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Abstract

The dihydronaphthalene derivative $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ reacts at room temperature with NH_3, n-$PrNH_2$ and $PhNH_2$ in THF solution to form high yields of $[(PhMe_2CCH_2)_2GaNHR]_2$ (R = H, n-Pr and Ph), $C_{10}H_{10}$ and NaCl. In contrast, the elimination reactions between $Ga(CH_2CMe_2Ph)_3$ with these same amines to form $[(PhMe_2CCH_2)_2GaNHR]_2$ and $PhCMe_3$ require temperatures of 150 °C. The cyclopentadiene elimination reaction between $(PhMe_2CCH_2)_2Ga(C_5H_5)$ and aniline occurs at -10 °C and is the fastest of these three. An X-ray structural study of $[(PhMe_2CCH_2)_2GaNHPh]_2$ identified it as the trans isomer.

The hydrocarbon elimination reaction is of fundamental importance to group 13 - 15 chemistry.[1] In its simplest terms for nitrogen compounds, an amine adduct can be converted by an elimination reaction to an amide derivative, to an imide derivative and then

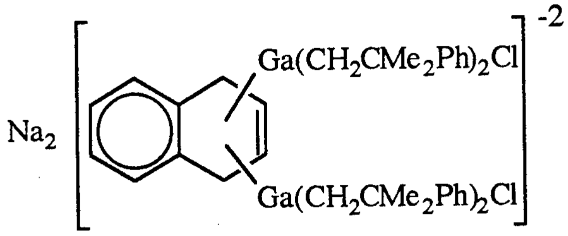
$$MR_3 + EH_3 \longrightarrow R_2MEH_2 + RH \quad (M = \text{group 13}, E = \text{group 15 element}) \qquad (1)$$

$$R_2MEH_2 \longrightarrow RMEH + RH \qquad (2)$$

$$RMEH \longrightarrow ME + RH \qquad (3)$$

to a nitride. Researchers have attempted to define the factors which determine the temperatures necessary to initiate these reactions but without definitive success. Each suceeding reaction in this sequence typically requires higher temperatures. Since these reactions provide a direct connection between group 13 -15 chemistry and the preparation of electronic materials such as GaN, InN, GaAs and InP, we have attempted to discover new hydrocarbon elimination reactions which occur at temperatures lower than those typically observed for the simple homoleptic organogallanes and group 15 bases ($ER_{3-n}H_n$, E = N, P, As; n = 1, 2, 3) because lower reaction temperatures minimize the possibility of decomposition reactions and, in turn, should lead to the formation of purer materials. This goal was realized with the discovery of the cyclopentadiene elimination reaction between $R_2Ga(C_5H_5)$ (R = Me[2], Et[3] and CH_2CMe_3[4]) and amines and phosphines. These reactions typically occur below room temperature or 100 to 200 °C lower than the temperatures needed for reactions of GaR_3 with the same bases. In this paper, elimination reactions of a diorganogallium derivative of dihydronaphthalene $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ are described.

The yellow dihydronaphthalene derivative[5, 6] $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$



reacts at room temperature with NH_3, n-$PrNH_2$ and $PhNH_2$ in THF solution to form $[(PhMe_2CCH_2)_2GaNHR]_2$ (R = H, n-Pr and Ph) as colorless crystalline solids in high yields, $C_{10}H_{10}$ and NaCl (eq 5). The time necessary for complete reaction was

$$2\ Ga(CH_2CMe_2Ph)_2Cl + C_{10}H_8 + 2\ Na \xrightarrow{THF} Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\} \quad (4)$$

$$Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\} + 2\ RNH_2 \longrightarrow [(PhMe_2CCH_2)_2GaNHR]_2 + C_{10}H_8 + 2\ NaCl \quad (5)$$

indicated by the change in color of the solution from bright golden yellow to colorless at completion in all three cases. Aniline reacted fastest and required approximately 6 h for complete reaction whereas n-propylamine, the strongest base, was slowest and took 5 days. Ammonia required 4 days. The reaction of the neopentyl derivative $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ with ammonia[7], which was described previously, required only 18 h to go to completion. Thus, the neophyl derivative reacts significantly slower than the neopentyl derivative.

Since the dihydronaphthalene derivative $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ decomposes at room temperature to form $Ga(CH_2CMe_2Ph)_3$, $[Ga(CH_2CMe_2Ph)]_n$ and NaCl, the question of whether $[(PhMe_2CCH_2)_2GaNHR]_2$ (R = H, n-Pr and Ph) is formed by an elimination reaction between the amine and $C_{10}H_8[Ga(CH_2CMe_2Ph)_2]_2$ or from some other gallium compounds which could be in solution must be addressed. All experimental data are consistent with the conclusion that $C_{10}H_8[Ga(CH_2CMe_2Ph)_2]_2$ is the reactive compound. The simple elimination reactions of $Ga(CH_2CMe_2Ph)_3$ with the amines were studied independently and found to require temperatures in the order of 150 °C to initiate elimination (eq 6). No reaction was observed at room temperature. Second, if

$$\mathrm{Ga(CH_2CMe_2Ph)_3 + RNH_2 \longrightarrow 1/2\ [(PhMe_2CCH_2)_2GaNHR]_2 + PhCMe_3} \quad (6)$$

$Ga(CH_2CMe_2Ph)_3$ had been formed from the decomposition of $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$, $[Ga(CH_2CMe_2Ph)]_n$, a reddish brown compound[5, 6], would also have been formed. However, the solution changed from lemon yellow to bright golden yellow to colorless and never was reddish brown. These observations suggest that $[Ga(CH_2CMe_2Ph)]_n$ was not present. Furthermore, the closely related low oxidation state gallium compound $[Ga(CH_2CMe_3)]_n$ has been reacted with ammonia[7] but temperatures around 450 °C were required to initiate a reaction. The products were GaN, H_2 and CMe_4. Third, the initial lemon yellow color is due to $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$. When the amine was added, a colorless precipitate (assumed to be NaCl) was formed and the color of the solution changed to bright golden yellow. These observations are consistent with the formation of an amine adduct, $C_{10}H_8[Ga(CH_2CMe_2Ph)_2]_2{\bullet}2$amine, the species which eventually is transformed into $[(PhMe_2CCH_2)_2GaNHR]_2$ and $C_{10}H_{10}$.

