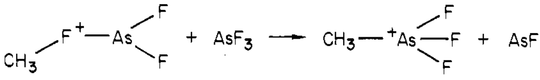
ternatively, a bimolecular isomerization (reaction 25) could



(25)

III IV

also occur, making it extremely probable that any $CH_3FAsF_2^+$ observed at long reaction time has structure IV. This reaction is essentially a CH_3^+ transfer from a less basic to a more basic site of AsF_3.

Conclusion

The above results demonstrate that the trifluoroarsonium ion displays an unusual reactivity among its group 5 trifluoride congeners. The $As_2F_5^+$ adduct produced via nucleophilic addition–elimination rections with AsF_3 has a known analogy in synthetic inorganic chemistry in the $Sb_2F_5^+$ cation found in $Sb_2F_5^+Sb_2F_{11}^-$ which has been shown by crystallographic methods to have a bridging fluoronium ion structure. Our results indicate that such a structure for $As_2F_5^+$ is not unreasonable.

The reactions of bases with $HAsF_3^+$ also suggest that, by a judicious choice of reaction conditions to simulate the gas-phase conditions as closely as possible in synthetic experiments, a number of salts of unusual cations might be produced. For example, a mixture of AsF_3 and HF–SbF_5 might conceivably yield $As_2F_5^+Sb_2F_{11}^-$. In addition, in the presence of a large excess of another weakly basic species, salts such as $AsF_2CO^+Sb_2F_{11}^-$ might be produced.

Through our continuing studies of gas-phase basicities of inorganic main-group oxides, fluorides, and oxofluorides, we hope to develop further routes to novel gas-phase ionic species which can suggest synthetic pathways to new compounds which exhibit unusual bonding.

Acknowledgment. The financial support of the National Research Council of Canada and the University of New Brunswick is gratefully acknowledged. We also acknowledge useful discussions with Professors F. Bottomley and J. Passmore.

Registry No. NF_3, 7783-54-2; AsF_3, 7784-35-2; PF_3, 7783-55-3; $HAsF_3^+$, 74203-18-2; $F_3NAsF_2^+$, 74203-19-3; AsF_5^+, 12446-59-2.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Organometallic Gallium(I) Anions Prepared by a Reductive Elimination Reaction

O. T. BEACHLEY, JR.,* and RANDALL G. SIMMONS

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A series of ((trimethylsilyl)methyl)gallium(I) compounds, $M^IGa(CH_2SiMe_3)_2$ (M^I = Na, K) and $M^IGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ (M^I = Li, Na), have been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements in benzene solution, solubility properties, and infrared and ^1H and ^{13}C NMR spectral data. These novel compounds represent a new class of organometallic derivative, which incorporate low oxidation state, main-group, metallic anions. The preparative route to these organogallium(I) compounds involves an apparent reductive elimination reaction between $Ga(CH_2SiMe_3)_3$ with alkali-metal hydrides in benzene or dimethoxyethane. All available data including the high solubility in aliphatic and aromatic solvents, low melting points, and molecular weight measurements are consistent with the covalent molecular formulas $[KGa(CH_2SiMe_3)_2]_2$, $[NaGa(CH_2SiMe_3)_2]_3$, and $[LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe]_x$. Structures involving gallium–gallium bonds are proposed to account for observed molecular association and chemical properties.

Introduction

Organometallic compounds have been known for over 100 years. Much of the development of the chemistry of the transition-metal derivatives can be ascribed to the synthetic utility of redox reactions and metal carbonyl anions.[1] In contrast the chemistry of the organometallic derivatives of the main-group elements has focused on the properties and reactions of compounds with the metals in their highest oxidation states.[2] Consequently, the literature contains very few examples of well-defined, kinetically stable, low oxidation state organometallic compounds or of reactions in which the main-group metal in an organometallic derivative changes oxidation state. The compounds[3,4] $In(C_5H_5)$ and $Tl(C_5H_5)$ are the only examples of low oxidation state group 3 organometallic derivatives. Both of these compounds[5,6] exist in the solid state as linear polymers with the cyclopentadienyl ring exhibiting η^5 coordination. In group 4 chemistry, the unique low oxidation state compounds[7] $M^{IV}(CH(SiMe_3)_2)_2$ (M^{IV} = Ge, Sn, Pb) have been prepared and thoroughly characterized. An X-ray structural study[7] of the tin compound confirms a dimeric structure which has an apparent bent tin–tin double bond using the available electron pair and vacant orbital on each tin(II) atom.

