Facile Reactions for the Preparation of 
[(Me₃CCH₂)₂GaNH₂]₂ and of GaN

O. T. Beachley, Jr., John C. Pazik and Matthew J. Noble

Department of Chemistry
State University of New York at Buffalo
Natural Sciences Complex
Buffalo, NY 14260-3000

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

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Four reactions of neopentylgallium compounds with ammonia have been investigated. The dihydronaphthalene derivative C₁₀H₈[Ga(CH₂CM₃)₂]₂·2NaCl has been observed to react with anhydrous ammonia at low temperature (−78°C) to form (Me₃CCH₂)₂GaNH₂, dihydronaphthalene (C₁₀H₉) and NaCl whereas the related elimination reaction between Ga(CH₂CM₃)₃ and NH₃ occurred at 140 – 150 °C. The new compound (Me₃CCH₂)₂GaNH₂ also was prepared by reacting Ga(CH₂CM₃)₂Cl with sodium in liquid ammonia at −70 °C. Bisneopentylgallium amide was fully characterized and exists as a dimer at room temperature in benzene solution. Neopentylgallium(I) [Ga(CH₂CM₃)]ₙ has been observed also to react with NH₃ at 460 – 480 °C to form GaN(s), CMe₄ and H₂.
Facile Reactions for the Preparation of \( [(\text{Me}_3\text{CCH}_2)_2\text{GaNH}_2)_2 \]

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O. T. Beachley, Jr.*, John C. Pazik and Matthew J. Noble
Department of Chemistry
State University of New York at Buffalo
Buffalo, NY 14260-3000

Abstract

Four reactions of neopentylgallium compounds with ammonia have been investigated. The dihydronapthalene derivative \(\text{C}_{10}\text{H}_8\{\text{Ga(CH}_2\text{CMe}_3)\}_2\cdot 2\text{NaCl}\) has been observed to react with anhydrous ammonia at low temperature (\(-78^\circ\text{C}\)) to form \((\text{Me}_3\text{CCH}_2)_2\text{GaNH}_2\), dihydronaphthalene \((\text{C}_{10}\text{H}_{10})\) and \(\text{NaCl}\) whereas the related elimination reaction between \(\text{Ga(CH}_2\text{CMe}_3)_2\) and \(\text{NH}_3\) occurred at 140 - 150 °C. The new compound \((\text{Me}_3\text{CCH}_2)_2\text{GaNH}_2\) also was prepared by reacting \(\text{Ga(CH}_2\text{CMe}_3)_2\text{Cl}\) with sodium in liquid ammonia at \(-70^\circ\text{C}\). Bisneopentylgallium amide was fully characterized and exists as a dimer at room temperature in benzene solution. Neopentylgallium(I) \([\text{Ga(CH}_2\text{CMe}_3)]_n\) has been observed also to react with \(\text{NH}_3\) at 460 - 480 °C to form \(\text{GaN}_{0.9}\), \(\text{CMe}_4\) and \(\text{H}_2\).
Low oxidation state gallium clusters\(^1\) \([\text{Ga(CH}_2\text{CMe}_3]\)\(_n\) \((n = 6 - 12)\) have been prepared by the reduction of dineopentylgallium chloride by using either sodium or lithium with naphthalene in THF solution. When the reagents were combined at -78 °C, a yellow dihydronaphthalene gallium(III) derivative \(\text{C}_{10}\text{H}_8[\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)]\(_2\)\(\cdot\)\(2\text{MCl M = Li, Na}\) was formed. Upon warming to room temperature, this intermediate was converted to gallium(I) clusters \((\text{GaR})_n\) \((n = 6 - 12)\), \(\text{GaR}_3\) and \(\text{MCl}\). We have investigated the reaction of this yellow dihydronaphthalene gallium(III) intermediate \(\text{C}_{10}\text{H}_8[\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)]\(_2\)\(\cdot\)\(2\text{NaCl}\) with anhydrous ammonia because of our interest in the reactions of gallium compounds which have two different organic substituents.\(^2\)\(^3\)\(^4\) The reactivity of this dihydronaphthalene derivative with ammonia was compared, in turn, with that for \(\text{Ga(CH}_2\text{CMe}_3]\)\(_3\). Two additional reactions of organogallium compounds are also reported: (1) the reaction of the low oxidation state gallium cluster \([\text{Ga(CH}_2\text{CMe}_3]\)\(_n\) with ammonia and (2) the reaction of \(\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)\(\cdot\)\(2\text{Cl}\) with sodium in liquid ammonia.