The dihydronaphthalene elimination reaction between $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ and aniline was compared directly with the cyclopentadiene elimination reaction between $(PhMe_2CCH_2)_2Ga(C_5H_5)$ and aniline. The latter was prepared *in situ* by a stoichiometric ligand redistribution reaction between $Ga(CH_2CMe_2Ph)_3$ and $Ga(C_5H_5)_3$.[4] After a stoichiometric amount of aniline was added to the solution of $(PhMe_2CCH_2)_2Ga(C_5H_5)$, the reaction mixture was maintained at -10 °C and after 24 h $[(PhMe_2CCH_2)_2GaNHPh]_2$, a slightly soluble solid, was isolated in higher than 70 % yield. Thus, the unsymmetrically substituted neophylgallium compounds $(PhMe_2CCH_2)_2GaC_5H_5$ and $[(PhMe_2CCH_2)_2Ga]_2(C_{10}H_8)$ both undergo elimination reactions with amines at room temperature (or below) to form $[(PhMe_2CCH_2)_2GaNHR]_n$, but the cyclopentadiene elimination reaction is faster.

Three gallium nitrogen compounds $[(PhMe_2CCH_2)_2GaNHR]_2$ (R = H, n-Pr[8] and Ph) were prepared and characterized in this study but only $[(PhMe_2CCH_2)_2GaNHPh]_2$ was characterized by an X-ray structural study. The products formed at room temperature have sharper and slightly higher melting points and are probably more pure than those formed in sealed tubes at 140 - 150 °C. Cryoscopic molecular weight data demonstrated the presence of dimers. ^1H NMR spectral data show the trans isomer being the predominant species in benzene solution. The cis isomer was observed in 7 % abundance but only in those benzene solutions of $[(PhMe_2CCH_2)_2GaNHPh]_2$ which had been prepared from the dihydronaphthalene derivative at room temperature. A benzene solution of $[(PhMe_2CCH_2)_2GaNHPh]_2$ which had been prepared in a sealed tube at 140 - 150 °C consisted of 100 % trans isomer. When the ^1H NMR spectrum of a CH_2Cl_2 solution of $[(PhMe_2CCH_2)_2Ga\text{-}NHPh]_2$ which had been prepared by the dihydronaphthalene elimination reaction was recorded, 16 % cis isomer was observed. Benzene solutions of $[(PhMe_2CCH_2)_2GaNH(n\text{-}Pr)]_2$ prepared by either route contained only the 100 % trans isomer.

An X-ray structural study of $[(PhMe_2CCH_2)_2GaNHPh]_2$ showed the crystal to be composed solely of the trans isomer. The crystallographic asymmetric unit consists of one-half of each of two crystallographically independent molecules, each of which lies about a center of symmetry. Molecule 1 lies about 0, 1/2, 0 (Wyckoff notation c), while molecule 2 lies about 1/2, 1/2, 1/2 (Wyckoff notation h).[9] All molecules are separated by normal van der Waals' distances and there are no anomalously short intermolecular contacts (Figure 1). The labeling scheme used for "Molecule 1" is shown in Figure 2. Note that the two crystallographically independent molecules are chemically equivalent and vary only in minor differences of orientation about Ga-C or Ga-N linkages. Bond distances and angles for both molecules are presented in Tables 1 and 2, respectively.

The presence of centers of symmetry necessitates that each Ga_2N_2 molecular core be strictly planar. Each four-membered ring is slightly distorted from its possible D_{2h} symmetry. Gallium-nitrogen bond lengths range from 2.037(3) Å to 2.082(4) Å. The cross-ring distances associated with the Ga_2N_2 molecular core are Ga(1)•••Ga(1A) = 3.008 Å and N(3)•••N(3A) = 2.815 Å (3.018Å and 2.780 Å, respectively, for the second molecule). These data may be compared with the corresponding data for the closely related compound $[(PhMe_2CCH_2)_2Ga\text{-}NH(n\text{-}Pr)]_2$.[8] The Ga-N distances were slightly shorter at 2.013(2) and 2.029(2) Å and the Ga_2N_2 molecular core was slightly more compact with the two Ga atoms separated by 2.938(1) Å and the two nitrogen atoms by 2.776(3) Å. The internal ring angle about Ga was 86.7(1)° whereas about N it was 93.3(1)°.

