(COT), 62422-35-9; $Ru(C_6Me_6)(COT)$, 62422-36-0; $Os(C_6H_6)(COT)$, 72765-31-2; $Os(C_6H_3Me_3)(COT)$, 72765-30-1; $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$, 52462-29-0; $[RuCl_2(HMB)]_2$, 67421-02-7; $[RuCl_2(1,5\text{-}COD)]_n$, 50982-13-3; $[RuCl_2(C_6H_5\text{-}t\text{-}Bu)]_2$, 72765-29-8; $OsCl_2(C_6H_6)(CH_3CN)$, 72765-28-7; $[Fe(C_6H_3Me_3)_2](PF_6)_2$, 31666-55-4; $[Fe(C_6H_6)_2](PF_6)_2$, 71108-19-3; $[Fe(HMB)_2](PF_6)_2$, 53382-63-1; $Fe(HMB)_2$, 55280-55-2; $[RuCl_2(C_6H_3Me_3)]_2$, 52462-31-4; $RuCl_2(C_6H_3Me_3)py$, 52490-90-1; $RuCl(acac)(C_6H_3Me_3)$, 72778-73-5; $[RuCl_2(HMB)]_2$, 67421-02-7; $[RuCl_2(C_6H_6)]_2$, 37366-09-9; $RuCl_2(C_6H_6)py$, 68012-51-1.

Supplementary Material Available: Listings of structure factor amplitudes and nonbonded contacts (7 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of ((Trimethylsilyl)methyl)gallium(III) Compounds

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A series of neutral organogallium(III) compounds which incorporate the (trimethylsilyl)methyl ligand, $Ga(CH_2SiMe_3)_nX_{3-n}$ (n = 3, 2, 1; X = Cl, Br), have been prepared and fully characterized by elemental analyses, ^1H NMR and infrared spectroscopy, molecular weight data, solubility properties, and Lewis acid–base chemistry. The parent compound $Ga(CH_2SiMe_3)_3$ was prepared from $GaCl_3$ by a standard Grignard reaction in diethyl ether. The halogen derivatives were prepared from $Ga(CH_2SiMe_3)_3$ by elimination reactions with HCl or HBr and exchange reactions with $GaCl_3$ or $GaBr_3$. The following molecular formulas are supported by all available data: $Ga(CH_2SiMe_3)_3$, $[Ga(CH_2SiMe_3)_2Cl]_x$, $[Ga(CH_2SiMe_3)_2Br]_2$, $[Ga(CH_2SiMe_3)Cl_2]_2$, and $[Ga(CH_2SiMe_3)Br_2]_2$. It is noteworthy that the (trimethylsilyl)methyl ligand significantly influences the chemistry of only $Ga(CH_2SiMe_3)_3$ and $[Ga(CH_2SiMe_3)_2Cl]_x$. The Lewis acidity of $Ga(CH_2SiMe_3)_3$ has been greatly diminished as diethyl ether can be readily removed by simple vacuum distillation. The chemical and physical properties of $Ga(CH_2SiMe_3)_2Cl$, which could only be prepared in low yield by the elimination reaction, suggest that the compound might have an unusual structure. A "ladder" polymer or a linear polymer with one bridging chlorine atom per gallium atom is proposed. All other ((trimethylsilyl)methyl)gallium–halogen compounds have properties analogous to those of other known organogallium–halogen compounds.

Introduction

The enhanced thermal stability of the ((trimethylsilyl)methyl)metal compounds and their potential for unusual chemistry as imposed by the steric restraints of the organometallic ligand provide the impetus for synthesizing new compounds.[1,2] The (trimethylsilyl)methyl derivatives of the group 3 elements, boron,[3] aluminum,[4] and indium,[1] have been prepared and fully characterized. The boron derivative,[3] $B(CH_2SiMe_3)_3$, is readily made from $BF_3 \cdot O(C_2H_5)_2$ by a standard Grignard reaction in refluxing diethyl ether solution. Available data suggest that $B(CH_2SiMe_3)_3$ has a trigonal-planar structure. The aluminum compound,[4] $Al(CH_2SiMe_3)_3$, prepared from $Hg(CH_2SiMe_3)_2$[5] and aluminum foil, exists as a mixture of monomeric and dimeric species in benzene solution. Only in the case of indium[1] has a series of (trimethylsilyl)methyl derivatives $In(CH_2SiMe_3)_xCl_{3-x}$ (x = 1, 2, 3) been studied. The parent compound, $In(CH_2SiMe_3)_3$, prepared by the Grignard reaction, exists as a monomeric three-coordinate species. The chloroindium derivatives[1] were prepared from $In(CH_2SiMe_3)_3$ by means of exchange reactions with $InCl_3$ or elimination reactions with HCl. Available data suggest that both the mono- and dichloroindium derivatives exist as chlorine-bridged dimers, but $[In(CH_2SiMe_3)Cl_2]_2$ probably has more extensive association in the solid state.[1] It is noteworthy that neither chloroindium compound formed a stable adduct with any base examined in a Lewis acid–base study. The bases included $N(CH_3)_3$, CH_3CN, $O(C_2H_5)_2$, tetrahydrofuran, and dimethoxyethane.

