Notes

Facile Reactions for the Preparation of $[(Me_3CCH_2)_2GaNH_2]_2$ and of GaN

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Summary: Four reactions of neopentylgallium compounds with ammonia have been investigated. The dihydronaphthalene derivative $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2NaCl$ has been observed to react with anhydrous ammonia at low temperature (−78 °C) to form $(Me_3CCH_2)_2GaNH_2$, dihydronaphthalene ($C_{10}H_{10}$), and NaCl, whereas the related elimination reaction between $Ga(CH_2CMe_3)_3$ and NH_3 occurred at 140−150 °C. The new compound $(Me_3CCH_2)_2GaNH_2$ was also prepared by reacting $Ga(CH_2CMe_3)_2Cl$ with sodium in liquid ammonia at −70 °C. Bis(neopentyl)gallium amide was fully characterized and exists as a dimer at room temperature in benzene solution. Neopentylgallium(I) $[Ga(CH_2CMe_3)]_n$ has been observed also to react with NH_3 at 460−480 °C to form GaN(s), CMe_4, and H_2.

Low oxidation state gallium clusters[1] $[Ga(CH_2CMe_3)]_n$ ($n = 6-12$) have been prepared by the reduction of bis(neopentyl)gallium 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 $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2MCl$ (M = Li, Na) was formed. Upon warming to room temperature, this intermediate was converted to gallium(I) clusters $(GaR)_n$ ($n = 6-12$), GaR_3, and MCl. We have investigated the reaction of this yellow dihydronaphthalene gallium(III) intermediate $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2NaCl$ with anhydrous ammonia because of our interest in the reactions of gallium compounds with two different organic substituents.[2−4] The reactivity of this dihydronaphthalene derivative with ammonia was compared, in turn, with that for $Ga(CH_2CMe_3)_3$. Two additional reactions of organogallium compounds are also reported: (1) the reaction of the low oxidation state gallium cluster $[Ga(CH_2CMe_3)]_n$ with ammonia and (2) the reaction of $Ga(CH_2CMe_3)_2Cl$ with sodium in liquid ammonia.

The yellow gallium(III) derivative of dihydronaphthalene $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2NaCl$ reacts with anhydrous ammonia at −78 °C to form $(Me_3CCH_2)_2GaNH_2$, $C_{10}H_{10}$, and NaCl in high yields (eq 1).

$$C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2NaCl + 2NH_3 \rightarrow 2(Me_3CCH_2)_2GaNH_2 + C_{10}H_{10} + 2NaCl \quad (1)$$

Hydrogen was not formed. Initially, the reaction mixture had 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] $[Ga(CH_2CMe_3)]_n$, a product from the decomposition of $C_{10}H_8[Ga(CH_2CMe_3)_2]_2$. Filtration of the final product mixture and removal of the solvent led to the isolation and subsequent identification of $(Me_3CCH_2)_2GaNH_2$, $C_{10}H_{10}$, 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 $Ga(CH_2CMe_3)_3$ and ammonia required heating at 140−150 °C for 4 days in a sealed tube to effect the formation of $(Me_3CCH_2)_2GaNH_2$ and CMe_4 (eq 2) in nearly quantitative yields. Thus,

$$Ga(CH_2CMe_3)_3 + NH_3 \rightarrow (Me_3CCH_2)_2GaNH_2 + CMe_4 \quad (2)$$

this elimination reaction occurs at ∼200 °C above the temperature needed for the reaction between the yellow dihydronaphthalene intermediate[1] and ammonia. The latter is known to decompose to $Ga(CH_2CMe_3)_3$, $[Ga(CH_2CMe_3)]_n$, and $C_{10}H_8$, but $(Me_3CCH_2)_2GaNH_2$ cannot have been formed by way of the initial decomposition of $C_{10}H_8[Ga(CH_2CMe_3)_2]_2$ and the subsequent elimination reaction of $Ga(CH_2CMe_3)_3$ with ammonia.