The yellow gallium(III) derivative of dihydronaphthalene \(\text{C}_{10}\text{H}_8[\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)]\(_2\)\(\cdot\)\(2\text{NaCl}\) reacts with anhydrous ammonia at -78 °C to form \((\text{Me}_3\text{CCH}_2)\text{GaNH}_2\), \(\text{C}_{10}\text{H}_{10}\) and \(\text{NaCl}\) in high yields (Eq 1). Hydrogen was not formed. Initially, the reaction mixture had

\[
\text{C}_{10}\text{H}_8[\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)]\(_2\)\(\cdot\)\(2\text{MCl} + 2\text{NH}_3 \rightarrow 2(\text{Me}_3\text{CCH}_2)\text{GaNH}_2 + \text{C}_{10}\text{H}_{10}\) (1)
\[+ 2\text{NaCl}\]

an intense golden-yellow color, which would be indicative of the dihydronaphthalene intermediate as an ammonia adduct. As the reaction mixture was stirred for 18 h at -78 °C, the yellow color disappeared and a colorless solution and a colorless precipitate (NaCl) formed. The solution never became brown, a color which would be indicative of the presence of the gallium(I) compound\(^1\) \([\text{Ga(CH}_2\text{CMe}_3]\)\(_n\), a product from the decomposition of \(\text{C}_{10}\text{H}_8[\text{Ga(CH}_2\text{CMe}_3]\)\(_2\)]\(_2\). Filtration of the final product mixture and removal of the solvent led to the isolation and subsequent identification of \((\text{Me}_3\text{CCH}_2)\text{GaNH}_2\), \(\text{C}_{10}\text{H}_{10}\).
and NaCl. All observations confirm the occurrence of a very facile elimination reaction between the dihydronaphthalene gallium(III) intermediate and ammonia and indicate the absence of an oxidation-reduction reaction. In comparison the elimination reaction between Ga(CH₂CMe₃)₃ and ammonia required heating at 140-150 °C for 4 days in a sealed tube to effect the formation of (Me₃CCH₂)₂GaNH₂ and CMe₄ (Eq 2) in nearly quantitative yields.

\[
\text{Ga(CH₂CMe₃)₃} + \text{NH₃} \rightarrow (\text{Me₃CCH₂})₂\text{GaNH₂} + \text{CMe₄}
\]  

(2)

Thus, this elimination reaction occurs at ~200 °C above the temperature needed for the reaction between the yellow dihydronaphthalene intermediate¹ and ammonia. The latter is known to decompose to Ga(CH₂CMe₃)₃, [Ga(CH₂CMe₃)]ₙ and C₁₀H₈ but (Me₃CCH₂)₂GaNH₂ cannot have been formed by way of the initial decomposition of C₁₀H₈[Ga(CH₂CMe₃)₂]₂ and the subsequent elimination reaction of Ga(CH₂CMe₃)₃ with ammonia.

Neopentylgallium(I) [Ga(CH₂CMe₃)]ₙ reacted with anhydrous ammonia in a sealed-tube but only at temperatures in the range of 460 - 480 °C. After 24 h the products were separated and identified as CMe₄, H₂ and GaNₙ with yields of 86, 70 and 88%, respectively, as based on Eq 3. Neopentane was identified by its characteristic ¹H NMR

\[
\frac{1}{n} [\text{Ga(CH₂CMe₃)}]_n + \text{NH₃} \rightarrow \text{GaNₙ} + \text{CMe₄} + \text{H₂}
\]  

(3)

spectrum whereas H₂ was identified by its typical properties in the vacuum line. The shiny black solid remaining in the tube was identified as GaN (hexagonal) by its X-ray powder pattern and ESCA spectrum. The ESCA spectrum confirmed the presence of gallium, nitrogen, carbon and oxygen. However, an elemental analysis of the shiny black solid revealed very low carbon contamination, 1.24 % C and 0.69 % H. It is of interest to note that when GaNₙ is prepared from GaMe₃ and NH₃, temperatures in the range of ~1000 °C
are needed. Thus, the lower temperatures used for the reaction of the gallium(I) compound with ammonia might reflect a significant relationship between the low oxidation state and intermediates in the pathway for the formation of group 13 - 15 materials.

The reaction between Ga(CH₃CMe₃)₂Cl and sodium in liquid ammonia also was studied. Addition of a stoichiometric quantity of Ga(CH₃CMe₃)₂Cl dissolved in ammonia at -70 °C to the deep blue solution formed between sodium and liquid ammonia resulted in the formation of a colorless solution and a heavy colorless precipitate. Subsequent use of the vacuum line revealed the formation of slightly less than one half mol of hydrogen gas per mol of Ga(CH₃CMe₃)₂Cl. Thus, the following balanced equation (Eq 4) describes the

$$\text{Ga(CH₃CMe₃)₂Cl} + \text{Na} + \text{NH₃} \rightarrow \text{(Me₃CCH₂)₂GaNH₂ + 1/2 H₂ (4) + NaCl}$$

reaction.