An attempt to prepare $Ga(CH_2SiMe_3)_3$ from gallium metal and $Hg(CH_2SiMe_3)_2$ was surprisingly unsuccessful.[4] Considering the success of the Grignard reaction for the preparation of the boron[3] and indium[1] derivatives and the subsequent ease of removing diethyl ether from $In(CH_2SiMe_3)_3$, the Grignard reaction of $GaCl_3$ was investigated. In this paper we report the high yield synthesis of $Ga(CH_2SiMe_3)_3$. The diethyl ether was very readily removed. Additional experiments lead to the syntheses of a series of neutral organogallium(III) compounds which incorporate the (trimethylsilyl)methyl ligand, $Ga(CH_2SiMe_3)_nX_{3-n}$ (X = Cl, Br; n = 1, 2, 3). All compounds have been fully characterized by elemental analyses, infrared spectra, molecular weight data, solubility properties, ^1H NMR data, and Lewis acid–base studies. Our results suggest that the (trimethylsilyl)methyl ligand introduces new chemical properties, reactivities, and structures in some of these organogallium(III) compounds.

Experimental Section

All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or a purified nitrogen or argon atmosphere. The solvents and reagents were purified by conventional means. New compounds were analyzed for gallium by EDTA titration.[6] Chlorine and bromine were determined by standard gravimetric procedures.

Synthesis of $Ga(CH_2SiMe_3)_3$. The compound $Ga(CH_2SiMe_3)_3$ was prepared from $GaCl_3$ and the Grignard reagent[7] Me_3SiCH_2MgCl in diethyl ether solution. An argon-purged flask, containing 10.000 g (56.796 mmol) of $GaCl_3$ and 200 mL of ether, was equipped with

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(1) Beachley, O. T., Jr.; Rusinko, R. N. *Inorg. Chem.* **1979**, *18*, 1966.

(2) (a) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209.

(3) (a) Seyferth, D. *J. Am. Chem. Soc.* **1959**, *81*, 1844. (b) Seyferth, D. U.S. Patent 2 831 009, 1958.

(4) Nyathi, J. Z.; Ressner, J. M.; Smith, J. D. *J. Organomet. Chem.* **1974**, *70*, 35.

(5) Seyferth, D., Freyer, W. *J. Org. Chem.* **1961**, *26*, 2604.

(6) Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233.

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Table I. Reactions of $Ga(CH_2SiMe_3)_3$ with Gallium Trihalides or Anhydrous Hydrogen Halides[a]

compd	stoichiometric ratios of reagents	product purifcn	% yield of $Si(CH_3)_4$[b]	% yield of prod[c]	mp, °C
$Ga(CH_2SiMe_3)_2Br$	1:1 GaR_3:HBr	recrystn from benzene	99.2	94.0	31.0–32.0
	2:1 GaR_3:$GaBr_3$	recrystn from benzene	. . .	99.1	
$Ga(CH_2SiMe_3)Br_2$	1:2 GaR_3:HBr	extracn with benzene	99.5	94.2	19.0–21.0
	1:2 GaR_3:$GaBr_3$	extracn with benzene	. . .	90.0	
$Ga(CH_2SiMe_3)Cl_2$	1:2 GaR_3:HCl	vacuum sublimn (50 °C)	99.6	91.0	48.0–49.0
	1:2 GaR_3:$GaCl_3$	vacuum sublimn (50 °C)	. . .	94.5	

[a] All reactions were carried out in benzene solution at 25 °C. [b] Tetramethylsilane was collected in a −196 °C trap. The percent yield of $Si(CH_3)_4$ is based upon $Ga(CH_2SiMe_3)_3$. [c] The percent yield of product is based upon $Ga(CH_2SiMe_3)_3$.

Table II. Analytical and Molecular Weight Data for ((Trimethylsilyl)methyl)gallium Compounds

	gallium anal.		halogen anal.		mol wt data		
compd	% calcd	% found	% calcd	% found	fw	calcd molality[a]	obsd mol wt
$Ga(CH_2SiMe_3)_3$	21.04	20.94			331	0.0918	379
						0.0588	378
$Ga(CH_2SiMe_3)_2Cl$	24.96	25.02	12.69	12.65	280	*b*	*b*
$Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$	20.62	20.56	10.48	10.31	339	0.0902	370
						0.0491	364
$Ga(CH_2SiMe_3)Cl_2$	30.61	30.52	31.13	31.10	228	0.1591	461
						0.0796	459
$Ga(CH_2SiMe_3)_2Br$	21.51	21.46	24.65	24.57	324	0.1852	649
						0.1384	648
$Ga(CH_2SiMe_3)Br_2$	22.03	21.96	50.49	50.35	317	0.1440	631
						0.0894	630

[a] Calculated molality of solution is based upon monomer. [b] Compound has insufficient solubility in benzene for molecular weight measurements.

a mechanical stirrer, condenser, dropping funnel, and inert-gas bubbler. Then the ether solution of the Grignard reagent (100 mL, 2.16 M) was added dropwise to the $GaCl_3$–ether solution over a period of 1 h. After addition was complete, the white pasty mixture was stirred for 24 h at room temperature. Diethyl ether was then removed by vacuum distillation. The product, $Ga(CH_2SiMe_3)_3$, a colorless mobile liquid at room temperature, was distilled from the reaction flask at 120 °C under high vacuum. The yield of $Ga(CH_2SiMe_3)_3$ was 17.207 g, 51.966 mmol, 91.5% based on $GaCl_3$. Analytical and molecular weight data are given in Table II. Typical solvents for $Ga(CH_2SiMe_3)_3$ include *n*-pentane, benzene, methylene chloride, acetonitrile, and diethyl ether.

