) W. J. Hamer and Y. C. Wu, *J. Phys. Chem. Ref. Data*, **1**, 1047 (1972).

13) O. Söhnel and P. Novotný, "Physical Sciences Data 22, Densities of Aqueous Solutions of Inorganic Substances," Elsevier, Amsterdam (1985).

14) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

15) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, New York (1964).

16) Y. Yoshino, *Bull. Chem. Soc. Jpn.*, **28**, 382 (1955).

17) A. W. Laubengayer, O. B. Billings, and A. E. Newkirk, *J. Am. Chem. Soc.*, **62**, 546 (1940).

18) D. A. Everest and J. C. Harrison, *J. Chem. Soc.*, **1957**,

1820.
19) R. S. Tobias, *Organomet. Chem. Rev.,* **1**, 93 (1966).
20) K. Moedritzer, *J. Organomet. Chem.,* **5**, 254 (1966).
21) R. G. Pearson, *J. Am. Chem. Soc.,* **85**, 3533 (1963).
22) A. Cassol, L. Magon, and R. Barbieri, *Inorg. Nucl. Chem. Lett.,* **3**, 25 (1967).
23) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes, Special Publication No. 17," The Chemical Society, London (1964).