Two neophyl ligands are bound to each gallium(III) center with Ga(1)-C(00) = 1.967(6) Å and Ga(1)-C(10) = 1.982(5) Å and an interligand angle of C(00)-Ga(2)-C(10) = 123.5(2)° (Ga(2)-C(30) = 1.988(5) Å, Ga(2)-C(40) = 1.982(5) Å and C(30)-Ga(2)-C(40) = 122.2(2)° the second molecule). The Ga-C distances for $[(PhMe_2CCH_2)_2Ga\text{-}NH(n\text{-}Pr)]_2$[8] were 1.992(2) and 1.994(3) Å. The twist associated with the neophyl ligands for $[(PhMe_2CCH_2)_2GaNHPh]_2$ in relation to the molecular core is 89.3° as defined by the intercept of the planes C(00)-Ga(1)-C(10) and N(3)-Ga(1)-N(3A) (C(30)-Ga(2)-C(40)/N(4)-Ga(2)-N(4A) = 88.1° for the second molecule). The α-carbon atoms of the neophyl ligands possess a distorted tetrahedral environment with expanded Ga-C(α)-C(β) angles of 116.6(3) to 119.9(4) °

Primary phenyl amide ligands bridge the gallium(III) metal centers. The nitrogen atoms of these ligands possess a distorted tetrahedral environment (Table 2, Section b). The hydrogen atoms of the amine moieties were located and refined successfully yielding N-H distances of 0.89(6) Å and 0.81(5)Å, respectively, for H(3) and H(4). The N-H distance in $[(PhMe_2CCH_2)_2Ga\text{-}NH(n\text{-}Pr)]_2$ was 0.82(3) Å.[8] The phenyl ring is bonded to the nitrogen atom with N(3)-C(21) = 1.437(8)Å (N(4)-C(51) = 1.436(7)Å. The phenyl rings intercept the plane of the molecular core at 85.8° and 81.6° for molecules 1 and 2, respectively (intercept of the planes Ga(1)-N(3)-Ga(1A)/ C(21)-C(22)-C(23) and Ga(2)-N(4)-Ga(2A)/ C(51)-C(52)-C(53)). The phenyl rings are close to parallel and are perpendicular to the appropriate Ga•••Ga axis, an orientation resulting from the arrangement of the neophyl ligands about the molecular core.

Experimental Section

All compounds described in this investigation were very sensitive to oxygen and moisture and were manipulated under a purified argon atmosphere in a Vacuum Atmospheres drybox equipped with a Dry Train or by using standard vacuum line techniques. The reagents $Ga(CH_2CMe_2Ph)_3$ and $Ga(CH_2CMe_2Ph)_2Cl$ were prepared by using literature procedures.[8] All solvents were purified before use. Elemental analyses were performed by E+R Microanalytical Laboratories, Corona, NY. The ^{1}H NMR spectra were recorded at 400 MHz by using a Varian VXR-400 spectrometer with samples in flame-sealed NMR tubes. Chemical shifts are reported in δ (ppm) and are referenced to tetramethylsilane (TMS) at $\delta = 0.00$ ppm and benzene at $\delta = 7.15$ ppm. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin Elmer 683 spectrometer. Melting points were observed with a Mel-Temp by using flame-sealed capillaries and are uncorrected. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[10]

Reaction of $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ with Anhydrous Amines. In a typical experiment the yellow gallium(III) dihydronaphthalene derivative[5, 6] $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ was prepared in a Solv-Seal reaction flask at -78 °C from sodium metal, naphthalene, $Ga(CH_2CMe_2Ph)_2Cl$ and 40 - 50 mL of THF. Then, a slight excess of the dry amine was added to the flask by vacuum distillation and the solution was warmed from -196 °C to -78 °C. A large amount of colorless precipitate (NaCl) formed as the solution became bright yellow. Finally, the reaction mixture was warmed with stirring to ambient temperature over 12 h. When reaction with the amine was complete, the mixture was colorless. THF and the other readily volatile materials were removed by vacuum distillation at 20 °C. After the bulk of the readily volatile material had been removed, the material remaining in the flask was subjected to dynamic vacuum for 24 h. The slightly volatile materials were collected in a small preweighed trap and the components were identified by ^{1}H NMR spectroscopy as $C_{10}H_{10}$, $C_{10}H_8$, and THF. The nonvolatile material was extracted with pentane in order to separate NaCl from the soluble gallium-nitrogen product. The latter was purified and then fully characterized. The following paragraph gives quantities of reactants, the time required at room temperature for complete reaction, quantities and percent yields of products and the characterization data for each colorless new compound.

$[(PhMe_2CCH_2)_2GaNH_2]_2$. Reagents: 0.0926 g Na (4.03 mmol), 0.517 g $C_{10}H_8$ (4.03 mmol); 1.49 g $Ga(CH_2CMe_2Ph)_2Cl$ (4.00 mmol), 4.22 mmol NH_3. Time at 20 °C for complete reaction: 4 d. Products: 0.231 g NaCl (3.95 mmol, 98.9 % yield based on Na, see Eq 1), 1.30 g $(PhMe_2CCH_2)_2GaNH_2$ (3.69 mmol, 92.2 % yield based on $Ga(CH_2CMe_2Ph)_2Cl$ (Eq 1), product purified by recrystallization from pentane at -30 °C). Characterization data: Mp: 99.1 - 101.1 °C. ^{1}H NMR (C_6D_6, δ): 7.16 (d, 4 H, *o*-Ar, $^3J_{CCH}$ = 7.59 Hz), 7.04 (t, 4 H, *m*-Ar, $^3J_{CCH}$ = 6.26 Hz), 6.90 (t, 2 H, *p*-Ar, $^3J_{CCH}$ = 6.33 Hz), 1.20 (s, 12 H, $-CMe_2$), 0.53 (s, 4 H, $-CH_2-$), - 0.94 (s, 1 H, $-NH_2$). IR (Nujol, cm^{-1}): 3378 (vs), 3310 (s), 3080 (s), 3075 (s), 3019 (s), 1951 (sh, m), 1943 (m), 1882 (m), 1867 (m), 1800 (m), 1744 (m), 1670 (m), 1597 (s), 1587 (m), 1275 (s), 1178 (s), 1155 (m), 1130 (m), 1098 (m), 1069 (s), 1061 (sh,s), 1027 (s), 998 (m), 960 (m), 942 (m), 925 (m), 901 (m), 848 (m), 848 (m), 838 (s), 821 (vs), 775 (m), 762 (vs), 715 (vs), 692 (vs), 635 (s), 615 (sh, m), 605 (sh, m), 585 (m), 554 (s), 508 (w), 445 (s), 269 (w). Anal. for $C_{20}H_{28}GaN$. Calcd: C, 68.21; H, 8.01. Found: C, 68.14; H, 7.98. Solubility: soluble in THF, pentane, and benzene.

