

Low Oxidation State Gallium Compounds. Synthesis and Characterization of $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$

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Received January 7, 1994*

The new organogallium(I) compound $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ has been prepared by the reduction of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ by using either sodium or lithium with naphthalene in THF. When the reagents were combined at -78°C , a yellow intermediate, a neopentylgallium(III) derivative of dihydronaphthalene $\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2]_2\cdot 2\text{MCl}$ ($\text{M} = \text{Li}, \text{Na}$) was formed. Warming of the solution to 0 – 25°C resulted in decomposition of the yellow intermediate and formation of a reddish brown solution of $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$, $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$, C_{10}H_8 , and either NaCl or LiCl . The gallium(I) product was a vitreous solid and was characterized by complete elemental analyses, hydrolyses with $\text{HCl}/\text{H}_2\text{O}$ and with $\text{DCl}/\text{D}_2\text{O}$, oxidation with HgCl_2 and with I_2 , cryoscopic molecular weight studies in benzene solution, and IR and NMR spectroscopic studies. All data support the conclusion that $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ exists as a mixture of species which are gallium cages. The numbers of gallium atoms in these cages might range from 6 to 12 atoms.

Introduction

The synthesis and characterization of organogallium compounds with gallium having an apparent oxidation state other than +3 provide interesting challenges. Previous preparative reactions have involved either metathesis reactions with or without concomitant disproportionation reactions or reduction reactions of appropriate gallium(III) derivatives. When metathesis reactions have been used, both the nature of the halogallium reactant and of the organic group appear to be of significance. The reaction of $\text{Ga}_2\text{Br}_4\cdot 2$ (dioxane) with a stoichiometric quantity of $\text{Li}[\text{CH}(\text{SiMe}_3)_2]$ provided $\text{Ga}_2[\text{CH}(\text{SiMe}_3)_2]_4$ as a yellow gallium(II) compound¹ with a gallium–gallium bond. When the gallium reactant was changed to $[\text{GaBr}_4]$ and was allowed to react with the same alkyl lithium $\text{LiCH}(\text{SiMe}_3)_2$, a gallium(III) product, $[\text{Ga}(\text{CH}(\text{SiMe}_3)_2)_3]$, and gallium metal were formed.¹ When the organic group was changed to $\text{C}(\text{SiMe}_3)_3$ but the gallium reactant was $\text{Ga}_2\text{Br}_4\cdot 2$ (dioxane), $[\text{GaC}(\text{SiMe}_3)_3]_4$, a dark red gallium(I) compound,² was formed along with many other uncharacterized products. The structural study of this gallium(I) product revealed an almost undistorted tetrahedral Ga_4 skeleton. Cryoscopic molecular weight studies in benzene suggested that the tetrahedral Ga_4 species was unstable in benzene solution. Trimers were observed for a 0.023 M solution and monomers were found at 0.0014 M . When $\text{Ga}_2\text{Br}_4\cdot 2$ (dioxane) was allowed to react with reagents which had a less sterically demanding organic group³ such as $\text{LiCH}_2\text{SiMe}_3$, $\text{LiGa}(\text{CH}_2\text{SiMe}_3)_4\cdot 1.5$ (dioxane) and gallium metal were formed. Similar observations³ were made when $\text{Ga}_2\text{Br}_4\cdot 2$ (dioxane) was allowed to react with $\text{LiCH}_2\text{CMe}_3$ in pentane as $\text{LiGa}(\text{CH}_2\text{CMe}_3)_4\cdot 1.5$ (dioxane) and gallium metal were formed. The reaction of $\text{Ga}_2\text{Cl}_4\cdot 2$ (dioxane) with $\text{LiC}_6\text{H}_2(\text{CF}_3)_3$ in diethyl ether leads to the formation of a gallium(II) product⁴ $\text{Ga}_2[\text{C}_6\text{H}_2(\text{CF}_3)_3]_4$ as a yellow microcrystalline solid. Alternatively, $\text{Ga}_2[\text{C}_6\text{H}_2$

$(\text{CF}_3)_3]_4$ was prepared by reduction of the gallium(III) precursor $\text{Ga}[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{Cl}$ with Na/K alloy in hexane at 25°C . The remaining gallium(I) compound⁵ to be described in the current literature is $\text{Ga}(\text{C}_5\text{H}_5)$. This compound was prepared by a metathesis reaction between a metastable solution of GaCl in toluene/diethyl ether and either $\text{Mg}(\text{C}_5\text{H}_5)_2$ or LiC_5H_5 at -78°C and precipitated by addition of pentane. However, the isolation of $\text{Ga}(\text{C}_5\text{H}_5)$ from its solution by removal of solvent in vacuo has not been successful. Experimental support for the formation of $\text{Ga}(\text{C}_5\text{H}_5)$ was provided by NMR studies and by mass spectral data.