The two potential routes to low oxidation state main-group organometallic compounds involve the alkylation of a low oxidation state halogen compound or the reduction of a high oxidation state organometallic derivative. The alkylation reaction has been applied to the syntheses of the $M^{IV}(CH(SiMe_3)_2)_2$ compounds from $M^{IV}Cl_2$ and the lithium alkyl.[7] In contrast the synthesis[3,8] of $In(C_5H_5)$ involves a reduction reaction since the starting material is $InCl_3$. The cyclopentadienide anion[8] is considered the reducing agent for $In(C_5H_5)_3$. Regrettably, both of these observed reactions are of limited use for the synthesis of other group 3 derivatives. The common low oxidation state halogen compounds incorporate the metal in both the low and high oxidation states,[9] for example, $Ga^+GaCl_4^-$.

The chemistry of the hydride derivatives of the heavier main-group metals suggests the potential occurrence of facile

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(1) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds"; Methuen: London, England; Vol. 2, 1968.

(2) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds"; Methuen: London, England; Vol. 1, 1967.

(3) Fischer, E. O.; Hofmann, H. P. *Angew. Chem.* **1957**, *69*, 639.

(4) (a) Fischer, E. O. *Angew Chem.* **1957**, *69*, 207. (b) Meister, H. *Ibid.* **1957**, *69*, 533.

(5) Cotton, F. A.; Reynolds, L. T. *J. Am. Chem. Soc.* **1958**, *80*, 269.

(6) Frasson, E.; Menegus, F.; Panattoni, C. *Nature (London)* **1963**, *199*, 1087.

(7) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(8) Poland, J. S.; Tuck, D. G. *J. Organomet. Chem.* **1972**, *42*, 307.

(9) Garton, G.; Powell, H. M. *J. Inorg. Nucl. Chem.* **1957**, *4*, 84.

0020-1669/80/1319-3042$01.00/0

Table I. Reactions of $Ga(CH_2SiMe_3)_3$ with Alkali-Metal Hydrides

compd	solvent/time, h/temp, °C	% yield of products[a]		mp, °C
		$Si(CH_3)_4$	Ga(I) compd	
$NaGa(CH_2SiMe_3)_2$	C_6H_6/24/45	98.5	97.8	59–60
$KGa(CH_2SiMe_3)_2$	C_6H_6/24/45	98.8	97.3	74–75
$NaGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$	$MeOC_2H_4OMe$/24/25	99.0	98.8	100–102
$LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$	$MeOC_2H_4OMe$/168/45	97.1	94.8	80–82

[a] The percent yields of products, $Si(CH_3)_4$ and organogallium(I) compounds, are based upon initial amounts of $Ga(CH_2SiMe_3)_3$ used in the preparative reaction.

Table II. Analytical Data for the Alkali-Metal ((Trimethylsilyl)methyl)gallium(I) Compounds

compd	% Ga		% alkali metal		CH_2SiMe_3/Ga mole ratio
	calcd	found	calcd	found	
$NaGa(CH_2SiMe_3)_2$	26.10	26.09	8.61	8.64	2.00
$KGa(CH_2SiMe_3)_2$	24.62	24.51	13.80	13.73	2.00
$NaGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$	19.51	19.52	6.44	6.41	1.98
$LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$	20.43	20.38	2.03	2.04	a

[a] Due to the limited solubility of $LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ in solvents useful for the quantitative formation and isolation of $Si(CH_3)_4$, the analytical data could not be obtained.

reduction reactions at the metallic center. Previous research[10] has shown $(HGaCl_2)_2$ to quantitatively form $Ga^+GaCl_4^-$ and H_2 at 25 °C. Trichlorogermane,[11] $HGeCl_3$, undergoes rapid evolution of HCl at 50 °C to generate the low oxidation state compound $GeCl_2$. This latter reaction is an apparent example of reductive elimination, a class of reaction which has been of little synthetic utility in main-group chemistry. Thus, a controlled reduction reaction of a hydride derivative might be a possible route to a kinetically stable, low oxidation state organometallic compound if associative and dissociative low-energy decomposition pathways for the product can be avoided. The ligands CH_2SiMe_3, $CH(SiMe_3)_2$, and $N(SiMe_3)_2$ have been observed to minimize the availability of these types of decomposition pathways.[12] Thus, the reactions of tris((trimethylsilyl)methyl)gallium(III) with alkali-metal hydrides were investigated as possible routes to low oxidation state gallium compounds. In this paper we report the syntheses and characterizations of organogallium compounds with the simplest formula, $KGa(CH_2SiMe_3)_2$ and $NaGa(CH_2SiMe_3)_2$. Since these formulas are consistent with the gallium being in the +1 oxidation state, these compounds represent a new class of organometallic derivatives, which incorporate low oxidation state, main-group metallic anions. The nature of the synthetic reaction path, the unusual properties of these novel compounds, and their possible structures based on available data are discussed.