$[(PhMe_2CCH_2)_2GaNH(n\text{-}Pr)]_2$. Reagents: 0.117 g Na (5.09 mmol), 0.653 g $C_{10}H_8$ (5.09 mmol); 1.86 g $Ga(CH_2CMe_2Ph)_2Cl$ (5.00 mmol), 0.301 g $n\text{-}PrNH_2$ (5.09 mmol). Time at 20 °C for complete reaction: 5 days. Products: 0.264 g NaCl (4.52 mmol, 90.3 % yield based on Na and Eq 1), 1.67 g $(PhMe_2CCH_2)_2GaNH(n\text{-}Pr)$ (4.23 mmol, 84.6 % yield based on $Ga(CH_2CMe_2Ph)_2Cl$, after product purified by recrystallization from pentane at -30 °C). Characterization data: Mp: 127.8 - 128.5 °C (lit[8] 129.3 - 131.0 °C). ^1H NMR (C_6D_6, δ): 7.35 (d, 4 H, *o*-Ar, $^3J_{CCH}$ = 8.10 Hz), 7.16 (t, 4 H, *m*-Ar, $^3J_{CCH}$ = 7.26 Hz), 7.00 (t, 2 H, *p*-Ar, $^3J_{CCH}$ = 7.14 Hz), 2.06 (q, 2 H, $-CH_2-$ (Pr), $^3J_{CCH}$ = 7.68 Hz), 1.33 (s, 12 H, $-CMe_2$ (neophyl)), 0.87 (s, 4 H, $-CH_2-$ (neophyl)), 0.82 (m, 2 H, $-NCH_2-$ (Pr)), 0.61 (t, 3 H, $-CH_3$ (Pr), $^3J_{CCH}$ = 7.14 Hz), - 0.04 (t, 1 H, -NH, $^3J_{CNH}$ = 7.50 Hz). The ^1H NMR spectrum indicated 100% trans isomer. Solubility: soluble in THF, pentane, and benzene.

$[(PhMe_2CCH_2)_2GaNHPh]_2$: Reagents: 0.115 g Na (5.01 mmol), 0.643 g $C_{10}H_8$ (5.01 mmol); 1.86 g $Ga(CH_2CMe_2Ph)_2Cl$ (5.00 mmol), 0.480 g $PhNH_2$ (5.15 mmol). Time at 20 °C for complete reaction: 6 h. Products: 0.272 g NaCl (4.65 mmol, 93.1 % yield based on Na and Eq 1), 1.75 g $(PhMe_2CCH_2)_2GaNHPh$ (4.08 mmol, 81.6 % yield based on $Ga(CH_2CMe_2Ph)_2Cl$ after product purified by recrystallization from toluene at -78 °C). Characterization data: Mp: 175.4 - 177.5 °C. ^1H NMR (C_6D_6, δ) 7.30 (d, 8 H, *o*-Ar (neophyl), $^3J_{CCH}$ = 7.60 Hz), 7.20 (t, 4 H, *m*-Ar (N-Ph), $^3J_{CCH}$ = 6.80 Hz), 7.17 (t, 8 H, *m*-Ar (neophyl), $^3J_{CCH}$ = 7.40 Hz), 7.03 (t, 4 H, *p*-Ar (neophyl), $^3J_{CCH}$ = 7.20 Hz), 6.85 (t, 2 H, *p*-Ar (N-Ph), $^3J_{CCH}$ = 7.40 Hz), 6.78 (d, 4 H, *o*-Ar (N-Ph), $^3J_{CCH}$ = 8.80 Hz), 3.15 (s-br, 2.1 H, -NH (trans + cis)), 1.07 (d, 4.0 H, $-CH_2-$ (trans), $^2J_{CH}$ = 13.6 Hz), 1.03 (s, 12.0 H, $-CMe_2$ (trans)), 1.01 (s, 12.9 H, $-CMe_2$ (trans + cis)), 0.77 (d, 3.8 H, $-CH_2-$ (trans), $^2J_{CH}$ = 13.6 Hz). The ^1H NMR spectrum for a C_6D_6 solution indicated an isomer distribution of 7% cis and 93% trans (± 5%). ^1H NMR (CD_2Cl_2, δ): 7.34, 7.33, 7.30, 7.28, 7.25, 7.15 - (m, 24 H, *o*-Ar (neophyl), *m*-Ar (neophyl), *p*-Ar (neophyl), *m*-Ar (N-Ph)), 6.99 (t, 2 H, *p*-Ar (N-Ph), $^3J_{CCH}$ = 6.00 Hz), 6.55 (d, 4 H, *o*-Ar (N-Ph), $^3J_{CCH}$ = 7.30 Hz), 2.94 (s-br, 2.5 H, -NH (trans + cis)), 1.22 (s, 2.30 H, $-CMe_2$ (cis)), 1.02 (s, 0.70 H, $-CH_2-$ (cis)), 0.96 (s, 25.9 H, $-CMe_2$ (trans + cis)), 0.87 (d, 4.2 H, $-CH_2-$ (trans), $^2J_{CH}$ = 13.7 Hz), 0.82 (s, 0.70 H, $-CH_2-$ (cis)), 0.58 (d, 4.2 H, $-CH_2-$ (trans),