In this paper, the synthesis and characterization of a new gallium(I) compound $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ is described. The best synthetic reaction involves an apparent reduction of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ by using either sodium or lithium and naphthalene in THF solution. The gallium(I) product is actually formed by decomposition of a soluble yellow intermediate, an organogallium(III) derivative of dihydronaphthalene, $\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2]_2\cdot 2\text{MCl}$ ($\text{M} = \text{Na}, \text{Li}$). As the new gallium product was a vitreous solid, elemental analyses, cryoscopic molecular weight studies, and chemical reactions with subsequent product identification were used to identify the oxidation state of gallium and to characterize the product.

Experimental Section

General. Compounds described in this investigation were extremely sensitive to oxygen and moisture and were handled in a standard vacuum line or under a purified argon atmosphere in a Vacuum/Atmospheres drybox. The starting compounds $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ and $\text{Ga}(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ were prepared and purified by literature methods.⁶ Solvents were dried by conventional procedures. Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY or E + R Microanalytical Laboratory, Inc., Corona, NY. Infrared spectra of Nujol mulls between CaI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were

* Abstract published in *Advance ACS Abstracts*, June 1, 1994.

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recorded at either 300 or 400 MHz by using either a Varian Gemini-300 or a Varian VXR-400 spectrometer, respectively. Proton chemical shifts are reported in δ units (ppm) and are referenced to C_6H_6 at δ 7.15 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries under purified argon. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver and Drezdron.⁷ Mass spectral analyses were performed by Dr. Timothy Wachs at Cornell University on either a Finnigan 3300 Quadrupole Spectrometer or a AES-MS-902 Double-Focusing Mass Spectrometer.

Reaction of $Ga(CH_2CMe_3)_2Cl$ with $Na/C_{10}H_8$. In a typical experiment, a 100-mL two-neck reaction flask charged with sodium metal (0.119 g, 5.19 mmol) cut into small pieces and naphthalene (0.671 g, 5.24 mmol) was attached to a side-arm dumper charged with $Ga(CH_2CMe_3)_2Cl$ (1.28 g, 5.19 mmol). Tetrahydrofuran (50 mL) was added by vacuum distillation. The flask was warmed to ambient temperature and the contents were stirred for 18 h to form the dark green sodium naphthalenide solution. A small amount of THF (10–20 mL) was then transferred by vacuum distillation into the side-arm dumper to dissolve the $Ga(CH_2CMe_3)_2Cl$. The reaction flask and side-arm dumper were simultaneously cooled to $-78^\circ C$ and then the $Ga(CH_2CMe_3)_2Cl/THF$ solution was slowly added to the sodium naphthalenide solution over 30 min. The solution was stirred for 18 h at $-78^\circ C$. The solution changed from brown/green to bright yellow. Only a trace amount of colorless precipitate was observed in the flask. As the initial yellow solution was warmed, more colorless precipitate formed and the color changed from bright yellow to dark reddish-brown at 0 to $10^\circ C$. The solution was stirred finally for 12 h at room temperature and then the THF was removed by rapid vacuum distillation. The remaining less-volatile materials were subjected to dynamic vacuum for 24 h, and 1.74 g of volatile materials was isolated in a small weighed trap. The sample was diluted with CH_2Cl_2 and then the components were identified by 1H NMR spectroscopy as $Ga(CH_2CMe_3)_3$ (0.569 g, 2.01 mmol, 77.5% yield based on $Ga(CH_2CMe_3)_2Cl$ and eq 1), $C_{10}H_8$ (0.585 g, 4.56 mmol, 87.1% recovered based on the initial amount of $C_{10}H_8$), and THF. The nonvolatile material was separated into soluble and insoluble components by three extraction-filtrations with 50 mL of pentane through a fine glass frit. The insoluble, light brown product, impure NaCl (0.334 g, 5.71 mmol, 110% yield based on Na), had positive analyses for sodium and chloride ions. The nonvolatile, soluble product was isolated as a reddish/brown, vitreous solid and identified as neopentylgallium(I), $[Ga(CH_2CMe_3)]_n$ (0.280 g, 1.99 mmol, 76.8% based on $Ga(CH_2CMe_3)_2Cl$ and eq 1). When $Ga(CH_2CMe_3)_2Cl$ and $Na/C_{10}H_8$ were combined as THF solutions at room temperature, $[Ga(CH_2CMe_3)]_n$ (93% yield), $Ga(CH_2CMe_3)_3$, NaCl, and $C_{10}H_8$ were formed after purification as described above.