Experimental Section

Materials. 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 were purified by refluxing with an appropriate drying agent and vacuum distilled just prior to use. The drying agents for the solvents dimethoxyethane, benzene, and methylene chloride were sodium–benzophenone ketyl, sodium ribbon, and phosphorus pentoxide, respectively. The alkali-metal hydrides were purchased from Alfa Inorganics as an oil dispersion. The oil was removed by repeated extraction with dry pentane. Tris((trimethylsilyl)methyl)gallium(III),[13] $Ga(CH_2SiMe_3)_3$, was prepared from $GaCl_3$ by a standard Grignard reaction in diethyl ether.

Synthesis of ((Trimethylsilyl)methyl)gallium (I) Compounds: $M^IGa(CH_2SiMe_3)_2$ (M^I = Na, K) and $M^IGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ (M^I = Li, Na). The low oxidation state derivaties $M^IGa(CH_2SiMe_3)_2$ (M^I = Na, K) and $M^IGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ (M^I = Li, Na) were prepared from $Ga(CH_2SiMe_3)_3$ and the appropriate alkali-metal hydride in benzene or dimethoxyethane, respectively. The nature of the product depends on both the reducing agent and solvent. For illustration of the experimental procedure, the preparation of $NaGa(CH_2SiMe_3)_2$ is described in detail. All other compounds were prepared in a similar manner. Table I gives the specific reaction conditions, melting point data, and the percent yields of the products. Analytical data for the new compounds are given in Table II; molecular weight, infrared, and NMR data in appropriate sections.

A 250-mL heavy-wall pyrolysis tube equipped with a side-arm break-seal was charged with 1.726 g (5.213 mmol) of $Ga(CH_2SiMe_3)_3$ and 0.313 g (13.0 mmol) of NaH in the drybox. Then, all of the following manipulations were carried out with the apparatus under high vacuum. Dry benzene, 20 mL, was distilled into the tube by using a −196 °C bath. The tube was sealed and the reaction mixture heated at 45 °C with stirring for 24 h. After the break-seal was opened, the reaction mixture was filtered to remove unreacted NaH. The volatile components were then separated by fractional distillation to yield benzene (−78 °C trap) and 0.452 g (5.13 mmol, 98.5% yield) of tetramethylsilane (−196 °C trap). The product, $NaGa(CH_2SiMe_3)_2$, was isolated as a colorless, crystalline solid (1.362 g, 5.098 mmol, 97.8% yield). No further purification was necessary.

The new low oxidation state compounds $NaGa(CH_2SiMe_3)_2$, $KGa(CH_2SiMe_3)_2$, and $NaGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ are very soluble in aliphatic and aromatic solvents as well as the more polar solvents methylene chloride, acetonitrile, and diethyl ether. In contrast, the lithium derivative, $LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$, has only limited solubility in pentane and benzene but is readily soluble in the polar solvents dimethoxyethane and tetrahydrofuran.

Analyses. The new ((trimethylsilyl)methyl)gallium(I) compounds were analyzed for gallium by EDTA titration.[14] The percentages of alkali metals (Li, Na, K) were determined by standard atomic absorption procedures using a Perkin-Elmer Model 503 spectrometer. The molar ratio CH_2SiMe_3 groups per gallium was determined by quantitatively converting the ligand into $Si(CH_3)_4$ by reaction of the organogallium(I) compound with anhydrous hydrogen chloride in benzene solution at room temperature. $Si(CH_3)_4$ was separated from all other volatile components in the reaction mixture by passage through a −78 °C trap and into a −196 °C trap on the vacuum line. The purity of $Si(CH_3)_4$ was confirmed by vapor pressure measurements and ^1H NMR and infrared spectroscopy. All analytical data are given in Table II.

