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13. ABSTRACT (Maximum 200 words) The dihydronaphthalene elimination reaction between $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ ($\text{R} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}$) and t-BuNH_2 provided a room temperature route to $[\text{R}_2\text{GaNH}(\text{t-Bu})]_2$. However, when $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ and t-BuNH_2 were reacted at $140 - 150^\circ\text{C}$, $\text{C}_6\text{H}_5\text{CMe}_3$ was eliminated and the product was $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$, a gallium(III) amide with one GaC_4 metallocyclic ring, rather than $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. X-ray structural studies confirmed the identity of this novel compound as well as that of the typical dimer. When the reaction temperature was increased to $210 - 230^\circ\text{C}$, the product was $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}[\text{CH}_2\text{CMe}_2(\text{C}_6\text{H}_4)]$, a species with two GaC_4 metallocyclic rings.				
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TECHNICAL REPORT NO. 52

Gallium-Nitrogen Compounds Prepared By Dihydronaphthalene
and Thermal Elimination Reactions. Crystal and Molecular

Structures of $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$ and
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by

O. T. Beachley, Jr.*, Matthew J. Noble,
Melvyn Rowen Churchill* and Charles H. Lake

Prepared for Publication

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Organometallics

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14260-3000

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by

O. T. Beachley, Jr.*, Matthew J. Noble, Melvyn Rowen Churchill* and Charles H. Lake

Department of Chemistry

State University of New York at Buffalo

Buffalo, NY 14260-3000

Abstract

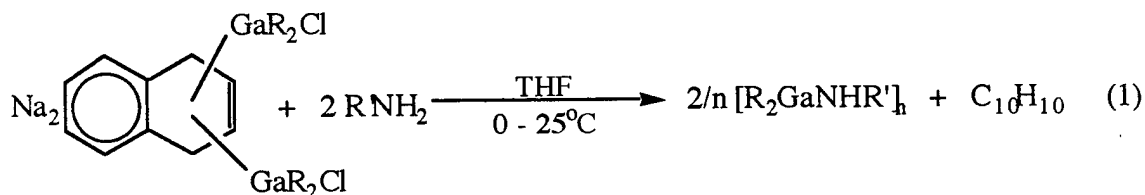
The dihydronaphthalene elimination reaction between $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ ($\text{R} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}$) and t-BuNH_2 provided a room temperature route to $[\text{R}_2\text{GaNH}(\text{t-Bu})]_2$. However, when $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ and t-BuNH_2 were reacted at 140 - 150 °C, $\text{C}_6\text{H}_5\text{CMe}_3$ was eliminated and the product was $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$, a gallium(III) amide with one GaC_4 metallocyclic ring, rather than $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. X-ray structural studies confirmed the identity of this novel compound as well as that of the typical dimer. When the reaction temperature was increased to 210 - 230 °C, the product was $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}[\text{CH}_2\text{CMe}_2(\text{C}_6\text{H}_4)]$, a species with two GaC_4 metallocyclic rings.

Introduction

The dihydronaphthalene derivatives $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ ($\text{R} = \text{CH}_2\text{CMe}_3$, $\text{CH}_2\text{CMe}_2\text{Ph}$) are members of a class of triorganogallium compounds which incorporate two different organic groups bonded to gallium in the monomeric unit. These molecules provide unique opportunities to investigate the relative propensity of the different organic substituents in the same molecule to undergo the hydrocarbon elimination reaction which is fundamental to group 13 chemistry.³ Thus, studies of elimination reactions between $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ and amines were undertaken in order to learn whether the dihydronaphthalenide ligand or the alkyl substituent would be eliminated preferentially and under what conditions the elimination reaction(s) would occur. Reactions of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$ with NH_3 ⁴ and of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}]_2\}$ with NH_3 ⁵, $n\text{-PrNH}_2$ ⁵ and PhNH_2 ⁵ demonstrated previously the selective elimination of the dihydronaphthalenide ligand and formation of $[\text{R}_2\text{GaNHR}']_2$ and $\text{C}_{10}\text{H}_{10}$ at room temperature. This paper describes the reactions of $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ and of GaR_3 ($\text{R} = \text{CH}_2\text{CMe}_3$, $\text{CH}_2\text{CMe}_2\text{Ph}$) with $t\text{-BuNH}_2$.