$[Ga(CH_2CMe_3)]_n$. MP $60-80^\circ C$ dec. 1H NMR (C_6H_6 , δ): 1.94 (s), 1.77 (s), 1.37 (s), 1.32 (s), 1.30 (s), 1.28 (s), 1.20 (s), 1.09 (s), 1.00 (s) (all lines appear to be part of a complex spectrum). See Results and Discussion for explanation of the 1H NMR spectrum. IR (Nujol, cm^{-1}): 1358 (vs), 1265 (m), 1234 (vs), 1123 (s), 1095 (m), 1042 (w), 1012 (m), 998 (m), 909 (w), 850 (w), 815 (w), 779 (m), 772 (w), 745 (sh, m), 732 (m), 719 (sh, m), 706 (m), 624 (m), 610 (m), 595 (m), 591 (sh, m), 520 (m), 475 (m), 450 (m), 382 (w), 228 (m). Anal. Calcd for GaC_5H_{11} : C, 42.63; H, 7.87; Ga, 49.50. Found: C, 42.32; H, 7.72; Ga, 49.97. Solubility: soluble in THF, pentane, and benzene. Cryoscopic molecular weight, formula weight 140.9 (obsd molality, obsd mol wt, association): 0.0600, 1256, 8.92; 0.0501, 1299, 9.22; 0.0282, 1357, 9.63; 0.0308, 1459, 10.3; 0.0260, 1475, 10.5; 0.0384, 1482, 10.5; 0.0314, 1519, 10.8.

Reactions of $Ga(CH_2CMe_3)_2Cl$ with Lithium and $C_{10}H_8$. The reagents $Li/C_{10}H_8$ and $2Li/C_{10}H_8$ were formed in THF

solution and then reacted with $Ga(CH_2CMe_3)_2Cl$ at $-78^\circ C$, as previously described. The solutions changed to bright yellow approximately 2–3 min after complete addition of $Ga(CH_2CMe_3)_2Cl$. After the solutions were warmed from $-78^\circ C$ to room temperature, the color changed to dark reddish-brown after 2–3 h at room temperature but no precipitate was observed. Both lithium reagents provided the analogous products ($[Ga(CH_2CMe_3)]_n$, $Ga(CH_2CMe_3)_3$, $C_{10}H_8$, and LiCl) as observed for the $Na/C_{10}H_8$ reaction. The characterization data for both gallium-containing products were identical to those described previously.

Reaction of $Ga(CH_2CMe_3)Cl_2$ with $2(Na/C_{10}H_8)$. A total of seven reduction reactions of $Ga(CH_2CMe_3)Cl_2$ with $Na/[C_{10}H_8]$ in a 1 to 2 mol ratio in THF solution were investigated. The procedures, quantities of reagents, and experimental observations were similar to those previously described. However, differences in detail were noted. When $Ga(CH_2CMe_3)Cl_2$ was added to the reducing agent at $-78^\circ C$, only a dark reddish-brown solution was observed initially and after complete addition. In contrast, when the reducing agent was added to $Ga(CH_2CMe_3)Cl_2$ at $-78^\circ C$ (reverse mode of addition), a bright yellow/orange solution was initially observed. As more reducing agent was added, the solution took a longer time to change to bright yellow/orange. After addition of approximately half of the reducing agent, the solution did not change to the bright yellow/orange but remained a dark reddish-brown. In both modes of addition, no precipitate was apparent at $-78^\circ C$. When the solution was slowly warmed, a precipitate formed when the temperature reached $-30^\circ C$ to $-20^\circ C$. The THF and volatile materials were isolated in a small weighed trap, as previously described. The nonvolatile materials were separated into insoluble and soluble components by pentane extractions. The nonvolatile, insoluble material (impure NaCl) was isolated as a light brown solid. The nonvolatile, soluble product were isolated as a reddish-brown vitreous solid. The percent yields of products were $[Ga(CH_2CMe_3)]_n$, 76–99%, NaCl, 98–109%, $C_{10}H_8$, 76–94%, and $Ga(CH_2CMe_3)_3$, 5–23%. The total recovered gallium from both products ranged from 90 to 100%. (See Results and Discussion). The decomposition temperature (melting point) of $[Ga(CH_2CMe_3)]_n$ was similar to that described previously. However, the analytical data for C and H were variable with only occasional samples consistent (within 0.4%) with calculated values. Similarly, hydrolyses of the reddish-brown solids with aqueous HCl provided variable amounts of H_2 (44–101%) and of neopentane (37–90%). These results suggest that the reddish-brown products were more impure than the product prepared by the reduction of $Ga(CH_2CMe_3)_2Cl$.