Molecular Weight Studies. Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.[15] The following molecular weight data for the new ((trimethylsilyl)methyl)gallium(I) compounds were observed. Calculated molality of the monomer (observed molecular weight): for $NaGa(CH_2SiMe_3)_2$ (fw 267), 0.2655 (811), 0.1610 (809), 0.1334 (816), 0.0834 (807); for $KGa(CH_2SiMe_3)_2$ (fw 284), 0.2165 (572), 0.1460 (572), 0.1355 (568), 0.1138 (572); for $NaGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ (fw 357), 0.0930 (854), 0.0917 (827), 0.0761 (778), 0.0505 (722), 0.0462 (699), 0.0320 (604); for $LiGa(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$ (fw 341), compound has insufficient solubility in benzene for molecular weight measurements.

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 Nujol mulls by using CsI plates. Absorption intensities were measured by using the method of Durkin, Glore, and Dehayes.[16]

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(10) (a) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 783. (b) Schmidbauer, H.; Findeiss, W.; Gast, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 152.

(11) Delwaulle, F. F.; Francois, F. *C. R. Hebd. Seances Acad. Sci.* **1949**, *228*, 1585.

(12) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.

(13) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 1021.

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

(15) Shiver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; p 159.

Table III. Proton NMR Data for the Alkali-Metal ((Trimethylsilyl)methyl)gallium(I) Compounds and Their Lewis Acid-Base Adducts[a]

	τ		
compd	Si–CH_3 protons	Si–CH_2 protons	Lewis base protons[b]
$LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	9.96	10.18	6.41 (singlet, CH_2) 6.57 (singlet, CH_3)
$NaGa(CH_2SiMe_3)_2$	9.95	10.80	
$NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	9.93	10.55	6.39 (singlet, CH_2) 6.55 (singlet, CH_3)
$NaGa(CH_2SiMe_3)_2 \cdot O(CH_2)_4$	9.92	10.63	6.15 (multiplet, CH_2) 8.05 (multiplet, CH_2)
$NaGa(CH_2SiMe_3)_2 \cdot N(CH_3)_3$	9.95	10.67	7.79 (singlet, CH_3)
$KGa(CH_2SiMe_3)_2$	9.93	10.01	
$KGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	9.92	10.14	6.64 (singlet, CH_2) 6.61 (singlet, CH_2)

[a] Chemical shifts are given in ppm relative to tetramethylsilane. Methylene chloride was used as solvent. [b] The chemical shifts (ppm) for the nonadducted Lewis base protons in methylene chloride relative to $Si(CH_3)_4$ are as follows: dimethoxyethane, 6.57, singlet, CH_2; 6.72, singlet, CH_3; tetrahydrofuran, 6.40, multiplet, α-CH_2; 8.25, multiplet, β-CH_2; trimethylamine, 7.79, singlet, CH_3.

The following are the spectral data [frequency, cm^{-1} (intensity: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder)]. Bands due to mulling agents have been omitted. $NaGa(CH_2SiMe_3)_2$: 1265 (s), 1252 (vs), 981 (s), 960 (s), 855 (vs), 835 (vs), 765 (m), 735 (m), 691 (w), 565 (w), 509 (s), 480 (m).

$KGa(CH_2SiMe_3)_2$: 1251 (s), 1238 (vs), 970 (s), 947 (s), 856 (vs), 834 (vs), 763 (m), 743 (m), 680 (w), 564 (w), 504 (s), 483 (m).

$LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$: 1255 (s), 1244 (vs), 1200 (m), 1130 (m), 1084 (m), 1032 (w), 969 (s), 865 (vs), 840 (vs), 770 (s), 765 (s), 699 (m), 559 (m), 518 (s), 481 (w).

$NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$: 1255 (s), 1245 (vs), 1198 (m), 1122 (m), 1085 (m), 982 (s), 960 (s), 855 (vs), 825 (vs), 760 (s), 740 (s), 685 (m), 565 (w), 508 (s), 475 (m).

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

The ^{13}C NMR spectra of benzene-d_6 solutions were recorded at 25.2 MHz and ambient temperature by using a Varian XL-100 spectrometer. All chemical shifts (ppm) are referenced to tetramethylsilane and are downfield of it: $[KGa(CH_2SiMe_3)_2]_2$ 4.49 ($SiCH_2$), 3.91 (SiMe); $[NaGa(CH_2SiMe_3)_2]_3$ 4.05 ($SiCH_2$), 3.85 (SiMe); $Ga(CH_2SiMe_3)_3$ 13.29 ($SiCH_2$), 3.06 ($SiCH_3$).

