Since benzene eluted with silacyclopentane on our GC columns, the above reaction can account for part (i.e., roughly one-third) of the apparent unexpectedly large yield increases of the latter at the highest study temperatures. The principal cause of this apparent increase, however, still remains a serious concern.

Secondary Free-Radical Reactions. Reaction rates in benzene were close to 3 times as fast as those under butadiene inhibition. Benzene is neither a free radical nor a silylene inhibitor; therefore, both silylene and free-radical chains can occur in the presence of benzene. Toluene should quench most of the free-radical-induced decomposition. Therefore, the differences in product yields observed in added benzene (Table IIB) and in added toluene (Table IIA) can be attributed mainly to free-radical processes. The yields of most of the products are about the same in the two studies; however, ethylene yields increase substantially. Ethylene, then, must be the major product of the free-radical-induced decomposition of *n*-butylsilane. This is reasonable on the basis of the expected products of the predicted Rice–Herzfeld type chains. Thus radical H abstraction from *n*-butylsilane can generate five different radicals whose possible decomposition pathways and rough statistical weights (based on reaction path degeneracies) are shown in reactions 28–33.

$$
\begin{array}{rcll}
 & & & \text{stat wt} \\
\cdot\mathrm{CH_2CH_2CH_2CH_2SiH_3} & \xrightarrow{29} & 2\mathrm{C_2H_4} + \cdot\mathrm{SiH_3} & 3 \\
\mathrm{CH_3\dot{C}HCH_2CH_2SiH_3} & \xrightarrow{30} & \mathrm{C_3H_6} + \cdot\mathrm{CH_2SiH_3} & 2 \\
\mathrm{CH_3CH_2\dot{C}HCH_2SiH_3} & \xrightarrow{31} & 1\text{-}\mathrm{C_4H_8} + \cdot\mathrm{SiH_3} & 1 \\
\mathrm{CH_3CH_2\dot{C}HCH_2SiH_3} & \xrightarrow{32} & \mathrm{CH_3}\cdot + \mathrm{CH_2{=}CHCH_2SiH_3} & 1 \\
\mathrm{CH_3CH_2CH_2\dot{C}HSiH_3} & \xrightarrow{33} & \mathrm{H}\cdot + \mathrm{C_2H_4} + \mathrm{CH_2{=}CHSiH_3} & 2 \\
\mathrm{CH_3CH_2CH_2CH_2\dot{S}iH_2} & \xrightarrow{34} & \mathrm{CH_3}\cdot + \mathrm{C_2H_4} + \mathrm{CH_2{=}SiH_2} & 3
\end{array}
$$

The above indicates that every 12 abstractions will produce roughly 11 ethylenes, four methanes, two propylenes, one 1-butene, and no 2-butenes. This correlates rather well with the observed yields of the two studies.

Conclusions

The main primary dissociation processes for *n*-butylsilane are 1,1- and 1,2-hydrogen eliminations: $\phi_{1,1}/\phi_{1,2} \simeq 2$. At high temperatures, C–C bond rupture also occurs. Alkylsilylenes (R > Me) decompose readily to olefins, and the mechanism of their decompositions is stepwise through silacyclic species formed by intramolecular silylene insertions into C–H bonds. Such insertions, involving 3-, 4-, and 5-centered cyclic transitions states, are all competitive at shock-tube reaction temperatures (i.e., $T > 1065$ K).

Acknowledgment. We are indebted to AFOSR for support under Grant 83-0209.

Registry No. *n*-BuSiH$_3$, 1600-29-9; silacyclopentane, 288-06-2.