Synthesis of $Ga(CH_2SiMe_3)_2Br$, $Ga(CH_2SiMe_3)Br_2$, and $Ga(CH_2SiMe_3)Cl_2$. The bromo derivatives and dichloro derivative were prepared from $Ga(CH_2SiMe_3)_3$ by either an exchange reaction with the appropriate gallium trihalide or an elimination reaction with the appropriate hydrogen halide in benzene solution. Different stoichiometries[1] were required for the different products. The procedure for the exchange reaction involved adding 5.0 mL of a benzene solution of $Ga(CH_2SiMe_3)_3$ to a mixture of the gallium trihalide and 10 mL of benzene at 25 °C. The experimental procedure for the elimination reaction was identical with that described for the synthesis of the corresponding indium derivatives.[1] Typical exchange and elimination reactions were run on a 5–10 mmol scale of $Ga(CH_2SiMe_3)_3$ for a period of 12 h at 25 °C. Specific synthetic conditions, product purification methods, percent yields of tetramethylsilane from elimination reactions, percent yields of ((trimethylsilyl)methyl)gallium–halide compounds, and their respective melting points are given in Table I. Analytical and molecular weight data are given in Table II. Typical solvents for these three organogallium compounds $Ga(CH_2SiMe_3)_2Br$, $Ga(CH_2SiMe_3)Br_2$, and $Ga(CH_2SiMe_3)Cl_2$ include *n*-pentane, benzene, methylene chloride, acetonitrile, and diethyl ether.

Synthesis of $Ga(CH_2SiMe_3)_2Cl$. The monochloro derivative was prepared by an elimination reaction between $Ga(CH_2SiMe_3)_3$ and hydrogen chloride under carefully controlled experimental conditions. However difficulty was encountered in obtaining reproducible results for this reaction. The following experimental conditions gave the greatest reproducibility and maximum yield of $Ga(CH_2SiMe_3)_2Cl$.

In a typical reaction 0.1212 g (0.3660 mmol) of $Ga(CH_2SiMe_3)_3$ dissolved in 1.0 mL of benzene contained in a 20-mL reaction vessel was reacted with a total of 0.0134 g (0.367 mmol) of hydrogen chloride. The hydrogen chloride was added in three equimolar portions by vacuum distillation at −196 °C. After each addition of hydrogen chloride, the reaction mixture was warmed to room temperature and stirred for 1 h. During this period a white solid precipitated from the solution. After reaction was complete, the volatile components were fractionally distilled to yield 0.0320 g (0.363 mmol, 99.2% yield) of tetramethylsilane (−196 °C trap) and benzene (−78 °C trap). Then, the nonvolatile reaction products were extracted twice with a 5.0-mL portion of *n*-pentane. The insoluble component was collected on a small glass frit and identified as $Ga(CH_2SiMe_3)_2Cl$ (0.0511 g, 0.183 mmol, 50.5% yield). The soluble fraction was a mixture of $Ga(CH_2SiMe_3)Cl_2$ and unreacted $Ga(CH_2SiMe_3)_3$. The product, $Ga(CH_2SiMe_3)_2Cl$, a white crystalline solid, had a sharp melting point of 159.5–160.0 °C and was soluble in polar solvents such as methylene chloride, acetonitrile, and diethyl ether but insoluble in benzene and *n*-pentane. Analytical data are given in Table II.

Synthesis of $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$. The Lewis acid–base adduct $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$ was prepared by an elimination reaction between $Ga(CH_2SiMe_3)_3$ and trimethylamine hydrochloride in benzene. In a typical reaction, 1.1010 g (3.3252 mmol) of $Ga(CH_2SiMe_3)_3$ dissolved in 5.0 mL of benzene was poured through a Teflon stopcock under high vacuum at 25 °C into a reaction flask containing 0.3141 g (3.326 mmol) of doubly sublimed $(CH_3)_3N{\cdot}HCl$ and 10 mL of benzene. Reaction was observed to proceed by the gradual disappearance of initially insoluble $(CH_3)_3N{\cdot}HCl$ over a period of 2 h. After reaction was complete, the volatile components were separated by vacuum distillation to yield 0.2870 g (3.326 mmol, 100% yield) of tetramethylsilane (−196 °C) and benzene (−78 °C trap). The crude product was purified by sublimation at 32 °C to give $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$ as a white crystalline solid (1.108 g, 3.276 mmol, 98.5% yield). The purified product had a melting point of 30.0–31.0 °C and was soluble in *n*-pentane, benzene, methylene chloride, acetonitrile, and diethyl ether. Analytical and molecular weight data are given in Table II. A compound with identical properties was prepared by reacting equimolar quantities of $Ga(CH_2SiMe_3)_2Cl$ and $N(CH_3)_3$ at 0 °C.

Molecular Weight Studies. Molecular weight measurements were obtained cryoscopically in benzene solution by using an instrument similar to that described by Shriver.[8] Molecular weight data for all compounds are given in Table II.