The compound (Me₃CCH₂)₂GaNH₂ was fully characterized by its melting point, ¹H NMR and IR spectra, C and H analyses and a cryoscopic molecular weight study in benzene solution. All data are consistent with the presence of a dimer in solution and in the solid state with a melting point of 58.0 - 60.5 °C. The corresponding methyl derivative Me₂GaNH₂ exists as a trimer with a higher melting point (100-101.5 °C).

**Experimental Section**

All compounds described in this investigation were very sensitive to oxygen and moisture and were manipulated by using standard vacuum line techniques or under a purified argon atmosphere in a Vacuum Atmospheres drybox equipped with a Dry Train. All solvents were purified before use. Elemental analyses were performed by E+R Microanalytical Laboratories, Corona, NY. Infrared spectra of samples as Nujol mulls between CsI plates were recorded by means of a Perkin Elmer 683 spectrometer. The ¹H
NMR spectra were recorded at 300 MHz by using a Varian Gemini 300 spectrometer. All samples for NMR spectra were contained in flame-sealed NMR tubes. Chemical shifts are reported in $\delta$ (ppm) and are referenced to tetramethylsilane (TMS) as $\delta = 0.00$ ppm and benzene as $\delta = 7.15$ ppm. X-ray photoelectron spectra were recorded by using a Perkin Elmer Physical Electronics (PHI) Model 5100 ESCA spectrometer with a Mg $K_{\alpha1,2}$ X-ray source (1253.6 eV) with a 180 degree hemispherical detector. The spectrometer was calibrated to the Ag$_{3d5/2}$ peak at 367.9 eV. Spectra were collected at an angle of 45°. The identity of elements at the surface were evaluated qualitatively with low resolution spectra (89.45 eV) whereas high resolution spectra (35.75 eV) were used to establish the binding energies and peak areas for quantitative analysis. X-ray powder diffraction data were recorded by using a Siemens D-500 X-ray diffractometer with Cu $K_{\alpha}$ radiation. Melting points were observed in a Mel-Temp by using flame-sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.7

**Reaction of C$_{10}$H$_{8}$Ga(CH$_2$CMe$_3$)$_2$•2NaCl with Anhydrous NH$_3$.** The yellow gallium(III) dihydronaphthalene derivative C$_{10}$H$_{8}$Ga(CH$_2$CMe$_3$)$_2$•2NaCl was prepared in THF at -78 °C as previously described$^1$ by using sodium metal (0.067 g, 2.9 mmol), naphthalene (0.380 g, 2.97 mmol) and Ga(CH$_2$CMe$_3$)$_2$Cl (0.721 g, 2.91 mmol). Then, excess dry NH$_3$ was added to the flask by vacuum distillation. Initially, the solution had an intense yellow color. As the solution was stirred at -78 °C for 18 h, the color disappeared and a colorless solution and a colorless precipitate formed. Pressure measurements at -196 °C on the vacuum line confirmed the absence of any noncondensable gas. The THF and excess NH$_3$ were removed by vacuum distillation. The remaining reaction products were subjected to dynamic vacuum for 40 h. The products which were volatile at room temperature were collected in a -196 °C trap and identified by $^1$H NMR spectroscopy as dihydronaphthalene with very small amounts of naphthalene and other unidentified impurities. Extraction of the nonvolatile products with pentane through a
glass frit separated NaCl (0.168 g, 2.88 mmol, 99.0 % yield based on Na) from a pentane soluble colorless solid. Sublimation of this solid at 55 °C led to the isolation and identification of (Me₃CCH₂)₂GaNH₂ (0.344 g, 1.51 mmol, 52 % yield based on Na).

(Me₃CCH₂)₂GaNH₂. Mp: 51.8 - 54.0 °C. ¹H NMR (C₆D₆): δ 1.10 (s, 9.3H, -CH₃), 0.63 (s, 2.2H, -CH₂-), 0.34 (s, br, 1.0H, -NH₂). IR (Nujol mull, cm⁻¹): 3870 (vw), 3400(m), 3325 (m), 3295 (vw), 3205 (w, br), 2735 (w), 2705 (m), 2400 (vw), 2370 (vw), 2280 (vw), 2270 (vw), 2100 (vw), 2010 (vw), 1982 (vw), 1650 (w), 1565 (w), 1355 (s), 1230 (s), 1133 (m), 1099 (s), 1013 (m), 997 (s), 930 (m), 908 (w), 846 (m), 800 (s), 743 (s), 700 (s), 628 (s), 590 (m), 574 (m), 520 (w), 455 (sh), 435 (vs), 382 (m), 328 (w), 288 (m), 245 (w).