$^2J_{CH}$ = 14.3 Hz). The ^{1}H NMR spectrum for the CH_2Cl_2 solution indicated an isomer distribution of 16% cis and 84% trans(± 5%). IR (Nujol mull, cm^{-1}): 3275 (s), 3082 (s), 3055 (s), 3015 (s), 2721 (m), 1949 (m), 1871 (m), 1809 (m), 1750 (m), 1595 (s), 1585 (sh, s), 1575 (m), 1489 (vs), 1279 (m), 1231 (s), 1210 (vs), 1175 (s), 1155 (m), 1139 (m), 1100 (m), 1070 (s), 1025 (s), 998 (m), 963 (m), 905 (m), 892 (s), 868 (sh, m), 862 (s), 852 (sh, m), 839 (m), 811 (m), 761 (vs), 750 (s), 725 (s), 712 (m), 699 (sh, vs), 692 (vs), 681 (sh, s), 665 (sh, m), 626 (m), 602 (w), 569 (m), 555 (m), 535 (w), 512 (w), 430 (sh, w), 418 (m), 408 (m), 250 (w), 235 (m). Anal. for $C_{26}H_{32}GaN$. Calcd: C, 72.92; H, 7.53. Found: C, 72.82; H, 7.59. Solubility: soluble in THF; slightly soluble in pentane, benzene, toluene and *m*-xylene. Compound had insufficient solubility in benzene for a cryoscopic molecular weight study.

Reactions of $Ga(CH_2CMe_2Ph)_3$ with NH_3 and with $PhNH_2$. In a typical experiment a break-seal reaction tube was charged with $Ga(CH_2CMe_2Ph)_3$ and the amine, evacuated, sealed and then heated for 4 days at 140-150 °C. After no noncondensable gas was observed to have been formed during the reaction by using the vacuum line, the more volatile product $C_6H_5CMe_3$ was transferred to an NMR tube by vacuum distillation at ambient temperature and identified as t-butylbenzene by ^{1}H NMR spectroscopy. The remaining colorless solid was washed out of the reaction tube with ~ 50 mL of pentane through a medium glass frit, purified by recrystallization from pentane and identified.

$[(PhMe_2CCH_2)_2GaNH_2]_2$. Reagents: 2.31 g $Ga(CH_2CMe_2Ph)_3$ (4.93 mmol); NH_3 (5.01 mmol). Products: 0.317 g $C_6H_5CMe_3$ (4.40 mmol, 93.2% yield based on $Ga(CH_2CMe_2Ph)_3$), 1.64 g $(PhMe_2CCH_2)_2GaNH_2$ (4.64 mmol, 94.2% based on $Ga(CH_2CMe_2Ph)_3$). Characterization data: Mp: 94.3 - 97.3 °C. Anal. calcd for $C_{20}H_{28}GaN$: C, 68.21; H, 8.01. Found: C, 68.48; H, 7.96. Cryoscopic molecular weight, benzene solution, formula weight 352.17 (obsd. molality, obsd. mol. wt., association): 0.0909, 686, 1.95; 0.0721, 695, 1.98; 0.0550, 708, 2.01. Spectroscopic data for this sample were identical within normal experimental error with the data for the compound prepared by the reaction of $C_{10}H_8[Ga(CH_2CMe_2Ph)_2]_2$ with NH_3. Solubility: soluble in pentane and benzene.

$[(PhMe_2CCH_2)_2GaNHPh]_2$: Reagents: 2.20 g $Ga(CH_2CMe_2Ph)_3$ (4.69 mmol); 0.503 g $PhNH_2$ (5.40 mmol). Products: 1.36 g $(PhMe_2CCH_2)_2GaNHPh$ (3.18 mmol, 67.8% yield based on $Ga(CH_2CMe_2Ph)_3$). Characterization data: Mp: 174.1 - 177.0 °C. Spectroscopic data for this sample were identical within normal experimental error with the data for the compound prepared from the reaction of $C_{10}H_8[Ga(CH_2CMe_2Ph)_2]_2$ with $PhNH_2$. Only the trans isomer was observed by ^1H NMR spectroscopy.

Synthesis of $(PhMe_2CCH_2)_2GaNHPh$ by Reacting $Ga(C_5H_5)_3$, $Ga(CH_2CMe_2Ph)_3$ and $PhNH_2$. A reaction flask was charged with $Ga(CH_2CMe_2Ph)_3$ (1.46 g, 3.11 mmol), $Ga(C_5H_5)_3$ (0.411 g, 1.55 mmol) and 20 - 25 mL of pentane. After the solution had been stirred for 1 h at 20 °C, the flask was cooled to -10 °C and a solution of $PhNH_2$ (0.434 g, 4.66 mmol) in 20 mL of pentane was added slowly. This solution was stirred for an additional 24 h and a large amount of colorless precipitate, the slightly soluble product, formed. After the pentane was removed by vacuum distillation, the residue was washed numerous times with fresh pentane at low temperature (-40 to -78 °C) to remove impurities. The resulting colorless solid was identified as pure $(PhMe_2CCH_2)_2GaNHPh$ (1.41 g, 3.30 mmol, 70.8% yield based on $Ga(CH_2CMe_2Ph)_3$). Crystallographic quality crystals were obtained by slowly cooling to ambient temperature a heated, saturated solution of the compound in *m*-xylene. The crystals were mounted directly from the *m*-xylene solution.