Neopentylgallium(I) $[Ga(CH_2CMe_3)]_n$ 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 CMe_4, H_2, and GaN(s) in yields of 86%, 70% and 88%, respectively, based on eq 3. Neopentane was identified by its

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characteristic ^{1}H NMR spectrum, whereas H_2 was

$$^1/_n\ [Ga(CH_2CMe_3)]_n + NH_3 \rightarrow GaN(s) + CMe_4 + H_2 \quad (3)$$

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 GaN(s) is prepared from $GaMe_3$ and NH_3, temperatures in the range of ~1000 °C are needed.[5] 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 $Ga(CH_2CMe_3)_2Cl$ and sodium in liquid ammonia also was studied. Addition of a stoichiometric quantity of $Ga(CH_2CMe_3)_2Cl$ 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 0.5 mol of hydrogen gas per mole of $Ga(CH_2CMe_3)_2Cl$. Thus, the balanced equation shown in eq 4 describes the reaction.

$$Ga(CH_2CMe_3)_2Cl + Na + NH_3 \xrightarrow{\text{Liquid ammonia}} (Me_3CCH_2)_2GaNH_2 + {}^1/_2H_2 + NaCl \quad (4)$$

The compound $(Me_3CCH_2)_2GaNH_2$ was fully characterized by its melting point, ^{1}H 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[6] Me_2GaNH_2 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 ^{1}H 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 δ (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$\alpha_{1,2}$ X-ray source (1253.6 eV) with a 180° 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 the 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 Kα 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 $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot NaCl$ with Anhydrous NH_3. The yellow gallium(III) dihydronaphthalene derivative $C_{10}H_8[Ga(CH_2CMe_3)_2]_2\cdot 2NaCl$ 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 $Ga(CH_2CMe_3)_2Cl$ (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 $(Me_3CCH_2)_2GaNH_2$ (0.344 g, 1.51 mmol, 52% yield based on Na).

$(Me_3CCH_2)_2GaNH_2$. Mp: 51.8−54.0 °C. ^{1}H NMR (C_6D_6): δ 1.10 (s, 9.3H, $-CH_3$), 0.63 (s, 2.2H, $-CH_2-$), 0.34 (s, br, 1.0H, $-NH_2$). 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 $Ga(CH_2CMe_3)_3$ with NH_3 at 140−150 °C. A break-seal tube was charged with $Ga(CH_2CMe_3)_3$ (1.42 g, 5.02 mmol) and purified NH_3 (5.03 mmol) and then sealed by fusion. The tube was heated at 140−150 °C for 4 days 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 ^{1}H NMR spectroscopy. The colorless solid remaining in the tube was sublimed at 60−80 °C and identified as $(Me_3CCH_2)_2GaNH_2$ (0.996 g, 4.37 mmol, 87.3% yield based on $Ga(CH_2CMe_3)_3$.

$(Me_3CCH_2)_2GaNH_2$. 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 ^{1}H NMR and IR spectra were identical to those described above.

Reaction of $[Ga(CH_2CMe_3)]_n$ with Ammonia. A break-seal tube was charged with 0.440 g of $[Ga(CH_2CMe_3)]_n$ (3.13 mmol), and then 3.44 mmol of NH_3 was added by vacuum distillation. The tube was sealed by fusion and heated for 1 day at 460−480 °C. As the 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

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to −196 °C and opened, and the noncondenseable gas was transferred and measured by using a Toepler-pump−gas-buret 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_6D_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 drybox, 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_{1s}): $Ga_{3d3/2}$ 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. Found for GaN: C, 1.24; H, 0.69.

Reaction of $Ga(CH_2CMe_3)_2Cl$ 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 $Ga(CH_2CMe_3)_2Cl$ (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 $Ga(CH_2CMe_3)_2Cl$ 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 $Ga(CH_2CMe_3)_2Cl$ 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 Toepler-pump−gas-buret 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 $(Me_3CCH_2)_2GaNH_2$, which was identified by its melting point, ^{1}H NMR and IR spectra, and partial elemental analysis.

$(Me_3CCH_2)_2GaNH_2$. 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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