Reaction of Ga(CH₂CMe₃)₃ with NH₃ at 140 - 150 °C. A break-seal tube was charged with Ga(CH₂CMe₃)₃ (1.42 g, 5.02 mmol) and purified NH₃ (5.03 mmol) and then sealed by fusion. The tube was heated at 140 - 150 °C for 4 d in a tube furnace and then opened. Noncondensable gas (-196 °C) was absent. The volatile products were separated, weighed (0.384 g) and the neopentane was identified by ¹H NMR spectroscopy. The colorless solid remaining in the tube was sublimed at 60 - 80 °C and identified as (Me₃CCH₂)₂GaNH₂ (0.996 g, 4.37 mmol, 87.3 % yield based on Ga(CH₂CMe₃)₃).

(Me₃CCH₂)₂GaNH₂. Mp: 58.8 - 60.8 °C. Cryoscopic molecular weight, benzene solution, formula weight 228.03 (observed molality, observed mol wt, association): 0.0796, 490, 2.15; 0.0562, 477, 2.09; 0.0284, 499, 2.19. The ¹H NMR and IR spectra were identical to that described above.

Reaction of [Ga(CH₂CMe₃)]₉ with Ammonia. A break-seal tube was charged with 0.440 g of [Ga(CH₂CMe₃)]₉ (3.13 mmol) and then 3.44 mmol of NH₃ was added by vacuum distillation. The tube was sealed by fusion and heated for 1 d at 460 - 480 °C. As reaction occurred, the contents of the tube changed from dark reddish brown to light gray, to yellow gray and finally to shiny black. The tube was cooled to -196 °C, opened and the noncondensible gas was transferred and measured by using a Toepler
pump-gas burette assembly (2.20 mmol, 70.3 % based on Eq 3). The volatile, condensable material (0.195 g) was transferred by vacuum distillation to a small weighed trap. The $^1$H NMR spectrum of these volatile compounds in C$_6$D$_6$ identified neopentane (CMe$_4$, δ 0.99, 86 % yield based on Eq 3). The nonvolatile, shiny black solid was scraped out of the reaction tube in the dry box, ground into a fine powder and washed with 50 mL of pentane. This crystalline phase was identified as GaN (0.232 g, 2.77 mmol, 88.5 % based on Eq 3). GaN. X-ray powder diffraction (d spacings in Å): 2.76, 2.58, 2.44, 1.89, 1.60, 1.46, 1.37 (Lit.$^8$ for hexagonal GaN: 2.76, 2.59, 2.43, 1.88, 1.59, 1.46, 1.38). ESCA (Binding energy, eV; corrected to C$_1$: Ga$_{3d3/2}$ 20.3, Ga$_{2p3/2}$ 1119.5, N$_{1s}$ 398.3, C$_{1s}$ 285.0, O$_{1s}$ 531.7. (Lit.$^9$ for hexagonal GaN: Ga$_{3d3/2}$ 19.8, Ga$_{2p3/2}$ 1124.1, N$_{1s}$ 397.0, C$_{1s}$ 285.0, O$_{1s}$ 531.9). Surface ratio from ESCA (Ga:N): 1.32:1.00. Anal. for GaN: Found: C, 1.24; H, 0.69.

Reactor of Ga(CH$_2$CMe$_3$)$_2$Cl with Sodium in Liquid Ammonia. A Solv-seal flask was charged with 0.027 g of Na (1.2 mmol) and then connected with an 80° elbow to another flask which contained 0.290 g of Ga(CH$_2$CMe$_3$)$_2$Cl (1.17 mmol). Then liquid ammonia (25 mL) which had been previously dried by stirring over sodium at -70 °C was vacuum distilled onto the fresh sodium metal and stirred for 0.5 h to form a deep blue solution. After a small amount of ammonia was distilled onto the Ga(CH$_2$CMe$_3$)$_2$Cl to form a solution, the reagents were combined. The dark blue solution immediately turned light blue. More ammonia was distilled back into the flask which originally contained the Ga(CH$_2$CMe$_3$)$_2$Cl in order to ensure the quantitative transfer of the reagent. The final solution was colorless and contained a colorless precipitate. After the mixture was stirred for 1 h at -70 °C, the noncondensable gas was measured at -196 °C with a Toeppler pump - gas burette assembly (0.458 mmol H$_2$). The ammonia was removed and the products were extracted with pentane to separate NaCl (0.068 g, 1.2 mmol, 100 % yield) from (Me$_3$CCH$_2$)$_2$GaNH$_2$ which was identified by its melting point, $^1$H NMR and IR spectra and partial elemental analysis. (Me$_3$CCH$_2$)$_2$GaNH$_2$. Mp: 58.0 - 60.5 °C. Anal.
Calcd. for C_{10}H_{24}GaN: C, 52.56; H, 10.61. Found: C, 52.83; H 10.85. The $^1$H NMR and IR spectra were identical to that described above.

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References


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