Reaction of $Ga(CH_2CMe_3)Cl_2$ with $2(Li/C_{10}H_8)$. In a typical experiment the dark green lithium naphthalenide solution (0.0566 g, 8.15 mmol Li; 1.05 g, 8.16 mmol $C_{10}H_8$) in 50 mL of THF was allowed to react with $Ga(CH_2CMe_3)Cl_2$ (0.859 g, 4.06 mmol) at $-78^\circ C$, as previously described. A dark reddish-brown solution was observed after complete addition at $-78^\circ C$ and remained dark reddish-brown after slowly warming to ambient temperature. No precipitate was observed. The solution was stirred an additional 18 h, and then the THF and volatile materials were removed by vacuum distillation. The remaining materials were subjected to dynamic vacuum for 24 h. The volatile materials (1.56 g) were collected in a small weighed trap and the components identified by 1H NMR spectroscopy as $Ga(CH_2CMe_3)_3$ (0.0690 g, 0.244 mmol, 6.0% yield based on $Ga(CH_2CMe_3)Cl_2$), $C_{10}H_8$ (0.920 g, 7.18 mmol, 88.0% recovered based on the initial amount of $C_{10}H_8$), and THF. The nonvolatile material was separated into soluble and insoluble components by pentane extractions. The insoluble light brown product, LiCl (0.306 g, 7.22 mmol, 88.9% yield based on $Ga(CH_2CMe_3)Cl_2$), had positive analyses for lithium and chloride ions. The nonvolatile, soluble product was isolated as a reddish-brown, vitreous solid and identified as $[Ga(CH_2CMe_3)]_n$ (0.491 g, 3.49 mmol, 86.0% based on $Ga(CH_2CMe_3)Cl_2$). The total amount of gallium recovered was 3.73 mmol, 91.9% based on $Ga(CH_2CMe_3)Cl_2$.

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[Ga(CH₂CMe₃)₂]₂. Mp 60.0–80.0 °C dec. ¹H NMR (C₆D₆, δ): 1.78 (s), 1.74 (s), 1.62 (s), 1.55 (s), 1.42 (s), 1.40 (s), 1.36 (s), 1.35 (s), 1.34 (s), 1.33 (s), 1.31 (s), 1.27 (s), 1.25 (s), 1.22 (s), 1.18 (s), 1.17 (s), 1.15 (s), 1.12 (s), 1.09 (s), 1.07 (s), 1.03 (s) (all lines appear to be part of a complex spectrum). Anal. Calcd C, 42.63; H, 7.87. Found: C, 42.44; H, 7.50. Hydrolysis: 0.143 g, 1.02 mmol produced 0.892 mmol (88.1%) H₂. Cryoscopic molecular weight, benzene solution, formula weight 140.9 (obsd molality, obsd mol wt, association): 0.0384, 1482, 10.5; 0.0314, 1519, 10.8; 0.0219, 1564, 11.1. Solubility: soluble in THF, pentane, and benzene.

Reaction of Ga(CH₂CMe₃)₂Cl with Na/C₁₀H₈ at -78 °C Followed by the Addition of Anhydrous HCl. Identification of Nonvolatile Products. The reagents, Ga(CH₂CMe₃)₂Cl (1.1 mmol), Na (1.1 mmol), and C₁₀H₈ (1.1 mmol) were allowed to react at -78 °C in 50 mL of THF to form the bright yellow solution, as previously described. Then, 1.18 mmol of anhydrous HCl was added. The solution became colorless. No noncondensable gas was formed as indicated by pressure measurements at -196 °C. The volatile components were removed by vacuum distillation and the resulting viscous liquid was subjected to dynamic vacuum for 18 h. The resulting solid was then dissolved in 25 mL of pentane and the insoluble portion was repeatedly washed. The pentane-insoluble product, NaCl (0.058 g, 0.99 mmol), was isolated in 92% yield based on Ga(CH₂CMe₃)₂Cl. A slightly impure sample of Ga(CH₂CMe₃)₂Cl (0.220 g, 0.889 mmol) was isolated in 82.3% yield based on the initial amount of Ga(CH₂CMe₃)₂Cl.

Ga(CH₂CMe₃)₂Cl as Reaction Product. Mp 59.5–63.5 °C (lit.⁶ 70.0–71.5 °C). ¹H NMR (C₆H₆, δ): 1.33 (s, 2H, CH₂) and 1.13 (s, 10H, CMe₃) (lit.⁶ 1.31 (CH₂), 1.10 (CMe₃)).