Infrared Spectra. The infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. The spectra were recorded as neat liquids or as Nujol mulls by using

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(8) Shriver, D. F. "The Manipulations of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; p 159.

Table III. Proton NMR Data for ((Trimethylsilyl)methyl)gallium Compounds and Their Lewis Acid–Base Adducts[a]

		τ, ppm		
Lewis acid	Lewis base	Si–Me	$SiCH_2$	Lewis base protons
$Ga(CH_2SiMe_3)_3$		9.91	10.15	
	$O(CH_2)_4$	9.91	10.35	6.13 (multiplet, CH_2) 8.05 (multiplet, CH_2)
	$N(CH_3)_3$	9.90	10.68	7.84 (singlet, CH_3)
$Ga(CH_2SiMe_3)_2Cl$		9.88	9.73	
	$O(CH_2)_4$	9.85	10.23	6.04 (multiplet, CH_2) 7.91 (multiplet, CH_2)
	$N(CH_3)_3$	9.90	10.42	7.53 (singlet, CH_3)
$Ga(CH_2SiMe_3)Cl_2$		9.88	9.47	
	$CH_3OC_2H_4OCH_3$	9.85	9.89	5.95 (singlet, CH_2) 6.31 (singlet, CH_3)
	$O(C_2H_5)_2$	9.85	9.92	5.83 (quartet, CH_2) 8.59 (triplet, CH_3)
	CH_3CN	9.86	9.94	7.50 (singlet, CH_3)
	$O(CH_2)_4$	9.87	9.97	5.81 (multiplet, CH_2) 7.89 (multiplet, CH_2)
	$N(CH_3)_3$	9.85	10.12	7.37 (singlet, CH_3)
$Ga(CH_2SiMe_3)_2Br$		9.82	9.59	
	$O(CH_2)_4$	9.86	10.08	5.93 (multiplet, CH_2) 7.93 (multiplet, CH_2)
	$N(CH_3)_3$	9.86	10.29	7.47 (singlet, CH_3)
$Ga(CH_2SiMe_3)Br_2$		9.86	9.19	
	$O(C_2H_5)_2$	9.85	9.73	5.75 (quartet, CH_2) 8.60 (triplet, CH_3)
	$CH_3OC_2H_4OCH_3$	9.86	9.74	5.98 (singlet, CH_2) 6.33 (singlet, CH_3)
	CH_3CN	9.88	9.78	7.44 (singlet, CH_3)
	$O(CH_2)_4$	9.88	9.80	5.61 (multiplet, CH_2) 7.90 (multiplet, CH_2)
	$N(CH_3)_3$	9.86	9.98	7.36 (singlet, CH_3)

[a] The chemical shifts (ppm) for the nonadducted Lewis base protons in methylene chloride relative to $Si(CH_3)_4$ are the following: diethyl ether, 6.58 (quartet, CH_2), 8.81 (triplet, CH_3); dimethoxyethane, 6.57 (singlet, CH_2), 6.72 (singlet, CH_3); tetrahydrofuran, 6.40 (multiplet, α-CH_2), 8.25 (multiplet, β-CH_2); acetonitrile, 8.05 (singlet, CH_3); trimethylamine, 7.79 (singlet, CH_3).

CsI plates. Absorption intensities were measured by using the method of Durkin, Glore, and DeHayes.[9]

The following are the spectral data [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder; vs, very strong)]. Bands due to mulling agents have been omitted.

$Ga(CH_2SiMe_3)_3$ (neat liquid): 2936 (vs), 2882 (s), 2802 (m), 1441 (m), 1403 (m), 1381 (m), 1354 (m), 1299 (w), 1266 (s), 1251 (vs), 1201 (m), 1130 (w), 990 (s), 957 (s), 860 (vs), 831 (vs), 759 (s), 725 (s), 693 (s), 681 (sh), 535 (m), 512 (m).

$Ga(CH_2SiMe_3)_2Cl$ (Nujol mull): 1269 (s), 1254 (vs), 1973 (s), 1018 (s), 982 (m), 864 (vs), 835 (vs), 771 (m), 725 (m), 700 (w), 583 (m), 545 (m), 282 (s), 263 (sh).

$Ga(CH_2SiMe_3)_2Cl\cdot N(CH_3)_3$ (Nujol mull): 1265 (s), 1250 (vs), 1112 (w), 995 (s), 975 (s), 861 (vs), 832 (vs), 760 (s), 740 (s), 692 (m), 591 (m), 575 (m), 515 (m), 501 (sh), 278 (s), 262 (sh).

$Ga(CH_2SiMe_3)Cl_2$ (Nujol mull): 1269 (s), 1252 (vs), 1013 (s), 980 (m), 861 (vs), 832 (vs), 776 (m), 721 (m), 698 (m), 581 (m), 541 (m), 369 (m), 342 (s), 316 (vs).

$Ga(CH_2SiMe_3)_2Br$ (Nujol mull): 1260 (s), 1253 (vs), 1198 (w), 1110 (s), 978 (m), 850 (vs), 838 (vs), 816 (m), 763 (m), 732 (m), 698 (m), 578 (m), 560 (sh), 548 (m).