Lewis Acidity Studies. The Lewis acidities of the ((trimethylsilyl)methyl)gallium(I) compounds, $M^IGa(CH_2SiMe_3)_2$ (M^I = Na, K), were studied by reacting a stoichiometric quantity of the desired acid with excess base (trimethylamine, acetonitrile, diethyl ether, tetrahydrofuran, dimethoxyethane). The reaction mixture was stirred at room temperature for 2 h. The volatile components were then removed 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 temperature for the acid–base pairs $KGa(CH_2SiMe_3)_2$–dimethoxyethane and $NaGa(CH_2SiMe_3)_2$–dimethoxyethane, –tetrahydrofuran, and –trimethylamine.

Results and Discussion

A novel class of organometallic derivatives of gallium as exemplified by $KGa(CH_2SiMe_3)_2$, $NaGa(CH_2SiMe_3)_2$, and $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ have been prepared by a new synthetic reaction and fully characterized. The composition of these sharp-melting, colorless, crystalline solids is consistent with gallium being classified in the +1 oxidation state. Thus, these novel, kinetically stable, low oxidation state compounds represent the first examples of anionic, σ-bonded organometallic derivatives of gallium(I).

The new gallium compounds were prepared from tris((trimethylsilyl)methyl)gallium(III), $Ga(CH_2SiMe_3)_3$, and an alkali-metal hydride by a stoichiometric reaction as summarized by the idealized equation (1), where the solvent is C_6H_6

$$Ga(CH_2SiMe_3)_3 + M^IH \xrightarrow{\text{solvent}} M^IGa(CH_2SiMe_3)_2 + Si(CH_3)_4 \quad (1)$$

for M^I = K, Na and $MeOC_2H_4OMe$ for M^I = Na, Li. There are several aspects of this particular reaction which are synthetically and experimentally attractive. The specific nature of the gallium(I) product can be easily changed by using different alkali-metal hydrides and solvents in a reaction which is carried out under very mild conditions. When benzene is used as solvent, only KH and NaH react at 45 °C to form the simple compounds $KGa(CH_2SiMe_3)_2$ and $NaGa(CH_2SiMe_3)_2$. In the case of dimethoxyethane, lower reaction temperatures (25 °C) can be employed, but the final product incorporates 1 mol of solvent, $NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, and $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$. Since the gallium(I) product is soluble in the reaction medium, the excess, insoluble metal hydride is easily separated by simple filtration. Finally, the extent of reaction is readily monitored by the evolution of tetramethylsilane. The reaction is observed to be stoichiometric, giving essentially quantitative yields of both tetramethylsilane and the gallium(I) product (Table I).

The stoichiometry of the preparative reaction, the analytical data, and the chemical and spectral properties of the products confirm the occurrence of an oxidation–reduction reaction. The gallium(III) reactant is converted to a gallium(I) product, a reduction process. The only other product, $Si(CH_3)_4$, must then be the product of the oxidation reaction. The reaction sequence (2) summarizes the proposed path for KH but it is

$$KH + Ga(CH_2SiMe_3)_3 \rightarrow KGa(CH_2SiMe_3)_3H$$

$$KGa(CH_2SiMe_3)_3H \xrightarrow[\text{elimination}]{\text{reductive}} KGa(CH_2SiMe_3)_2 + Si(CH_3)_4 \quad (2)$$

equally applicable to the other metal hydrides. All experimental data suggest that the gallium(I) product is formed by a reductive elimination reaction of a gallium(III) hydride intermediate, $KGa(CH_2SiMe_3)_3H$. The gallium(III) hydride intermediate is formed in a Lewis acid–base reaction between $Ga(CH_2SiMe_3)_3$ and the alkali-metal hydride, a thoroughly studied class of reactions for electron-deficient compounds.[2] The observed order of reactivity of the different metal hydrides for forming the gallium(I) products, KH > NaH > LiH, is identical with that observed for forming the simple Lewis acid–base adducts of the aluminum alkyls,[2] $MAlR_3H$. Thus, a primary factor controlling reactivity is probably related to the relative magnitude of the lattice energies of the alkali-metal hydrides. The quantitative formation of products in the preparative reaction, the lack of any infrared bands in the 2100–1800-cm^{-1} region, and the analytical data confirm that the gallium(III) hydride intermediate is readily converted to the gallium(I) product. The nature of the proposed facile reductive elimination reaction (step 2) was investigated by using NaD. Mass spectral data show that the deuterium is quantitativly incorporated into the tetramethylsilane as $(CH_3)_3SiCH_2D$. These results suggest that the reductive elimination reaction might occur as a nonradical, possibly concerted, process. Nonradical reactions should produce only $(CH_3)_3SiCH_2D$, whereas the existence of radical paths would

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

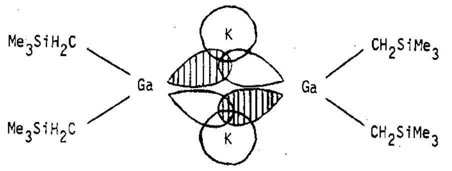


Figure 1. Proposed structure and bonding scheme for [KGa(CH$_2$SiMe$_3$)$_2$]$_2$.

lead to $Si(CH_3)_4$ by hydrogen abstraction from the solvent.