$[(PhMe_2CCH_2)_2GaNHPh]_2$: Mp: 173.6 - 176.0 °C. ^1H NMR (C_6D_6, δ) (400 MHz): 7.28 (d, 8.0 H, *o*-Ar (neophyl), $^3J_{CCH}$ = 8.0 Hz), 7.19 (t, 4.0 H, *m*-Ar (N-Ph), $^3J_{CCH}$ = 7.80 Hz), 7.17 (t, 8.0 H, *m*-Ar (neophyl), $^3J_{CCH}$ = 7.80 Hz), 7.02 (t, 4.0 H, *p*-Ar (neophyl), $^3J_{CCH}$ = 7.40 Hz), 6.84 (t, 2.0 H, *p*-Ar (N-Ph), $^3J_{CCH}$ = 7.40 Hz), 6.76 (d, 4.0 H, *o*-Ar (N-Ph), $^3J_{CCH}$ = 8.00 Hz), 3.14 (s-br, 2.0 H, -NH (trans)), 1.06 (d, 3.9 H, -

CH_2- (trans), $^2J_{CH}$ = 14.0 Hz), 1.02 (s, 11.8 H, -CMe_2 (trans)), 1.00 (s, 11.8 H, -CMe_2 (trans)), 0.76 (d, 3.9 H, -CH_2- (trans), $^2J_{CH}$ = 13.6 Hz). Only the trans isomer was observed by ^{1}H NMR spectroscopy. Anal. for $C_{26}H_{32}GaN$. Calcd.: C, 72.92; H, 7.53. Found: C, 72.93; H, 7.44. Solubility: slightly soluble in pentane, benzene, and *m*-xylene.

Collection of X-Ray Diffraction Data for $[(PhMe_2CCH_2)_2GaNHPh]_2$. A well-defined crystal of approximate orthogonal dimensions 0.30 × 0.25 × 0.15 mm was sealed into a thin-walled glass capillary under an argon atmosphere inside the drybox maintained under anaerobic and moisture-free conditions. The crystal was inspected under a binocular microscope to ensure that it was indeed a single crystal and then was centered on a Siemens R3m/V automated four-circle diffractometer. The unit cell parameters were determined as described previously.[11] Intensity data (Mo Kα radiation, $\lambda = 0.710730$Å)[12] were collected at ambient temperature (25±1 °C) with graphite-monochromatized radiation. The observed Laue symmetry (C_i or $\bar{1}$ only) and the non-occurrence of systematic absences indicate that the crystal belongs to the triclinic system. The centrosymmetric space group $P\bar{1}$ (No. 2) was selected on the basis of intensity statistics and frequency of occurrence[13] and was confirmed by the successful solution of the structure. A total of 6373 reflections were collected and merged to yield 6004 unique reflections of which 3711 (61.8%) had $|F_o| > 6.0\sigma(F_o)$. Details appear in Table 3.

Determination of Crystal Structure of $[(PhMe_2CCH_2)_2GaNHPh]_2$. All crystallographic calculations were carried out on a VAX station computer with the use of the Siemens SHELXTL PLUS (Release 4.11 (VMS)) program package.[14, 15] The analytical expressions of the scattering factors for neutral atoms[16a] were corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[16b] The structure was solved via a combination of Patterson maps, difference-Fourier syntheses and least-squares refinement. Positional and anisotropic thermal parameters for the unique N-bonded hydrogen atom of each independent phenylamido group were also refined; all remaining hydrogen atoms were placed in calculated positions, based upon d(C-H) = 0.96Å[17] and the appropriate idealized trigonal or staggered tetrahedral geometry. Refinement of the ordered model converged with R = 3.43% and wR = 3.62% for those 3711 data with $|F_o| > 6.0\sigma(|F_o|)$, and R = 6.94% for all data.

Acknowledgment. This work was supported in part by the Office of Naval Research (O.T.B.). The purchase of the X-ray diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supporting Information Available. One Figure (showing labeling of atoms in "Molecule 2"); complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms for the X-ray study (11 pp). Ordering information is given on any current masthead page.

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is thus secure.

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Table 1

Selected Bond Distances (Å) for $[(PhMe_2CCH_2)GaNHPh]_2$.

MOLECULE 1		MOLECULE 2	
(a) Distances Associated with the Gallium(III) Atoms			
Ga(1)–N(3)	2.082(4)	Ga(2)–N(4)	2.066(4)
Ga(1)–C(00)	1.977(6)	Ga(2)–C(30)	1.988(5)
Ga(1)–C(10)	1.982(5)	Ga(2)–C(40)	1.982(5)
Ga(1)•••Ga(1A)	3.008(1)	Ga(2)•••Ga(2A)	3.018(1)
Ga(1)–N(3A)	2.037(3)	Ga(2)–N(4A)	2.037(5)
(b) Bond Lengths within the Bridging Amide Ligands			
N(3)–H(3)	0.89(6)	N(4)–H(4)	0.81(5)
N(3)–C(21)	1.437(8)	N(4)–C(51)	1.436(7)
N(3)–Ga(1A)	2.037(3)	N(4)–Ga(2A)	2.037(5)
C(21)–C(22)	1.375(9)	C(51)–C(52)	1.365(7)
C(21)–C(26)	1.377(6)	C(51)–C(56)	1.392(9)
C(22)–C(23)	1.389(10)	C(52)–C(53)	1.397(10)
C(23)–C(24)	1.392(8)	C(53)–C(54)	1.370(13)
C(24)–C(25)	1.358(13)	C(54)–C(55)	1.365(9)
C(25)–C(26)	1.368(10)	C(55)–C(56)	1.375(9)

Table 2

Selected Bond Angles (deg) for $[(PhMe_2CCH_2)GaNHPh]_2$.