Chemistry of Methylgallium(III) Compounds in Protic Solvents

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The chemical properties of as well as routes to the formation of methylgallium(III) compounds in aqueous acidic solutions and in other protic solvents have been investigated. Aqueous perchloric acid solutions of Me_2GaClO_4 at room temperature are surprisingly resistant to hydrolytic cleavage of the gallium–carbon bond. Only 14% of the available methyl groups of Me_2GaClO_4 when dissolved in 0.0171 M $HClO_4$ are converted to CH_4 after a 3-month time period. In contrast, Me_2GaClO_4 undergoes a significantly faster methyl-transfer reaction with $Ga(ClO_4)_3$ in aqueous $HClO_4$ solution to form $MeGa^{2+}$(aq) which in turn hydrolyzes to form Ga^{3+}(aq) and methane. Approximately 36% of the initially available methyl groups form CH_4 in 3 months. The dimethylgallium cation also methylates Hg^{2+}(aq) to form $MeGa^{2+}$(aq) and $MeHg^+$(aq) in aqueous solution, but Me_2Ga^+(aq) does not react with Al^{3+}(aq), Zn^{2+}(aq), or Na^+(aq). In a second series of experiments the methylation of gallium(III) by Me_2Co(BDM1,3pn) (BDM1,3pn = {*N,N′*-propane-1,3-diyl[bis(biacetyl monooxime imino)]}) was investigated in ethanol and acetone solutions by using UV titration and ^{1}H NMR data. The observed stoichiometry of the reaction requires 1 mol of $Ga(ClO_4)_3$ for every 2 mol of Me_2Co(BDM1,3pn). The identified products are Me_2Ga^+ and MeCo(BDM1,3pn)$^+$. In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

Introduction

Methylgallium compounds can exist in aqueous solution,[1] and these solutions are exceedingly toxic.[2,3] The inorganic derivatives of gallium are also poisonous.[3] However, relatively little is known about the hydrolytic stability, the chemical reactions, or the modes of formation of methylgallium compounds in aqueous solution. The hydrolysis of trimethylgallium is very rapid until the first methyl group has been removed, and then further hydrolysis becomes slow.[1,4,5] The removal of the second and third methyl groups has been described as being particularly slow.[1,4,5] For example, the reaction of a diethyl ether solution of Me_3GaOEt_2 with a slight excess of water gives Me_2GaOH, which in turn reacts readily with both aqueous

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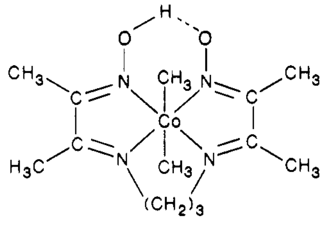
acids and bases at room temperature without rupture of the gallium–carbon bonds.[5] No methane evolution[5] was reported when either excess HNO_3, $HClO_4$, or NaOH was added to Me_2GaOH. However, after the resulting solutions had been at room temperature for several hours, very small quantities of a gas were observed.[5] No further details regarding the extent of hydrolysis or the reaction products have been described in the literature.

The presence of toxic organometallic compounds in the aqueous environment has prompted numerous studies of reactions of metal ions with a variety of methylcobalt complexes. Mercury(II),[6,7] chromium(II),[8] and thallium(III)[9] have been observed to react with either {*N*,*N*′-propane-1,3-diyl[bis(biacetyl monooxime imino)]}dimethylcobalt(III) [$Me_2Co(BDM1,3pn)$] or bis(dimethylglyoximato)monomethylcobalt(III) to form $MeHg^+$, $MeCr^{2+}$, and $MeTl^{2+}$, respectively. Zinc(II), cadmium(II), and lead(II) also react with 2 mol of $Me_2Co(BDM1,3pn)$ in 2-propanol to initially form $ZnMe_2$, $CdMe_2$, and $PbMe_2$, respectively, which then rapidly hydrolyze in the reaction solvent to liberate 2 mol of methane/mol of metal.[10]

The increasing importance of methylgallium compounds to the electronics industry as well as the potential presence and impact of methylgallium compounds in the environment leads us to study the chemical properties of methylgallium compounds in aqueous solution and in protic solvents. In this paper we report the results of our investigations of the hydrolytic stability of methylgallium compounds in dilute perchloric acid solution and of methyl-transfer reactions between aqueous solutions of dimethylgallium(III) cations and gallium(III), aluminum(III), and zinc(II) perchlorate salts and mercury(II) nitrate. Secondly, we report on the methylation of gallium(III) by $Me_2Co(BDM1,3pn)$ in protic solvents. Our results demonstrate that aqueous solutions of dimethylgallium(III) cations are stable to hydrolysis of the gallium–carbon bond over a limited time period, but methyl-transfer reactions can occur between $Me_2Ga^+(aq)$ and $Ga^{3+}(aq)$ and $Hg^{2+}(aq)$. Furthermore, $Me_2Co(BDM1,3pn)$ reacts with gallium(III) perchlorate in a 2:1 stoichiometry in ethanol solution to produce Me_2Ga^+ as the only methylgallium(III) product. These reactions represent the first examples of the methylation of gallium(III) in protic solvents.