Reaction of Ga(CH₂CMe₃)₂Cl with Na/C₁₀H₈ at -78 °C Followed by Addition of Anhydrous HCl. Identification of Volatile Components. The reagents, Ga(CH₂CMe₃)₂Cl (1.0 mmol), Na (1.0 mmol), and C₁₀H₈ (1.1 mmol), were allowed to react at -78 °C in 50 mL of THF to form the bright yellow solution. Then anhydrous HCl (1.04 mmol) was vacuum distilled onto the resulting yellow solution. A colorless solution formed after the reaction mixture was warmed to room temperature. The volatile components were removed by vacuum distillation at 0 °C to yield a colorless, sticky solid. The flask was then fitted with an 85° bent elbow connected to a 100-mL side-arm flask. The flask containing the sticky solid was heated to approximately 50 °C and the naphthalene and hydronaphthalene derivatives were vacuum sublimed into the 100-mL side-arm flask which was cooled to -196 °C. The flask containing the nonvolatile components was fitted with a medium frit filter connected to a 100-mL side arm flask. Pentane (25 mL) was vacuum distilled into the flask containing the sticky solid and the nonvolatile, pentane-soluble and -insoluble products were isolated. The insoluble product was identified as NaCl (0.043 g, 0.74 mmol, 71% yield based on Na) and the pentane-soluble product was identified as Ga(CH₂CMe₃)₂Cl⁶ (0.130 g, 0.525 mmol, 50.2% yield based on the initial amount of gallium present). The volatile components isolated by sublimation at 50 °C consisted of naphthalene, dihydronaphthalene, and trace quantities of THF, as identified by ¹H NMR spectroscopy. ¹H NMR (CDCl₃, δ): 7.79 and 7.41 (m, 76H, C₁₀H₈), 7.01 (m, 17H, aromatic C₁₀H₁₀), 6.39 (m, 3H, C₁₀H₁₀), 5.95 (m, 5H, C₁₀H₁₀), 4.06 (m, 1.5H, THF), 3.35 (s, minor impurity), 2.76 (m, C₁₀H₁₀), 2.26 (m, 5H, C₁₀H₁₀), 1.96 (m, 1.5H, THF), 1.08 (s, minor impurity).

Reaction of Ga(CH₂CMe₃)₂Cl with HCl/H₂O and with DCl/D₂O. A sealed tube was charged with 0.137 g of Ga(CH₂CMe₃)₂Cl (0.973 mmol) prepared from Ga(CH₂CMe₃)₂Cl and Na/C₁₀H₈, as previously described. The tube was evacuated and approximately 10 mL of dilute aqueous HCl was added to the Ga(CH₂CMe₃)₂Cl through the neck of the tube. Gas evolution was observed. The tube was placed in a 100 °C oil bath for 3 d after which time the noncondensable gas was measured. Hydrogen gas (0.828 mmol, 85.1% yield based on the oxidation of Ga⁺¹ to Ga⁺³) was collected by using a Toepler pump-gas buret assembly. The volatile, condensable gas was fractionated through two -78 °C traps, and 0.0565 g of neopentane (0.783 mmol, 80.5% yield based on Ga(CH₂CMe₃)₂Cl) was isolated. Ratio of H₂/CMe₄: 1.06.

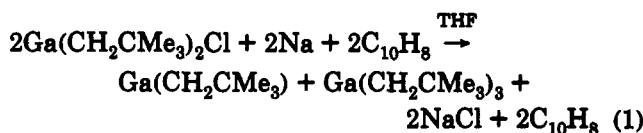
In a similar experiment, a 0.0759-g sample of Ga(CH₂CMe₃)₂Cl (0.539 mmol) prepared from Ga(CH₂CMe₃)₂Cl and Na/C₁₀H₈ was reacted with a dilute D₂O solution of DCl (~95 atom % D). After stirring for 8 d at 110 °C, 0.415 mmol of D₂ (77.0% yield) was collected. In addition, 0.444 mmol of Me₃CCH₂D was isolated as previously described. Ratio of D₂/Me₃CCH₂D: 1.07. Mass spectra of the noncondensable and condensable gas were recorded. **Noncondensable Gas.** Relative intensity (*m/e*) assignment: 4, 100.0, D₂; 3, 8.8, HD; 2, Trace, H₂. The sample is composed of 91.9% D₂ and 8.1% HD. **Condensable Gas.** Relative intensity (*m/e*) assignment: 58, 100, CMe₃CH₂D⁺; 57, 41.5, CMe₃⁺; 43, 32, CMeCH₂D⁺; 42, 42.6, CMe₂⁺. The sample corresponds to 93.5% CMe₃CH₂D and 6.5% CMe₄.