The new organometallic gallium(I) compounds have properties of typical covalent substances—low melting points and solubility in hydrocarbon solvents. The cryoscopic molecular weight measurements in benzene solution indicate that molecular association is an important structural feature for these compounds. The potassium derivative $[KGa(CH_2SiMe_3)_2]_2$ exists in benzene solution as a dimer whereas $[NaGa(CH_2SiMe_3)_2]_3$ is a trimer. These degrees of molecular association suggest that the properties of the alkali-metal ions, including their steric and thermodynamic effects, influence the specific nature of the molecule. The unique solubility properties and low melting points of the gallium(I) compounds are also consistent with relatively weak interactions between associated molecular units. The structures and nature of bonding of the molecules, infrared, ^{1}H, and ^{13}C NMR data, and Lewis acidity studies for these gallium(I) compounds will be discussed in turn.

Molecular association of the monomeric formula units can occur by metal–metal or alkyl-bridge bonding. All available data suggest that both the dimer $[KGa(CH_2SiMe_3)_2]_2$ and trimer $[NaGa(CH_2SiMe_3)_2]_3$ exist with metal–metal bonds. The proposed dimeric structure for $[KGa(CH_2SiMe_3)_2]_2$ (Figure 1) is analogous to that defined by an X-ray structural study[7] for $[Sn(CH(SiMe_3)_2]_2$. Since the number of metal-centered electron pairs and the number of vacant orbitals in the SnR_2 and GaR_2^- monomeric units are identical, analogous modes of bonding can be proposed. The gallium dimer would have the equivalent of a bent gallium–gallium double bond, which results from a pairwise orbital-overlap scheme between the filled nonbonding orbital of one $Ga(CH_2SiMe_3)_2^-$ unit with the vacant orbital of the other. This bonding scheme requires the gallium(I) atoms to function simultaneously as both a Lewis acid and base, a condition which leads to "synergic bonding". The potassium atoms are most likely situated near the sites of orbital overlap between the two gallium atoms. Bonding might involve a three-centered interaction. The nature of the (trimethylsilyl)methyl groups could provide a hydrocarbon sheath around the periphery of the molecule and possibly cover the potassium atoms. Thus, intermolecular interactions between the dimeric units would be minimized. The existence of metal–metal bonding in gallium chemistry is well documented. Gallium metal consists of dimeric (Ga_2) units arranged in deformed sets of hexagonal rings.[17] The anion[18] $[Cl_3Ga–GaCl_3]^{2-}$ has been prepared by the anodic oxidation of gallium metal in 6 M HCl. The dioxane adduct of Ga_2Cl_4, $[GaCl_2{\cdot}O_2C_4H_8]_2$, has a structure which incorporates a gallium–gallium bond.[19] In the last two examples, the metal–metal bond was verified by a Raman band around 235 cm^{-1}. Similar attempts to confirm the gallium–gallium bond in the new ((trimethylsilyl)methyl)gallium(I) derivatives were thwarted by the extremely low quality of Raman spectra due to high fluorescence.

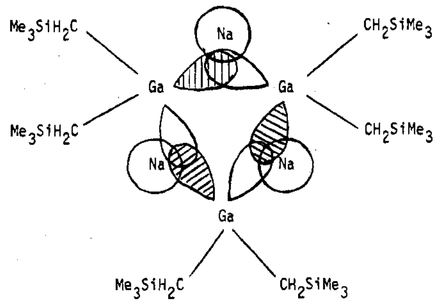
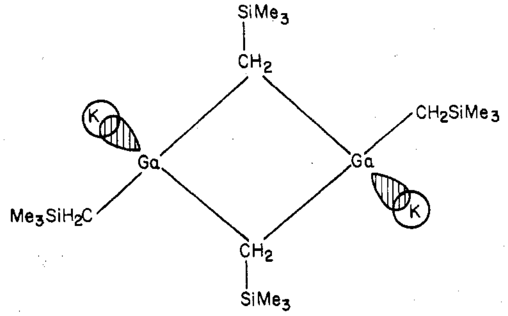


Figure 2. Proposed structure and bonding scheme for [NaGa(CH$_2$SiMe$_3$)$_2$]$_3$.