$Me_2Co(BDM1,3pn)$

Experimental Section

General Data. All of the compounds used in these studies, with the exception of trimethylgallium diethyl etherate, were handled on the laboratory bench top. Trimethylgallium diethyl etherate was prepared from $GaCl_3$ and the methyl Grignard reagent in diethyl ether under an argon atmosphere. Dimethylgallium hydroxide was prepared from isolated and purified $Me_3Ga{\cdot}OEt_2$ and water in diethyl ether at room temperature.[5] Dimethylgallium perchlorate[5] was prepared from Me_2GaOH and $HClO_4$. The cobalt complex $Me_2Co(BDM1,3pn)$ was prepared from $Co(BDM1,3pn)[ClO_4]_2$ by using previously published methods.[10,11] The formation of CH_4 from the hydrolysis of methylgallium(III) compounds was confirmed after isolation by fractional vacuum distillation and identification by vapor pressure measurements at −196 °C (10 mm).

Spectral Measurements. Infrared spectra were recorded in the range 4000–250 cm^{-1} by using either a Perkin-Elmer 457 or 683 spectrometer. Spectra of solids were observed as Nujol mulls by using KBr or CsI windows. Ultraviolet spectra were recorded by using a Perkin-Elmer 575 UV–visible spectrometer and 1-cm quartz cells. Proton NMR spectra were recorded by using a Varian EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) with internal references of benzene (δ 7.13) or sodium 3-(trimethylsilyl)-1-propanesulfonate (δ 0.00). The following chemical shifts (reference benzene, 7.13 ppm) of starting materials were observed: Me_2GaOH (acetone-d_6) −0.56 (Me, s), 4.28 (H, s); $Me_2Ga(ClO_4)$ (acetone-d_6) −0.29 (Me, s); $Me_2Co(BDM1,3pn)$ (acetone-d_6) −0.19 (Me, s), 1.94 (s), 1.84 (m), 2.04 (s), 4.52 (s).

Determination of Hydrolytic Stability of Me_2GaClO_4 in Aqueous Solutions by Measuring the Evolved Methane. The hydrolytic stability of an aqueous acidic solution of Me_2GaClO_4 was monitored by measuring the evolved CH_4 by using a Toepler pump–gas buret assembly. The following data were observed for a solution of 2.23 mL that was 0.994 M Me_2GaClO_4 (2.217 mmol), 0.0171 M $HClO_4$, and 1.27 M acetone [time (mmol of CH_4, % available methyl groups converted to CH_4)]: 6 (0.0629, 1.42), 13 (0.121, 2.73), 20 (0.166, 3.74), 27 (0.210, 4.74), 34 (0.254, 5.73), 48 (0.356, 8.02), 105 days (0.647, 14.6).

In a second series of experiments, the methane evolved from an aqueous solution of 2.96 mL that was 1.02 M Me_2GaClO_4 (3.008 mmol), 0.884 M $Ga(ClO_4)_3$ (2.617 mmol), 0.0164 M $HClO_4$, and 1.00 M acetone was investigated. The following measurements of evolved CH_4 were observed [time (mmol of CH_4, % available methyl groups converted to CH_4)]: 6 (0.157, 2.61), 13 (0.336, 5.59), 20 (0.478, 7.94), 27 (0.610, 10.1), 34 (0.761, 12.6), 48 (1.12, 18.6), 76 (1.93, 32.1), 103 days (2.22, 36.9).

Determination of Hydrolytic Stability of Me_2GaClO_4 in Aqueous Solution by Using ^1H NMR Spectroscopy. The hydrolytic stability of Me_2GaClO_4 contained in sealed NMR tubes was evaluated by using ^1H NMR spectral data. For one series of experiments an aqueous solution that was 1.25 M Me_2GaClO_4, 0.020 M $HClO_4$, and 1.25 M acetone was prepared. The relative intensity of the single line due to Me_2GaClO_4 vs. the line due to acetone was monitored over a period of 150 days. The following data were observed time (Integration ratio $Me_2Ga^+(aq)$/acetone): 0 (1.0), 0.79 (0.95), 1.01 (1.0), 2.04 (0.86), 5.96 (0.96), 13.00 (0.99), 14.00 (0.96), 34.00 (0.99), 150.00 days (1.0). After 150 days, an extremely small line due to $MeGa^{2+}(aq)$ was just barely visible in the spectrum.