MOLECULE 1		MOLECULE 2	
(a) Angles around the gallium(III) centers			
N(3)–Ga(1)–C(00)	108.5(2)	N(4)–Ga(2)–C(30)	106.1(2)
N(3)–Ga(1)–C(10)	107.8(2)	N(4)–Ga(2)–C(40)	109.9(2)
C(00)–Ga(1)–C(10)	123.5(2)	C(30)–Ga(2)–C(40)	122.2(2)
N(3)–Ga(1)–N(3A)	86.2(1)	N(4)–Ga(2)–N(4A)	85.3(2)
C(00)–Ga(1)–N(3A)	111.5(2)	C(30)–Ga(2)–N(4A)	113.6(2)
C(10)–Ga(1)–N(3A)	112.6(2)	C(40)–Ga(2)–N(4A)	113.0(2)
(b) Angles around the nitrogen atoms			
Ga(1)–N(3)–Ga(1A)	93.8(1)	Ga(2)–N(4)–Ga(2A)	94.7(2)
Ga(1)–N(3)–C(21)	117.6(3)	Ga(2)–N(4)–C(51)	118.7(3)
Ga(1A)–N(3)–C(21)	125.2(3)	Ga(2A)–N(4)–C(51)	123.8(3)
Ga(1)–N(3)–H(3)	96(3)	Ga(2)–N(4)–H(4)	102(3)
Ga(1A)–N(3)–H(3)	113(4)	Ga(2A)–N(4)–H(4)	107(4)
C(21)–N(3)–H(3)	107(4)	C(51)–N(4)–H(4)	108(4)
(c) Angles about C(α) of the neophyl groups			
Ga(1)–C(00)–C(01)	119.9(4)	Ga(2)–C(30)–C(31)	116.6(3)
Ga(1)–C(10)–C(11)	118.3(4)	Ga(2)–C(40)–C(41)	119.3(4)

Table 3.

Data for the X-Ray Crystallographic Studies of $[(PhMe_2CCH_2)GaNHPh]_2$

mol formula	$C_{52}H_{64}Ga_2N_2$
cryst syst	triclinic
space Group	$P\bar{1}$ (No. 2)
a, Å	11.0545(19)
b, Å	11.4532(22)
c, Å	20.5023(36)
α, °	86.599(15)
β, °	83.524(14)
γ, °	62.713(13)
V, $Å^3$	2292.11(73)
Z	2
molec wt	856.5
D, g/cm^3	1.240
μ(Mo Kα), mm^{-1}	1.204
F(000)	904
2θ range, deg	5 - 45
h	0 to +11
k	-10 to +12
ℓ	-21 to +22
no. of rflns collected	6373
no. of indep reflns	6004 (R_{int} =1.23 %)

Table 3 (Cont.)

no. of rflns above 6σ	3711
absorption correction	Semi-empirical
min./max. transmission	0.5747 / 0.7027
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0013F^2$
no. of params refined	514
final R indices (all data), %	R = 6.94
	R_w = 5.65
R indices (6σ data), %	R = 3.43
	R_w = 3.62
goodness of fit	0.93
largest and mean Δ/σ	0.002, 0.001
data-to-param ratio	11.7:1
largest diff peak, $e\text{Å}^{-3}$	0.42
largest diff hole, $e\text{Å}^{-3}$	-0.42

Caption to Figures.

Figure 1. Packing diagram for $[(PhMe_2CCH_2)_2GaNHPh]_2$, viewed down *a*.. The defined "Molecule 1" (centered about 0, ½, 0) lies to the left and "Molecule 2" (centered about ½, ½, ½) is in the center of this diagram. (The *c*-axis is horizontal and the *b*-axis is vertical).

Figure 2. Labeling of atoms for "Molecule 1" of $[(PhMe_2CCH_2)_2GaNHPh]_2$. ORTEP2 diagram, 30% probability ellipsoids for non-hydrogen atoms and with all hydrogen atoms artifically reduced.