$Ga(CH_2SiMe_3)Br_2$ (Nujol mull): 1262 (s), 1256 (vs), 1105 (s), 978 (m), 860 (vs), 842 (vs), 765 (m), 730 (m), 705 (m), 585 (m), 550 (m).

Proton Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz and ambient temperature with a Jeolco Model MH-100 spectrometer. All chemical shifts (τ) are given in ppm (Table III) and are referenced to tetramethylsilane as 10.00 ppm. The spectra of all ((trimethylsilyl)methyl)gallium compounds were observed as methylene chloride solutions.

Lewis Acidity Studies. The Lewis acidities of the ((trimethylsilyl)methyl)gallium compounds were studied by reacting a stoichiometric quantity of the desired acid with excess base (trimethylamine, acetonitrile, diethyl ether, tetrahydrofuran, and dimethyloxyethane). The reaction mixture was stirred at room temperature for 2 h. The volatile components were then removed by pumping on the sample until no dissociation pressure was observed. If a stoichiometric quantity of base was retained by the acid, the stable adduct was characterized by its ^1H NMR spectrum (Table III). In those cases in which a nonstoichiometric quantity of base was retained, the product was not further characterized.

Stable 1:1 adducts were isolated at room temperatures for the following acid–base pairs: $Ga(CH_2SiMe_3)_3$–tetrahydrofuran and –trimethylamine; $Ga(CH_2SiMe_3)_2Cl$–tetrahydrofuran and –trimethylamine; $Ga(CH_2SiMe_3)Cl_2$–diethyl ether, –dimethoxyethane, –acetonitrile, –trimethylamine, and –tetrahydrofuran; $Ga(CH_2SiMe_3)_2Br$–tetrahydrofuran and –trimethylamine; $Ga(CH_2SiMe_3)Br_2$–diethyl ether, –dimethoxyethane, –acetonitrile, –trimethylamine, and –tetrahydrofuran.

Results and Discussion

A series of neutral organogallium(III) compounds which incorporate the (trimethylsilyl)methyl ligand $Ga(CH_2SiMe_3)_nX_{3-n}$ (where X = Cl, Br; n = 1, 2, 3) have been prepared and fully characterized. The elemental analyses, ^1H NMR and infrared spectroscopy, molecular weight data, and solubility properties suggest the following molecular formulas: $Ga(CH_2SiMe_3)_3$, $[Ga(CH_2SiMe_3)_2Cl]_x$, $[Ga(CH_2SiMe_3)_2Br]_2$, $[Ga(CH_2SiMe_3)Cl_2]_2$, and $[Ga(CH_2SiMe_3)Br_2]_2$. These new organogallium(III) compounds exhibit the high thermal stability expected for (trimethylsilyl)methyl derivatives. It is noteworthy that the (trimethylsilyl)methyl ligand significantly influences the chemistry of $Ga(CH_2SiMe_3)_3$ and $Ga(CH_2SiMe_3)_2Cl$ when compared with other organogallium compounds. The Lewis acidic behavior of $Ga(CH_2SiMe_3)_3$ has been greatly diminished, and the chemical and physical properties of $Ga(CH_2SiMe_3)_2Cl$ suggest that the compound might have an unusual structure. These changes in chemical behavior contrast the similarities in properties exhibited by related simple organo- and ((trimethylsilyl)methyl)indium(III) derivatives.[1]

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(9) Durkin, T.; Glore, J.; DeHayes, L. *J. Chem. Educ.* **1971**, *48*, 452.

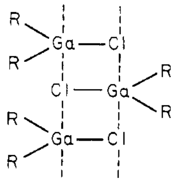
The parent compound of the series, $Ga(CH_2SiMe_3)_3$, was readily prepared in 91% yield by a standard Grignard reaction in diethyl ether solution at room temperature. The best synthetic conditions involved adding a 13% excess of the Grignard reagent to the $GaCl_3$ in diethyl ether solution. The product, $Ga(CH_2SiMe_3)_3$, was isolated as a colorless, mobile liquid at room temperature. A significant feature in the preparative scheme is that diethyl ether is readily separated from $Ga(CH_2SiMe_3)_3$ by vacuum distillation at 25 °C over a period of 3 h. The steric restraints imposed by the bulky (trimethylsilyl)methyl ligand apparently reduce the Lewis acidity of $Ga(CH_2SiMe_3)_3$ compared with other organogallium(III) compounds.[10,11] The compound $Ga(CH_2SiMe_3)_3$ like the analogous aluminum compound[4] $Al(CH_2SiMe_3)_3$ is spontaneously flammable in air and reacts violently with water. It is of interest that the gallium(III) compound $Ga(CH_2SiMe_3)_3$ is exceedingly more reactive than $In(CH_2SiMe_3)_3$.[1] The chemical properties of $Ga(CH_2SiMe_3)_3$ are indicative of a simple three-coordinate gallium compound analogous to $Ga(CH_3)_3$.[11] Cryoscopic molecular weight measurements have shown the compound to exist as a monomeric species in benzene solution. Our infrared data are also fully consistent with this formulation. The asymmetrical $Ga-C_3$ stretching vibrations give rise to an intense doublet at 535 and 512 cm^{-1}. There were no absorptions observed in the region 510–300 cm^{-1} in which the symmetrical $Ga-C_3$ vibrations would be expected. This is in full agreement with our proposed three-coordinate structure for $Ga(CH_2SiMe_3)_3$ since the symmetrical $Ga-C_3$ vibrations would be infrared inactive in a planar molecule.[10]