The second possible mode of molecular association is by three-centered electron-deficient alkyl-bridge bonding as shown by structure I. However, this type of bonding is inconsistent with our experimental data, including the lack of reaction of $[KGa(CH_2SiMe_3)_2]_2$ with amines and strong oxygen bases, and ^{1}H NMR chemical shift data for solutions containing these types of bases. The details of these experimental results are discussed in a following section. Bridge bonding has not been previously observed in gallium chemistry.[2] There are no alkyl-substituted gallium compounds which are associated in solution by alkyl-bridge bonding. Lastly, it is important to realize that the proposed electron precise gallium–gallium bonds in the low oxidation state compounds should be energetically more favorable than electron-deficient alkyl-bridge bonds.



I

The proposed structure for the trimer, $[NaGa(CH_2SiMe_3)_2]_3$ (Figure 2), is closely related to the proposed structure of $[KGa(CH_2SiMe_3)_2]_2$. The addition of another monomeric $Ga(CH_2SiMe_3)_2$ unit to the dimer leads to a triangular arrangement of gallium atoms linked by gallium–gallium single bonds. The sodium atoms would be similarly placed near sites of orbital overlap between gallium atoms and occupy positions along the edges of the gallium atom triangle. The smaller size and stronger bonding interactions of the sodium atoms compared with potassium might be responsible for the observed increase in degree of molecular association. Since the structure and nature of bonding of the dimer and trimer are very closely related, similar chemical and physical properties are observed. It is noteworthy that the structures proposed for the dimer and trimer are analogous to the type observed for the rhenium halides[20-22] $Re_2Cl_8^{2-}$ and Re_3Cl_9.

The NMR spectral data are fully consistent with the proposed structures. Since the (trimethylsilyl)methyl groups in $[KGa(CH_2SiMe_3)_2]_2$ and $[NaGa(CH_2SiMe_3)_2]_3$ occupy magnetically equivalent positions, only two sharp lines are observed in both the ^{1}H and ^{13}C NMR spectra for each compound (Table III). One line is assigned to the methyl-hydrogen

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(17) Bradley, A. J. *Z. Kristallogr. Kristallgeom., Kristallphys., Kristallchem.* **1935**, *91*, 302. Laves, F.; *Ibid.* **1933**, *84*, 256.

(18) (a) Evans, C. A.; Tan, K. H.; Tapper, S. P.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1973**, 988. (b) Brown, K. L.; Hall, D. *Ibid.* **1973**, 1843.

(19) Beanisk, J. C.; Small, R. W. H.; Worrall, I. J. *Inorg. Chem.* **1979**, *18*, 220.

(20) Cotton, F. A.; Lippard, S. J.; Mague, J. T. *Inorg. Chem.* **1965**, *4*, 508.

(21) Bennett, M. J.; Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1563.

(22) Cotton, F. A.; DeBoer, B. G.; Jeremic, J. *Inorg. Chem.* **1970**, *9*, 2143.

or -carbon atoms whereas the second line corresponds to the methylene-hydrogen or -carbon atoms. It is interesting that the methylene proton resonance shifts to higher field as the molecular association increases from dimer to trimer. These data would suggest that the methylene protons have more negative charge due to the inductive effects in a nominally trianionic species compared to a dianionic species. However, further comparisons with $Ga(CH_2SiMe_3)_3$ in order to determine the effects of oxidation state on NMR chemical shift would not be valid because the coordination number around gallium has changed significantly. In the potassium dimer gallium has an apparent coordination number of 5 whereas in the sodium trimer it is 6, and in $Ga(CH_2SiMe_3)_3$ it is only 3. Similarly, direct comparisons of infrared frequencies assigned to the gallium–carbon stretching modes for the various ((trimethylsilyl)methyl)gallium compounds are also unwarranted.