Reaction of Ga(CH₂CMe₃)₂Cl with HgCl₂. In a typical experiment, a 100-mL Solv-Seal flask was charged with 0.435 g (3.09 mmol) of Ga(CH₂CMe₃)₂Cl prepared from Ga(CH₂CMe₃)₂Cl and Na/C₁₀H₈ and 0.820 g (3.02 mmol) of HgCl₂. The flask was evacuated and 50 mL of THF were vacuum distilled into the reaction flask. The reaction mixture was subjected to ultrasound for 2.5 h and the formation of a gray precipitate was noted. The solution was then stirred at ambient temperature for 5 d followed by an additional 2 d of stirring in a 80–90 °C oil bath. Beads of mercury metal were observed in the flask and the color of the solution changed from brown to nearly colorless. The THF was removed by vacuum distillation and a viscous, colorless liquid remained. A ¹H NMR spectrum of a benzene solution of the viscous liquid confirmed its identity as [Ga(CH₂CMe₃)₂Cl]₂·THF⁶ (0.788 g, 2.78 mmol, 91.9% yield based on HgCl₂). ¹H NMR (C₆H₆, δ): 3.49 (m, 4H, THF), 1.13 (s, 9H, CH₃), 1.01 (s, 2H, CH₂), 0.99 (m, 4H, THF) and 0.60 (s, trace impurity). Metallic mercury (0.0501, 2.50 mmol) was identified by its physical appearance and was isolated in 82.6% yield based on HgCl₂.

Reaction of Ga(CH₂CMe₃)₂Cl with I₂. A freshly prepared sample of Ga(CH₂CMe₃)₂Cl (0.222 g, 1.58 mmol) (prepared from Ga(CH₂CMe₃)₂Cl and Na/C₁₀H₈) was placed in a 100-mL Solv-Seal flask equipped with a low hold-up side-arm charged with 20 mL of a THF solution of I₂ (0.399 g, 1.57 mmol). The apparatus was evacuated and an additional 20 mL of THF was vacuum distilled into the flask containing the Ga(CH₂CMe₃)₂Cl. The reagents were combined; the I₂ color was discharged immediately and then the reaction mixture was stirred for 2 d at room temperature. The flask was then placed in a 60 °C oil bath for an additional 10 d. The resulting solution was slightly yellow. The THF was removed by vacuum distillation, and a gray viscous liquid remained. Pentane (30 mL) was vacuum distilled onto the gray material and the resulting solution was filtered through a fine glass frit. After removing the pentane, a colorless, sticky solid was obtained. The ¹H NMR spectrum of the product was identical to that of an authentic sample of Ga(CH₂CMe₃)₂Cl·THF. The product, Ga(CH₂CMe₃)₂Cl·THF (0.506 g, 1.27 mmol) was isolated in 80.9% yield based on I₂. ¹H NMR (C₆H₆, δ): 3.47 (m, 5.5 H, THF), 1.35 (s, 2.0 H, CH₂), 1.16 (s, 11.6 H, CH₃) and 0.99 (m, 6.0 H, THF). ¹H NMR (Ga(CH₂CMe₃)₂Cl·THF prepared from Ga(CH₂CMe₃)₂Cl⁶ and THF, C₆H₆): 3.48 (m, 4.3 H, THF), 1.36 (s, 2.0 H, CH₂), 1.18 (s, 9.6 H, CH₃), 1.04 (m, 4.8 H, THF).

Results and Discussion

The reaction between Ga(CH₂CMe₃)₂Cl and sodium or lithium naphthalenide in THF lead to the formation of neopentylgallium(I), trineopentylgallium(III), sodium (lithium) chloride, and naphthalene in nearly quantitative yields according to the following balanced equation.

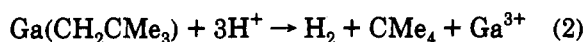


Gallium metal, an obvious reduction product, was not observed during any stage of the synthetic process. The

gallium(I) product $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ was isolated as a pentane-soluble, dark reddish-brown, vitreous solid (glass). All attempts to form crystals of $\text{Ga}(\text{CH}_2\text{CMe}_3)$ by recrystallization techniques failed. The gallium(III) product was isolated as a slightly volatile, colorless liquid at room temperature as is characteristic of $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$.⁶ The sodium chloride was separated as a light brown, pentane-insoluble solid and identified by X-ray powder diffraction data. The light brown color suggests that the material was impure NaCl. The most likely light brown impurity would be a form of neopentylgallium(I).