For a second series of experiments an aqueous solution that was 1.12 M Me_2GaClO_4, 0.969 M $Ga(ClO_4)_3$, 1.12 M acetone, and 0.0179 M $HClO_4$ was monitored over a period of 150 days. During the course of this study, the ^1H NMR line due to $Me_2Ga^+(aq)$ decreased in intensity and a new line due to $MeGa^{2+}$ appeared but never became very large relative to the line due to acetone. The following data were observed time (integration ratio $Me_2Ga^+(aq)$/acetone, $MeGa^{2+}(aq)$/acetone): 0 (0.92, 0), 0.79 (0.89, 0.027), 1.01 (0.95, 0.025), 2.04 (0.90, 0.024), 5.96 (0.85, 0.063), 13.00 (0.74, 0.11), 34.00 (0.62, 0.17), 150.00 days (0.042, 0.31).

In order to determine the effects of other metal perchlorate salts on the hydrolytic stability of $Me_2Ga^+(aq)$, saturated aqueous solutions of Me_2GaClO_4 containing 0.0912 M $HClO_4$ were mixed with aqueous solutions of $Al(ClO_4)_3$, $Zn(ClO_4)_2$, and $NaClO_4$. The ^1H NMR spectrum of these resulting solutions were monitored over a 150-day time period. The line due to $Me_2Ga^+(aq)$ did not decrease in intensity, and no new lines suggesting the formation of $MeGa^{2+}(aq)$ or any other methylmetal species appeared.

Methyl-Transfer Reactions between Me_2GaClO_4 and $Hg(NO_3)_2$ in Aqueous $HClO_4$ Solution. The reaction between Me_2GaClO_4 and $Hg(NO_3)_2$ in aqueous perchloric acid was mon-

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itored by means of a ^1H NMR spectral titration. To an NMR tube that contained 1 mL of saturated Me_2GaClO_4 solution in 0.0912 M $HClO_4$ was added 0.173 M $Hg(NO_3)_2$ dropwise. The ^1H NMR spectrum was recorded after each Hg^{2+} addition. The data support the formation of $MeGa^{2+}(aq)$ and $MeHg^+(aq)$ (see Results and Discussion).

UV Spectral Titrations. Solutions of $Me_2Co(BDM1,3pn)$ in absolute ethanol (0.203–0.292 mM) were titrated with 4.14 mM $Ga(ClO_4)_3$ in absolute ethanol in 0.50-mL increments. The extent of reaction was monitored by following the change in the UV spectrum in the 390–500 nm range of a sample contained in 1-cm quartz cells after equilibrium was established. The addition of $Ga(ClO_4)_3$ was discontinued after at least three additions caused no change in the absorbance at 412 nm. The purity of $Me_2Co(BDM1,3pn)$ was verified before each titration by recording the spectrum, noting the presence of the absorption at 412 nm characteristic of $Me_2Co(BDM1,3pn)$ as well as the absence of the absorption at 470 nm characteristic of $MeCo(BDM1,3pn)^+$, and calculating the extinction coefficient of $Me_2Co(BDM1,3pn)$. Similar UV titrations were studied in order to detect a potential reaction between methylcobalamin and $Ga(ClO_4)_3$ in water.

Identification by ^1H NMR Data of the Methylated Gallium Species from the Reaction of $Ga(ClO_4)_3$ with $Me_2Co(BDM1,3pn)$. A small quantity of $Me_2Co(BDM1,3pn)$ was dissolved in the desired solvent, and the ^1H NMR spectrum was recorded. Then, a sample of $Ga(ClO_4)_3$ (0.50 mol/mol of $Me_2Co(BDM1,3pn)$) was added, and the spectrum was recorded a second time. The appearance of lines assigned to $MeCo(BDM1,3pn)^+$, Me_2Ga^+, and/or $MeGa^{2+}$ was noted. After the spectrum showed no further change with time, a small quantity of a known solution of Me_2GaClO_4 was added to verify the identity of the Me_2Ga^+ line. These studies were carried out in both acetone-d_6 and ethanol-d_6.