The behavior of $[NaGa(CH_2SiMe_3)_2]_3$ and $[KGa(CH_2SiMe_3)_2]_2$ as Lewis acids toward the Lewis bases diethyl ether, dimethoxyethane, tetrahydrofuran, acetonitrile, and trimethylamine was investigated in order to determine the relative strength and primary site of reaction, the alkali-metal ion or the gallium(I) atom. Our data suggest that $[NaGa(CH_2SiMe_3)_2]_3$ is the stronger acid and the base reacts primarily with the alkali metal ion. These conclusions are based on the range of bases which form stable 1:1 adducts at room temperature with a given acid and the relative ^1H NMR chemical shift data. The potassium derivative formed a stable adduct with only dimethoxyethane whereas the sodium compound formed adducts with dimethoxyethane, tetrahydrofuran, and trimethylamine. Similarly, the dimethoxyethane protons exhibit larger changes in NMR chemical shifts upon coordination to the sodium compound than those of the potassium compound. However, it is interesting to note that for the bases studied the protons in tetrahydrofuran exhibit the largest change in chemical shift upon coordination, but the magnitude is still small (0.25 ppm downfield) in comparison with the effects of the stronger Lewis acid[13] $[Ga(CH_2SiMe_3)_2Br]_2$ (0.47 ppm). It is also noteworthy that the chemical shift of the methyl (N) protons for free $N(CH_3)_3$ and $NaGa(CH_2SiMe_3)_2{\cdot}N(CH_3)_3$ are identical. All of these data suggest that the base coordinates with the alkali metal ion. If the base had coordinated to the gallium(I), the change in alkali-metal ion should have had a minor effect on the Lewis acidity of the low oxidation state compound. Furthermore, ethers are stronger bases than amines toward the alkali-metal ions whereas amines are usually stronger bases to gallium.[2] The anionic character of the $Ga(CH_2SiMe_3)_2^-$ moiety is probably responsible for the weak Lewis acidic behavior. An X-ray structural study[23] of $[NaBe(C_2H_5)_2H{\cdot}O(C_2H_5)_2]_2$ has shown the ether to be bound exclusively to the sodium ions rather than the beryllium atoms. Reactions of the gallium(I) anions as Lewis bases will be the subject of future publications.

The dimethoxyethane adduct $NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ was further characterized by cryoscopic molecular weight measurements in benzene solution. The apparent molecular weight depends upon the concentration of the solution. At higher concentrations, a molecular weight corresponding to the timer was observed. At the lowest concentration, the degree of association was 1.69. These data would suggest either that an equilibrium between monomer, dimer, and trimer exists in solution or, alternatively, the $[NaGa(CH_2SiMe_3)_2]_3$ trimer remains intact but has various numbers of bound dimethoxyethane molecules. The lithium derivative $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ was also prepared, but it was not sufficiently soluble in benzene for molecular weight measurements. Therefore, a structural hypothesis is not warranted at this time.

The successful synthesis of a low oxidation state organometallic anion of gallium opens a new area of chemistry. Periodic trends can be used to predict that analogous compounds might exist for indium and possibly aluminum. Similarly, the available electron pair on the main-group metal atom in the low oxidation state also implies the potential for nucleophilic reaction chemistry. Such aspects of the chemistry of these metal-based anions are being actively pursued.

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Registry No. $[NaGa(CH_2SiMe_3)_2]_3$, 74096-67-6; $[KGa(CH_2SiMe_3)_2]_2$, 74112-96-2; $[NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_3$, 74081-90-6; $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$, 74081-92-8; $[NaGa(CH_2SiMe_3)_2{\cdot}O(CH_2)_4]_3$, 74081-93-9; $[NaGa(CH_2SiMe_3)_2{\cdot}N(CH_3)_3]_3$, 74096-69-8; $[KGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_2$, 74081-95-1; $Ga(CH_2SiMe_3)_3$, 72708-53-3; NaH, 7646-69-7; LiH, 7580-67-8; KH, 7693-26-7.

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[23] Adamson, G. W.; Shearer, H. M. M. *Chem. Commun.* **1965**, 240.

Contribution from Rocketdyne, A Division of Rockwell International Corporation,
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Synthesis and Properties of $NF_4^+SO_3F^-$

KARL O. CHRISTE,* RICHARD D. WILSON, and CARL J. SCHACK

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The novel salt $NF_4^+SO_3F^-$ was prepared by metathesis between NF_4SbF_6 and $CsSO_3F$ in anhydrous HF solution at −78 °C. In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0 °C but slowly decomposes at +10 °C to produce $FOSO_2F$ and NF_3 in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and ^{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF, producing $CsSO_3F$ as the major product. Similarly, $CsPO_2F_2$, the Raman spectrum of which is reported, was found to react with HF to give $CsPF_6$ in quantitative yield.

Introduction

Among oxidizers, the NF_4^+ cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,[1] thereby permitting its combination with a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF_4^+ salt formation include

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[1] Christe, K. O.; Wilson, R. D.; Goldberg, I. B. *Inorg. Chem.* **1979**, *18*, 2572.

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