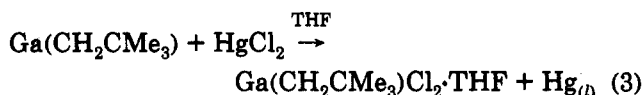
The new low oxidation state gallium compound $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ has been characterized by complete elemental analyses, hydrolysis by $\text{DCl}/\text{D}_2\text{O}$, oxidation with HgCl_2 and with I_2 , cryoscopic molecular weight studies in benzene solution, and NMR and IR spectroscopic data. The analytical data for C, H, and Ga are in excellent agreement with the simplest formula, $\text{GaC}_5\text{H}_{11}$ (within 0.3% by difference). The sum of the experimentally observed percentages of C, H, and Ga is 100.01%. Reproducible analytical data have been observed for multiple samples.

The reaction of $\text{Ga}(\text{CH}_2\text{CMe}_3)$ with aqueous hydrochloric acid provides support for the hypothesis that the reddish-brown solid is a gallium(I) compound with a σ -bonded neopentyl group.



Hydrolysis produced H_2 and CMe_4 in high yield (85.1 and 80.5%, respectively). The H_2/CMe_4 ratio of 1.06 strongly supports a formulation of one neopentyl group per gallium atom in the +1 oxidation state. Confirmation of oxidation-reduction during hydrolysis was achieved by reaction of $\text{Ga}(\text{CH}_2\text{CMe}_3)$ with $\text{DCl}/\text{D}_2\text{O}$ to form D_2 and monodeuterated neopentane ($\text{CMe}_3\text{CH}_2\text{D}$). The mass spectrum of the noncondensable gas indicated 91.9% D_2 and 8.1% HD. Similarly, the neopentane was 93.5% $\text{CMe}_3\text{CH}_2\text{D}$ and only 6.5% CMe_4 . These deuterated hydrolysis products rule out the possibility that the dark reddish-brown product is an organogallium(III) hydride. An organogallium(III) hydride with the simplest formula $\text{GaC}_5\text{H}_{11}$ would have hydrolyzed to form HD and CMe_3CHD_2 . Infrared bands suggestive of $\text{Ga}-\text{H}^{\delta}$ at either 2000 cm^{-1} (terminal) or $1200\text{--}1300\text{ cm}^{-1}$ (bridging) are also absent.

Conformation of the reddish-brown solid as neopentylgallium(I) was provided also by the characterization of products from oxidation-reduction reactions by using HgCl_2 and I_2 as oxidizing agents. Reaction of $\text{Ga}(\text{CH}_2\text{CMe}_3)$ with HgCl_2 in THF produced $\text{Ga}(\text{CH}_2\text{CMe}_3)\text{Cl}_2\cdot\text{THF}$ and elemental mercury in high yield according to the following equation.



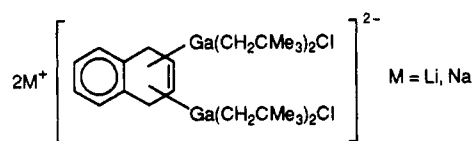
The ^1H NMR spectrum of the organogallium(III) product was identical to that for an authentic sample⁶ with the exception of a low-intensity resonance at 0.60 ppm. The unidentified resonance does not correspond to any known neopentylgallium(III) compound. Oxidation of $\text{Ga}(\text{CH}_2\text{CMe}_3)$ with I_2 in THF produced $\text{Ga}(\text{CH}_2\text{CMe}_3)\text{I}_2\cdot\text{THF}$ according to the following equation.



Again, the ^1H NMR spectrum of the product was identical with that for an authentic sample.

Cryoscopic molecular weight data in benzene solution suggest that neopentylgallium(I) exists as highly associated species. The average association values from observed molecular weight values ranged from 8.92 to 10.8. These data suggest that $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ most likely exists in solution as a mixture of cages or clusters with n varying from possibly 6 to 12. The suggestion of cages or clusters is supported by EPR data⁹ observed for the decomposition of the yellow intermediate and by the literature. The Zintl compounds KGa_3 ,¹⁰ $\text{Na}_7\text{Ga}_{13}$,¹¹ $\text{Na}_{22}\text{Ga}_{39}$,¹¹ RbGa_7 ,¹² and K_3Ga_{13} ¹³ have been shown to contain dodecahedral and icosahedral gallium cages or clusters. It is also significant that the closely related boron subhalides,¹⁴ B_4Br_4 , B_4Cl_4 , B_7Br_7 , B_8Cl_8 , B_9Cl_9 , B_9Br_9 and $\text{B}_{10}\text{Br}_{10}$, and $\text{B}_4(\text{t-Bu})_4$,¹⁵ exist as cages according to X-ray structural studies. These boron compounds have the same number of framework electrons for cage bonding as $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$. Another striking similarity between the boron subhalides¹⁴ and the proposed neopentylgallium(I) cages is their intense color. The lack of volatility and the ease of decomposition of $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ have prevented meaningful mass spectral data. The suggestion of gallium clusters with different degrees of association is also consistent with the complex (multiple closely spaced lines) ^1H NMR spectrum.