Results and Discussion

Our experimental results demonstrate that aqueous acidic solutions of Me_2GaClO_4, which are reported[5] to contain $Me_2Ga(H_2O)_2^+$ and are represented as $Me_2Ga^+(aq)$, are surprisingly resistant to hydrolytic cleavage of the gallium–carbon bond to produce methane. In contrast, $Me_2Ga^+(aq)$ undergoes a significantly faster methyl-transfer reaction with $Ga^{3+}(aq)$ in aqueous $HClO_4$ solution to form $MeGa^{2+}(aq)$ that in turn hydrolyzes to form $Ga^{3+}(aq)$ and methane. Available data also suggest that $MeGa^{2+}(aq)$ hydrolyzes much more rapidly than $Me_2Ga^+(aq)$. The dimethylgallium cation also methylates $Hg^{2+}(aq)$ to form $MeGa^{2+}(aq)$ and $MeHg^+(aq)$, but $Me_2Ga^+(aq)$ does not react with $Al^{3+}(aq)$, $Zn^{2+}(aq)$, or $Na^+(aq)$. Conversely, gallium(III) is methylated by $Me_2Co(BDM1,3pn)$ to form Me_2Ga^+ and $MeCo(BDM1,3pn)^+$ in ethanol and acetone solutions. These methylation reactions of gallium represent the first examples in which gallium–carbon bonds are formed in protic solvents, including water.

The hydrolytic stability of methylgallium cationic species in $HClO_4$ solution and the propensity of these cations to undergo methyl-transfer reactions were monitored by measuring the evolved CH_4 and by following the changes in the ^1H NMR spectrum of related solutions. In the ^1H NMR experiments, the intensities of the lines due to $Me_2Ga^+(aq)$ (−0.35 ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate) and acetone were compared for 0.02 M $HClO_4$ solutions equimolar in Me_2GaClO_4 and Me_2CO. The NMR signal due to $Me_2Ga^+(aq)$ did not decrease in intensity over a period of 5 months, and no other new signals of significant intensity appeared. In the experiments in which the CH_4 was measured, only 0.0642 *mmol* of CH_4 was formed after 6 days from 2.217 mmol of $Me_2Ga^+(aq)$ and only 0.647 mmol of CH_4 was measured after 105 days, less than 15% of the available methyl groups. Both types of observations confirm that the hydrolysis of $Me_2Ga^+(aq)$ in 0.02 M $HClO_4$ is exceedingly slow. However, when a 0.018 M $HClO_4$ solution equimolar in Me_2GaClO_4, $Ga(ClO_4)_3$, and Me_2CO was observed over the same time period, the intensity of the ^1H NMR line due to $Me_2Ga^+(aq)$ decreased with time and one new line at −0.14 ppm (referenced to sodium 3-(trimethylsilyl)propanesulfonate) due to $MeGa^{2+}(aq)$ appeared in the spectrum and grew slightly in intensity but never became very large relative to the acetone line. (The assignment of the new line to $MeGa^{2+}(aq)$ is based on a comparison of the chemical shift of this line to a line in the spectrum of $MeGaCl_2$ dissolved in a mixture of $HClO_4$, acetone, and water at the identical pH.) The $Me_2Ga^+(aq)$ line decreased to half of its original intensity in approximately 80 days. However, the sum of the intensities of the lines due to $Me_2Ga^+(aq)$ and $MeGa^{2+}(aq)$ decreased relative to the intensity of the internal acetone sample. In the quantitative experiments of evolved CH_4, 0.157 mmol of CH_4 was formed after 6 days from an acidic solution that initially contained 3.01 mmol of $Me_2Ga^+(aq)$ and 2.617 mmol of $Ga^{3+}(aq)$. This quantity of CH_4 is almost twice that observed for the solution that contained $Me_2Ga^+(aq)$ as the only initial gallium species. Our observations are consistent with the occurrence of a methyl-transfer reaction (eq 1) and the hydrolysis of the resultant $MeGa^{2+}(aq)$ (eq 2).

$$Me_2Ga^+(aq) + Ga^{3+}(aq) \rightarrow 2MeGa^{2+}(aq) \qquad (1)$$

$$MeGa^{2+}(aq) + H^+ \rightarrow Ga^{3+}(aq) + CH_4 \qquad (2)$$

Thus, $MeGa^{2+}(aq)$ is significantly more susceptible to gallium–carbon bond cleavage with methane formation than is $Me_2Ga^+(aq)$ in aqueous perchloric acid solution.