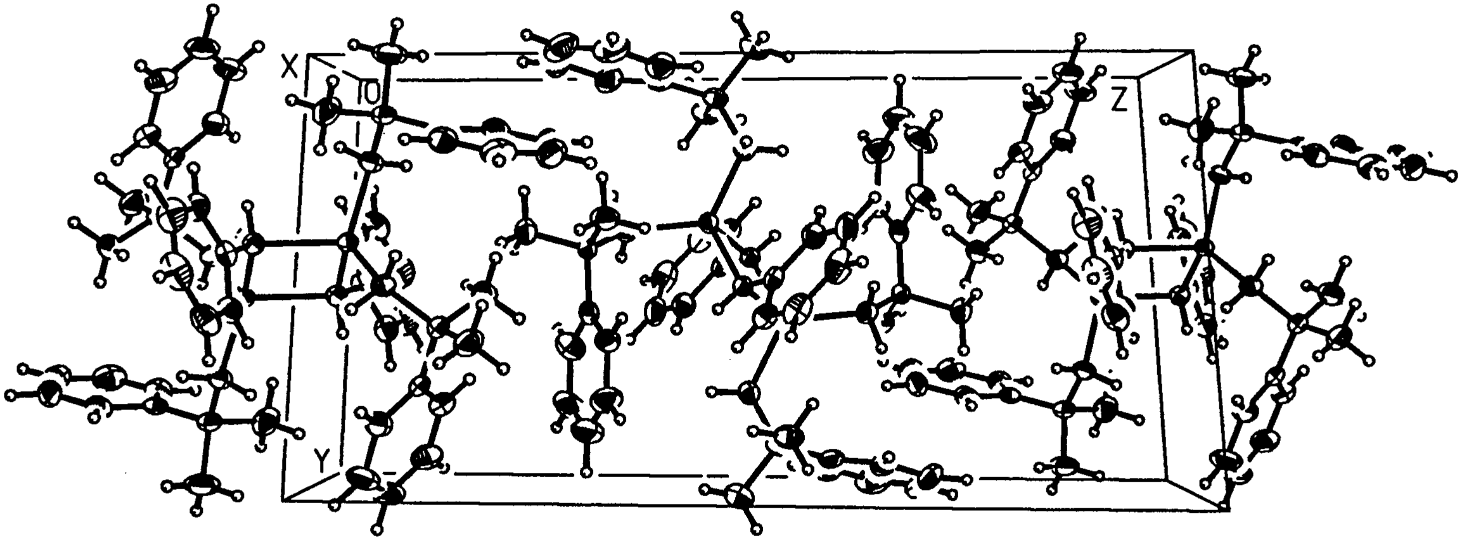

FIG. 1

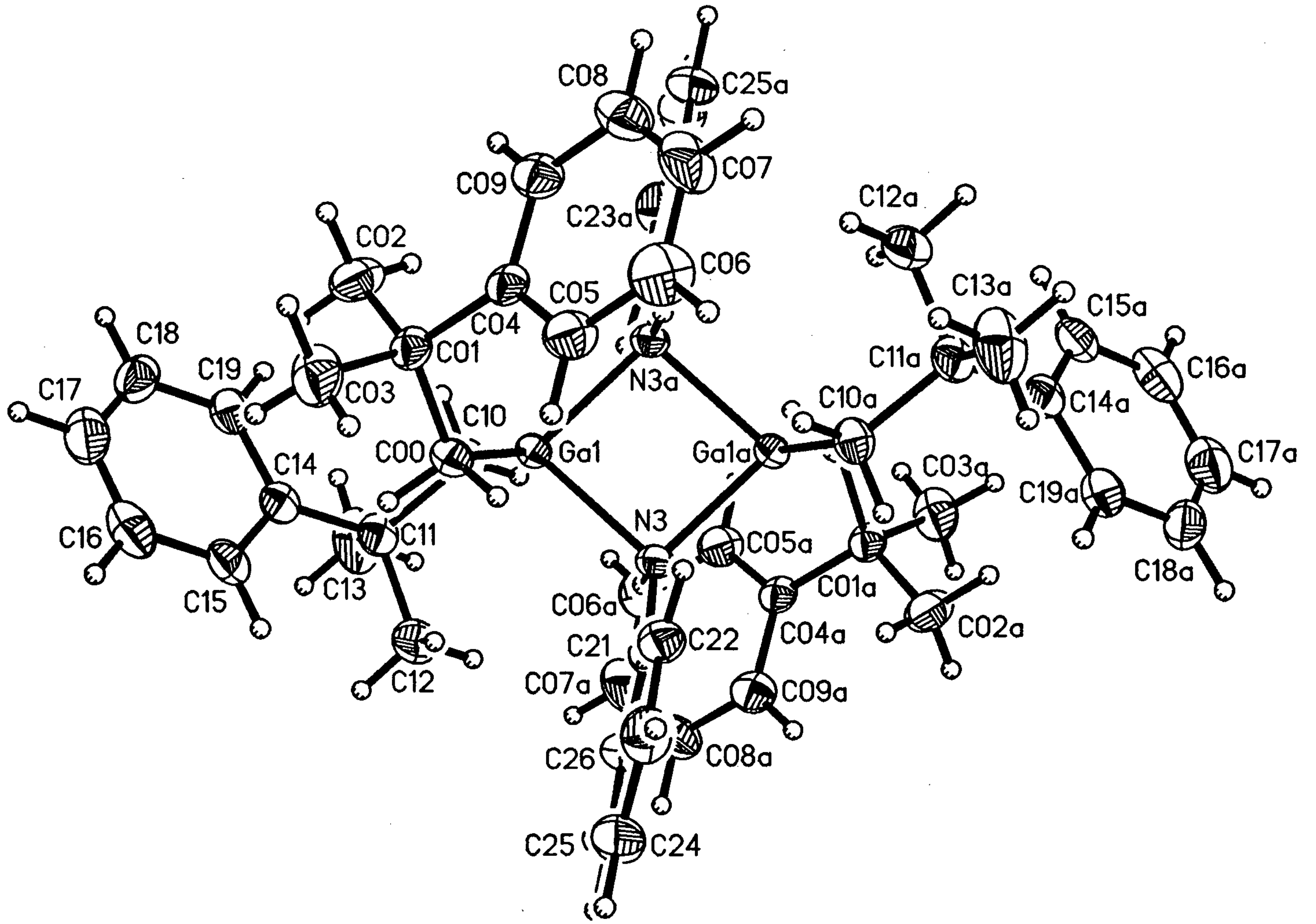
C08
C25a
C07
C09
C23a
C12a
C02
C06
C13a
C15a
C05
C04
C18
C01
C11a
C16a
C19
N3a
C17
C03
C10a
C14a
C10
C00
Ga1
Ga1a
C03a
C17a
C19a
C14
N3
C16
C11
C05a
C18a
C01a
C13
C15
C06a
C02a
C04a
C21
C22
C07a
C12
C09a
C26
C08a
C25
C24

FIG. 2.

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