The monobromo-, dibromo-, and dichloro((trimethylsilyl)methyl)gallium derivatives were readily prepared from $Ga(CH_2SiMe_3)_3$ by using stoichiometric quantities of gallium trihalide in an exchange reaction or anhydrous hydrogen halide in an elimination reaction. These reactions have been discussed in detail for the preparation of analogous ((trimethylsilyl)methyl)indium(III)–chloride derivatives.[1] Our available data suggest that these organogallium(III)–halide compounds exist as halogen-bridged dimers with the following molecular formulas: $[Ga(CH_2SiMe_3)_2Br]_2$, $[Ga(CH_2SiMe_3)Br_2]_2$, and $[Ga(CH_2SiMe_3)Cl_2]_2$. Dimeric species were shown to be present in benzene solution by cryoscopic molecular weight data. The ^1H NMR and infrared data are also fully consistent with these formulations. It is noteworthy that these ((trimethylsilyl)methyl)gallium(III)–halide compounds have properties more similar to those of the corresponding methylgallium–halide derivatives[12,13] than the related higher alkyl species. The compounds of the general formula R_nGaCl_{3-n} ($R = C_2H_5$ to C_4H_9 isomers; $n = 1, 2$) have chlorine-bridged dimeric structures and are liquids at room temperature.[14] Structural studies have confirmed the chlorine-bridged dimeric structures[15,16] for $[CH_3GaCl_2]_2$ and $[C_6H_5GaCl_2]_2$ which are analogous to that proposed for $[Ga(CH_2SiMe_3)Cl_2]_2$. In contrast the organoindium(III) derivative $In(CH_2SiMe_3)Cl_2$ is believed to have more extensive association in the solid state.[1] The indium atom is suggested to exist in a strongly distorted trigonal-bipyramidal coordination of one (trimethylsilyl)methyl group and four chlorines.

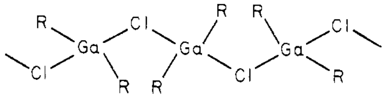
The monochloro-substituted derivative $Ga(CH_2SiMe_3)_2Cl$ was prepared in surprisingly low yields in comparison to the reactions which gave near quantitative yields of $[Ga(CH_2SiMe_3)_2Br]_2$ and $[In(CH_2SiMe_3)_2Cl]_2$.[1] The best procedure for the preparation of $Ga(CH_2SiMe_3)_2Cl$ involved small scale elimination reactions. Anhydrous hydrogen chloride was added in several equimolar portions to a benzene solution of $Ga(CH_2SiMe_3)_3$. Within 1 h a white crystalline solid, later identified as $Ga(CH_2SiMe_3)_2Cl$, precipitated from solution. The other products observed from the reaction included $Si(CH_3)_4$, $[Ga(CH_2SiMe_3)Cl_2]_2$, and unreacted $Ga(CH_2SiMe_3)_3$. The elemental analyses, ^1H NMR and infrared data, and the quantitative hydrolysis of (trimethylsilyl)methyl groups confirm the formula of the insoluble reaction product as $Ga(CH_2SiMe_3)_2Cl$. The chemical and physical properties of $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$ prepared from equimolar quantities of $Ga(CH_2SiMe_3)_2Cl$ and $N(CH_3)_3$ at 0 °C are identical in every respect with those of $Ga(CH_2SiMe_3)_2Cl{\cdot}N(CH_3)_3$ prepared from $Ga(CH_2SiMe_3)_3$ and $(CH_3)_3N{\cdot}HCl$. All data suggest that the low yields of $Ga(CH_2SiMe_3)_2Cl$ from the elimination reaction are related to further reaction. Unless $Ga(CH_2SiMe_3)_2Cl$ precipitates from solution, it reacts with a second mole of HCl to give $Ga(CH_2SiMe_3)Cl_2$. The ^1H NMR spectrum of $Ga(CH_2SiMe_3)_2Cl$ in CH_2Cl_2 solution suggests that $Ga(CH_2SiMe_3)_2Cl$ does not disproportionate to give the observed products of the preparative reaction.

Various reaction conditions were attempted to maximize the yield of $Ga(CH_2SiMe_3)_2Cl$ and increase the reproducibility of the reaction. Elimination reactions at low temperature (0, −46, −78 °C) using toluene as solvent or reactions at 25 °C in methylene chloride, diethyl ether, acetonitrile, or toluene gave decreased yields of $Ga(CH_2SiMe_3)_2Cl$. The exchange reaction between $Ga(CH_2SiMe_3)_3$ and $GaCl_3$ in benzene solution gave none of the desired product, $Ga(CH_2SiMe_3)_2Cl$. The monochloro derivative could not be isolated from a reaction mixture of $GaCl_3$ with 2 mol of the Grignard reagent Me_3SiCH_2MgCl in ether solution.

The unusual chemical and physical properties of $Ga(CH_2SiMe_3)_2Cl$ when compared with other monohalogallium derivatives suggest a unique structure probably involving extensive association of monomeric units in the solid state as shown in the following types of polymeric structures.