Methyl-transfer reactions also occur between $Me_2Ga^+(aq)$ and $Hg^{2+}(aq)$ in aqueous $HClO_4$ solution (eq 3), but this reaction is significantly faster than methyl transfer between $Me_2Ga^+(aq)$ and $Ga^{3+}(aq)$. The intensity of the ^1H NMR line due to $Me_2Ga^+(aq)$ at −0.35 ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate, in a solution initially equimolar in $Me_2Ga^+(aq)$ and $Hg^{2+}(aq)$, decreased to half of its original intensity in only 31 min, and two new lines at 1.08 and −0.14 ppm appeared in the spectrum. The line at 1.08 ppm is assigned to $MeHg^+(aq)$ by comparison with the literature[12] whereas the line at −0.14 ppm is due to $MeGa^{2+}(aq)$. The observed formation of $MeHg^+(aq)$ instead of $HgMe_2$ is consistent with previously observed methylation reactions of mercury(II). Others[9] have also observed that it is more difficult to methylate $MeHg^+(aq)$ than $Hg^{2+}(aq)$ due to the decreased electrophilic character of $MeHg^+(aq)$. It is significant to note that mercury(II) acetate is also methylated[13] by $Me_2Tl(MeCO_2)$, another group 3 alkyl, to yield $MeHg^+(aq)$ and $MeTl^{2+}(aq)$.

$$Me_2Ga^+(aq) + Hg^{2+}(aq) \rightarrow MeGa^{2+}(aq) + MeHg^+(aq) \qquad (3)$$

N,N'-Propane-1,3-diyl[bis(biacetyl monoxime imino)]dimethylcobalt(III), $Me_2Co(BDM1,3pn)$, methylates gallium(III) perchlorate and gallium(III) chloride in polar solvents. This reaction represents the first reported example of the formation of a dimethylgallium(III) species in a protic solvent. The stoichiometry of the reaction as shown by eq 4 is consistent with all UV titration data. In

$$Ga^{3+} + 2Me_2Co(BDM1,3pn) \rightarrow Me_2Ga^+ + 2MeCo(BDM1,3pn)^+ \qquad (4)$$

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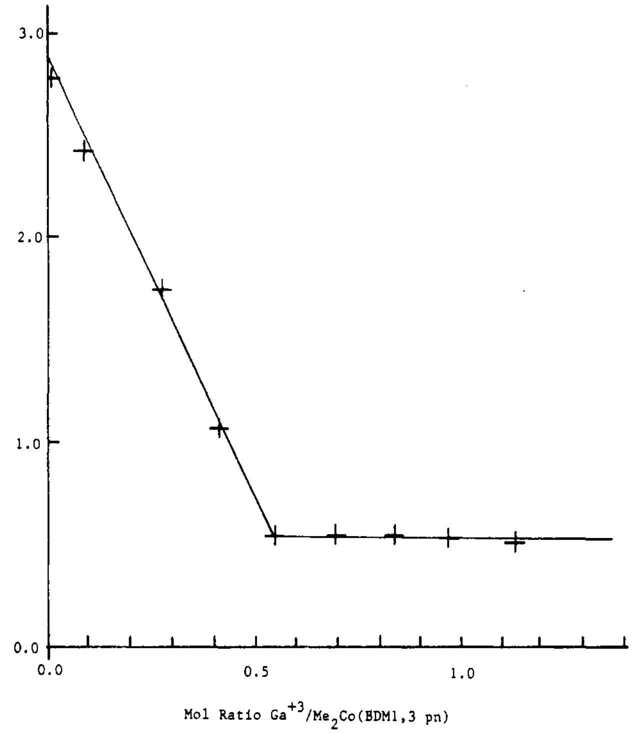

Figure 1. Titration of $Me_2Co(BDM1,3pn)$ with $Ga(ClO_4)_3 \cdot 6H_2O$.