The reactions of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ with either $\text{Na}/\text{C}_{10}\text{H}_8$, $\text{Li}/\text{C}_{10}\text{H}_8$, or $2\text{Li}/\text{C}_{10}\text{H}_8$ in THF solution proceed through the formation of a yellow intermediate, which in turn decomposes to form neopentylgallium(I). The yellow intermediate has been identified as a mixture of 1,2- and 1,4-dihydronaphthalene-organogallium(III) species. The



absence of a significant amount of precipitate suggests the lack of formation of the simple alkali metal halide, presumably due to the coordination of the chloride ion by a gallium(III) moiety. The ^1H NMR spectrum of the yellow intermediate at $-40\text{ }^\circ\text{C}$ is consistent with the presence of the dihydronaphthalene-organogallium(III) species. As the solution was warmed to room temperature, the intensities of the lines associated with the dihydronaphthalene species decreased and finally disappeared. Reaction of the yellow intermediate with a stoichiometric quantity of anhydrous HCl at $-78\text{ }^\circ\text{C}$ resulted in the isolation of a mixture of naphthalene, 1,4-dihydronaphthalene, and 1,2-dihydronaphthalene as identified by ^1H

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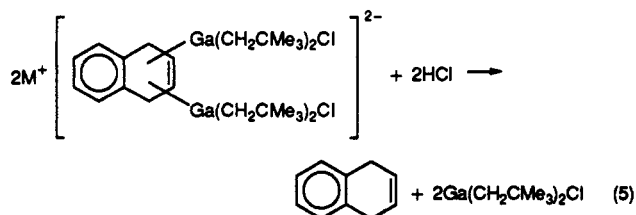
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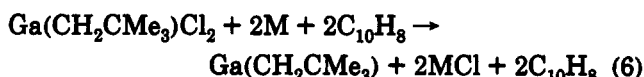
NMR spectroscopy. Bisneopentylgallium(III) chloride was



also isolated from the reactions of the yellow intermediate with anhydrous HCl. The gallium(III) product was identified as $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ by ^1H NMR and IR spectroscopic data, melting point, and hydrolysis data. The hydrolysis of the yellow intermediate with aqueous HCl further confirmed the presence of a gallium(III) rather than a gallium(I) species. No noncondensable gas (H_2) was formed. Thus, no low oxidation state gallium species could have been present. The identification of the yellow intermediate as a gallium(III) species suggests that the alkali metal naphthalenide acts as a nucleophile toward bisneopentylgallium(III) chloride to form the dihydronaphthalene intermediate. Related observations have been made in silicon chemistry.¹⁶ Reduction from gallium(III) to gallium(I) occurs when the yellow intermediate decomposes upon warming. It is interesting to note that the use of lithium naphthalenide reagents requires a higher temperature to decompose the yellow intermediate (room temperature) than for the sodium reagent (0–10 °C). The higher lattice energy of NaCl fosters the dissociation of the chloride ions from the dihydronaphthalene intermediate and, in turn, apparently enhances reduction. The decomposition of the yellow intermediate apparently occurs by a radical process. Appropriate EPR data will be presented in a later communication.⁹

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Reduction of gallium(III) to gallium(I) can also be achieved by reacting $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ with 2 mol of Na/ C_{10}H_8 or Li/ C_{10}H_8 in THF. The idealized balanced equation for the reaction is given by the following equation.



This reaction, according to the balanced equation, would appear to have a higher percent conversion of gallium(III) to gallium(I) as $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ should not be formed. However, $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ has been observed among the products. When lithium was used, 6% of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ was converted to $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ and the reddish-brown product had acceptable analytical data for C and H. When reducing agent was sodium, the yield of $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ varied from 6 to 23% and the reddish-brown product had poor analytical data. In addition, acid (HCl) hydrolysis of the reddish-brown solid from sodium reductions produced variable amounts of H_2 and typically low yields of neopentane. Thus, reduction of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ with sodium/naphthalene does not appear to be a useful route to pure samples of neopentylgallium(I).

The reduction of $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ by using lithium or sodium naphthalenide in THF to form $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ as a reddish-brown solid has been observed. These products are analogous to those formed by the reduction of $\text{Al}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ with potassium metal¹⁷ in hexane at 60 °C. The low oxidation state aluminum product was also a nonvolatile brown solid. Molecular weight studies by the isopiestic method in cyclopentane suggested a tetramer, $\text{Al}_4(\text{CH}_2\text{CMe}_3)_4$. Thus, organometallic compounds of aluminum and gallium have been observed as clusters, a series of observations which are consistent with boron chemistry.

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