I
"ladder polymer"



II
linear polymer

Structure I would minimize interactions between the (trimethylsilyl)methyl groups and maximize the coordination number of the gallium. The gallium atom would have severely distorted trigonal-bipyramidal coordination. Structure II would have the normal coordination number four around gallium but interactions between (trimethylsilyl)methyl groups would be greater than in structure I. Simple dimeric and monomeric structures as well as ion pair formulations are ruled out on the basis of chemical, physical, and spectral data. The high melting point, nonvolatile behavior up to 160 °C, and the limited solubility of $Ga(CH_2SiMe_3)_2Cl$ in benzene or pentane are in sharp contrast with all other organogallium–halogen compounds,[12,14] including $[Ga(CH_2SiMe_3)_2Br]_2$. All dimeric compounds of the general formula[14] $[GaR_nCl_{3-n}]_2$, where $R = CH_3$ to C_4H_9 isomers and $n = 1$ and 2, are volatile, low-melting solids or liquids at room temperature. All of these compounds are also soluble in nonpolar solvents such as benzene or pentane. Even, $[Ga(CH_2SiMe_3)_2Br]_2$, $[Ga(CH_2SiMe_3)Br_2]_2$, and $[Ga(CH_2SiMe_3)Cl_2]_2$ have low melting

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Table IV. Infrared Spectra of ((Trimethylsilyl)methyl)gallium and Methylgallium Compounds[a]

compd	ν(Ga–C), cm^{-1}	ν(Ga–Cl), cm^{-1}
$Ga(CH_2SiMe_3)_3$	535 (m), 512 (m)	
$Ga(CH_2SiMe_3)_2Cl$	583 (m), 545 (m)	282 (vs), 263 (sh)
$Ga(CH_2SiMe_3)Cl_2$	581 (m), 541 (m)	369 (m), 342 (s), 316 (vs)
$Ga(CH_2SiMe_3)_2Br$	578 (m), 548 (m)	*b*
$Ga(CH_2SiMe_3)Br_2$	585 (m), 550 (m)	*b*
$Ga(CH_3)_2Cl$	588 (s), 540 (m)	335 (m), 292 (s), 270 (vs)
$Ga(CH_3)Cl_2$	586 (s), 540 (m)	361 (vs), 335 (vs), 311 (m)

[a] Spectra observed as neat liquids or Nujol mulls. [b] Absorption due to Ga–Br vibrations occurs at frequencies below the range of our instrument.

points and are soluble in nonpolar solvents. Thus, $Ga(CH_2SiMe_3)_2Cl$ is the only organogallium(III)–chlorine compound which is not dimeric.

The infrared spectral data (Table IV) support the proposed dimeric structures for $[Ga(CH_2SiMe_3)_2Br]_2$, $[Ga(CH_2SiMe_3)Br_2]_2$, and $[Ga(CH_2SiMe_3)Cl_2]_2$, as well as a unique structure, possibly a "ladder polymer" for $[Ga(CH_2SiMe_3)_2Cl]_x$. The frequencies of the gallium–carbon and gallium–halogen vibrations are directly related to the structural backbones of the compound. All compounds have two absorptions assigned to gallium–carbon vibrations. The dimeric methylgallium compounds $[(CH_3)_2GaCl]_2$ and $[CH_3GaCl_2]_2$ also have two ν(Ga–C) absorptions at frequencies similar to those observed for the corresponding (trimethylsilyl)methyl derivatives. The dichlorogallium compounds $[Ga(CH_2SiMe_3)Cl_2]_2$ and $[CH_3GaCl_2]_2$ also have similar ν(Ga–Cl) absorptions, indicative of similar structures. In contrast, the infrared spectra of $Ga(CH_2SiMe_3)_2Cl$ and $[(CH_3)_2GaCl]_2$ are very different which is indicative of different structures. A unique structure is proposed for $Ga(CH_2SiMe_3)_2Cl$. The dimer $[(CH_3)_2GaCl]_2$ has three Ga–Cl bands whereas $Ga(CH_2SiMe_3)_2Cl$ has one very intense band at 282 cm^{-1} with a shoulder at 263 cm^{-1}. The intensity of the Ga–Cl band is consistent with the proposed arrangement of groups around gallium in the "ladder" polymer. The high coordination number of gallium in the proposed "ladder polymer" could lead to the relatively low frequency observed for the band. The two Ga–C absorptions are consistent with an angular arrangement of (trimethylsilyl)methyl groups and discount a linear symmetry which might occur in an ionic type structure.[17]