the UV titrations, absolute ethanol solutions of $Ga(ClO_4)_3$ were added to ethanol solutions of $Me_2Co(BDM1,3pn)$. The linear decrease in the absorbance at 412 nm, characteristic of $Me_2Co(BDM1,3pn)$,[10] as well as the increase in the absorbance at 470 nm, characteristic of the methylcobalt(III) product[10] $MeCo(BDM1,3pn)^+$, were used to determine the extent of reaction. A plot of the absorbance at 412 nm vs. the mole ratio $Ga^{+3}/Me_2Co(BDM1,3pn)$ had a distinct break at 0.532 mol of Ga^{3+}/mol of $Me_2Co(BDM1,3pn)$ (Figure 1). The observation of only the absorbance at 470 nm[10] at the end of the titration demonstrates the formation of $MeCo(BDM1,3pn)^+$ and precludes the possibility that both methyl groups are removed from cobalt.

The proposed stoichiometry of the Ga^{3+}–$Me_2Co(BDM1,3pn)$ reaction and the identity of the products are also supported by ^1H NMR spectral data. The products observed after reaction were $MeCo(BDM1,3pn)^+$ and Me_2Ga^+. The NMR spectrum of $Me_2Co(BDM1,3pn)$ in acetone is characterized by a sharp singlet at −0.16 ppm (referenced to benzene at 7.13 ppm) for the methyl groups bound to cobalt. This resonance disappeared as $Ga(ClO_4)_3$ was added, and two new sharp lines at 0.51 and −0.26 ppm due to methyl groups of $MeCo(BDM1,3pn)^+$ and Me_2Ga^+, respectively, appeared. The identity of the species responsible for the −0.26 ppm line, Me_2Ga^+, was verified by examining the ^1H NMR spectrum of the product mixture after the addition of a solution of pure Me_2GaClO_4. The stoichiometry of the methylation reaction of gallium(III) by $Me_2Co(BDM1,3pn)$ and identity of the reaction products were independent of the solvent, ethanol, acetone, or acetonitrile, and the gallium(III) reactant, $Ga(ClO_4)_3$ and $Ga(NO_3)_3$.

Gallium species other than simple solvated Ga^{3+} ions have also been shown to undergo methyl-transfer reactions with $Me_2Co(BDM1,3pn)$ in acetone and ethanol solutions. Anhydrous $GaCl_3$ dissolves in ethanol, and acetone but the exact nature of the solubilized species is unknown. Therefore, the gallium(III) solute[14] will be referred to as $[GaCl_n]^{(3-n)+}$. These solutions react readily with $Me_2Co(BDM1,3pn)$ in a 1:2 stoichiometry to yield $MeCo(BDM1,3pn)^+$ and a dimethylgallium(III) product according to data from UV spectroscopic titrations and ^1H NMR studies. It is also significant that $[GaCl_n]^{(3-n)+}$ undergoes a faster methyl-transfer reaction with Me_2Ga^+ in acetone than Ga^{3+} from $Ga(ClO_4)_3$ does in water. The intensity of the ^1H NMR line due to Me_2Ga^+ decreased to half intensity in 112 h in the presence of excess $[GaCl_n]^{(3-n)+}$ in acetone solution, and a new line due to $MeGa^{2+}$ appeared.

The methylcobalt(III) complex $Me_2Co(BDM1,3pn)$ is considered to be of high reactivity for the methylation of metal ions whereas methylcobalamin is significantly less reactive.[10] Since Ga^{3+} reacted so readily with $Me_2Co(BDM1,3pn)$ to form Me_2Ga^+, the reactivity of methylcobalamin toward $Ga(ClO_4)_3$ in aqueous solution was studied by UV titration experiments. However, no reaction occurred. The absorbance of the bands of methylcobalamin at 520 and 350 nm did not change significantly as an aqueous solution of $Ga(ClO_4)_3$ was added. Thus, it is unlikely that exceedingly toxic methylgallium species will be formed directly by methylcobalamin methylation in the aqueous environment.

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Registry No. Me_2GaClO_4, 21978-10-9; $Hg(NO_3)_2$, 10045-94-0; $MeGa^{2+}$, 106733-82-8; $MeHg^+$, 22967-92-6; $Me_2Co(BDM1,3pn)$, 33569-60-7; $Ga(ClO_4)_3$, 19854-31-0.

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