Lewis acidity studies indicate the following order of increasing acid strength for ((trimethylsilyl)methyl)gallium(III) compounds: $Ga(CH_2SiMe_3)_3 < Ga(CH_2SiMe_3)_2X < Ga(CH_2SiMe_3)X_2$ (X = Cl, Br). It is of interest that the chloro and bromo compounds showed very similar Lewis acidic behavior. This order is indicated by the range of bases which formed stable adducts at room temperature with a given acid and by relative ^1H NMR chemical shift data (Table III). The Lewis bases studied included diethyl ether, dimethoxyethane, acetonitrile, tetrahydrofuran, and trimethylamine. The weakest Lewis acid of the series is $Ga(CH_2SiMe_3)_3$. It formed stable 1:1 adducts with only trimethylamine and tetrahydrofuran, the strongest bases. Our experimental data suggest that the diethyl ether complex is extensively dissociated at 25 °C. Diethyl ether could be removed from $Ga(CH_2SiMe_3)_3$ by vacuum distillation at 25 °C in only 3 h. In contrast, diethyl ether cannot be removed from $Ga(CH_3)_3$ at room temperature.[10] The $(CH_3)_3GaO(C_2H_5)_2$ complex is only extensively dissociated in the vapor phase.[10] The monohalo derivatives $Ga(CH_2SiMe_3)_2Cl$ and $Ga(CH_2SiMe_3)_2Br$ also formed stable 1:1 adducts with only trimethylamine and tetrahydrofuran. However, the ease with which diethyl ether can be removed from these acids would suggest that they are slightly stronger acids than $Ga(CH_2SiMe_3)_3$. There are no available data which permit a clear distinction between the Lewis acidities of $Ga(CH_2SiMe_3)_2Cl$ and $Ga(CH_2SiMe_3)_2Br$. In contrast to the limited number of stable adducts observed for $Ga(CH_2SiMe_3)_3$ and $Ga(CH_2SiMe_3)_2X$ (X = Cl, Br), the dihalo derivatives formed stable 1:1 adducts with all bases studied. The ^1H NMR chemical shift data of all stable adducts compared to the free acid are consistent with the previously observed order of Lewis acidity.

The studies[1] of the interactions of the ((trimethylsilyl)methyl)indium(III) compounds with an identical range of Lewis bases gave significantly different results than those observed for the gallium(III) compounds. The strongest Lewis acid of the indium series[1] is $In(CH_2SiMe_3)_3$. It formed a stable 1:1 adduct with only trimethylamine. The compound $[In(CH_2SiMe_3)_2Cl]_2$ did not exhibit any acidic properties whereas $[In(CH_2SiMe_3)Cl_2]_2$ formed weak adducts with appreciable dissociation pressures.

All data indicate the Lewis acidities of ((trimethylsilyl)methyl)gallium(III) compounds increase with increasing halogen substitution at gallium. The steric interactions between two (trimethylsilyl)methyl groups is most likely the controlling factor. The weakly acidic properties of $Ga(CH_2SiMe_3)_3$ enable the compound to be synthesized from $GaCl_3$ and the Grignard reagent in diethyl ether solution. Furthermore, the steric interactions between the two (trimethylsilyl)methyl groups of $Ga(CH_2SiMe_3)_2Cl$ might be responsible for preventing dimer formation. The tendency for coordination saturation about gallium would lead to the proposed polymeric type of structures. The dimer $[Ga(CH_2SiMe_3)_2Br]_2$ might be stable because the longer gallium–bromine bridge bonds allow a greater distance to be maintained between (trimethylsilyl)methyl groups. It is apparent that as the radius of the central atom decreases from indium to gallium, the (trimethylsilyl)methyl groups introduce unusual changes in the chemistry.

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Registry No. $Ga(CH_2SiMe_3)_3$, 72708-53-3; $Ga(CH_2SiMe_3)_2Br$, 72708-90-8; $Ga(CH_2SiMe_3)Br_2$, 72708-91-9; $Ga(CH_2SiMe_3)Cl_2$, 72708-92-0; $Ga(CH_2SiMe_3)_2Cl$, 72708-39-5; $Ga(CH_2SiMe_3)_2Cl\cdot N(CH_3)_3$, 72709-13-8; $Ga(CH_2SiMe_3)_3\cdot O(CH_2)_4$, 72709-14-9; $Ga(CH_2SiMe_3)_3\cdot N(CH_3)_3$, 72709-15-0; $Ga(CH_2SiMe_3)_2Cl\cdot O(CH_2)_4$, 72709-16-1; $Ga(CH_2SiMe_3)Cl_2\cdot CH_3OC_2H_4OCH_3$, 72708-93-1; $Ga(CH_2SiMe_3)Cl_2\cdot O(C_2H_5)_2$, 72708-94-2; $Ga(CH_2SiMe_3)Cl_2\cdot CH_3CN$, 72708-95-3; $Ga(CH_2SiMe_3)Cl_2\cdot O(CH_2)_4$, 72708-96-4; $Ga(CH_2SiMe_3)Cl_2\cdot N(CH_3)_3$, 72708-97-5; $Ga(CH_2SiMe_3)_2Br\cdot O(CH_2)_4$, 72708-98-6; $Ga(CH_2SiMe_3)_2Br\cdot N(CH_3)_3$, 72708-99-7; $Ga(CH_2SiMe_3)Br_2\cdot O(C_2H_5)_2$, 72709-00-3; $Ga(CH_2SiMe_3)Br_2\cdot CH_3OC_2H_4OCH_3$, 72709-01-4; $Ga(CH_2SiMe_3)Br_2\cdot CH_3CN$, 72709-02-5; $Ga(CH_2SiMe_3)Br_2\cdot O(CH_2)_4$, 72708-88-4; $Ga(CH_2SiMe_3)Br_2\cdot N(CH_3)_3$, 72708-89-5; $Ga(CH_3)_2Cl$, 6917-81-3; $Ga(CH_3)Cl_2$, 6917-74-4; $GaCl_3$, 13450-90-3; $GaBr_3$, 13450-88-9; Me_3SiCH_2Cl, 2344-80-1.

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