Results and Discussion

The dihydronaphthalene derivatives $\text{Na}_2[\text{C}_{10}\text{H}_8(\text{GaR}_2\text{Cl})_2]$ ($\text{R} = \text{CH}_2\text{CMe}_3$, $\text{CH}_2\text{CMe}_2\text{Ph}$) undergo stoichiometric elimination reactions with $t\text{-BuNH}_2$ at room temperature to form $\text{R}_2\text{GaNH}(t\text{-Bu})$ and dihydronaphthalene (eq 1). The neophyl dihydronaphthalene derivative required ~12 h to go to completion as shown by the



disappearance of its yellow color and $(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ was isolated in 96 % yield. In contrast, the neopentyl compound required a reaction time of ~4 - 5 days but only a 53 % yield of $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ was obtained. The final solution from the reaction of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}]_2\}$ with t-BuNH_2 was colorless whereas that from the reaction of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$ with t-BuNH_2 was reddish-brown due to the presence of the gallium(I) compound¹ $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$. Thus, the neopentyl dihydronaphthalene derivative underwent both elimination and reduction reactions. This hypothesis was confirmed by the isolation of $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ and $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$, the products from the reduction of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$.¹ The three isolated products accounted for 80 % of the initial gallium. It is noteworthy that t-BuNH_2 is the only amine in the series for which both the elimination and reduction reactions were observed. The other amines⁵ PhNH_2 , $n\text{-PrNH}_2$, NH_3 , t-BuNH_2 underwent only the elimination reaction. The order of reactivity of these amines for their elimination reactions with $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}]_2\}$ is $\text{PhNH}_2 \gg \text{t-BuNH}_2 > n\text{-PrNH}_2 \sim \text{NH}_3$. The weaker amine with the more acidic proton reacted fastest. It is also of interest that neophylgallium(III) compounds are stronger Lewis acids⁶ than are the corresponding neopentyl derivatives.

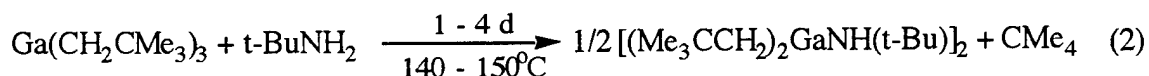
The two new compounds $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ and $(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ were fully characterized and only the latter was the subject of an X-ray structural study. All cryoscopic molecular weight and spectroscopic data are consistent with the existence of dimers in benzene solution. The X-ray structural study of $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$ identified discrete dimers with precise C_i symmetry as shown in Figure 1. Interatomic distances and angles are collected in Table 1. The Ga_2N_2 core defines a strictly planar parallelogram but is distorted slightly from the possible higher D_{2h} symmetry. Bond lengths are $\text{Ga}(1)\text{-N}(1) = \text{Ga}(1A)\text{-N}(1A) = 2.028(3)$ Å and $\text{Ga}(1)\text{-N}(1A) = \text{Ga}(1A)\text{-N}(1) = 2.073(3)$ Å. The angle at Ga(1) is acute ($\text{N}(1)\text{-Ga}(1)\text{-N}(1A) = 84.2(1)^\circ$) and the angle at nitrogen ($\text{Ga}(1)\text{-N}(1)\text{-Ga}(1A) = 95.8(1)^\circ$) is obtuse and

supplementary to the previous angle. The Ga(1)•••Ga(1A) distance of 3.044(1) Å is in the non-bonding regime. The crystallographic inversion center mandates that the two t-butyl ligands have a mutually trans disposition such that t-butyl groups appear on opposite faces of the planar Ga₂N₂ core, as do the N-H linkages. Two neophyl ligands are bonded to each gallium atom with Ga(1)-C(00) = 2.007(4) Å, Ga(1)-C(10) = 2.003(4) Å [Ga-C(aver) = 2.005(3) Å] and C(00)-Ga(1)-C(10) = 117.9(1) °. The Ga-C(α)-C(β) angles are substantially increased from the regular tetrahedral value of 109.5 °, with Ga(1)-C(00)-C(01) = 124.6(2) ° and Ga(1)-C(10)-C(11) = 128.9(2) °. Other structural features are normal. The closely related molecules [(PhMe₂CCH₂)₂GaNH(n-Pr)]₂⁶ and [(PhMe₂CCH₂)₂GaNHPh]₂⁵ have analogous planar Ga₂N₂ rings, trans orientations of organic groups on nitrogen and similar Ga-C and Ga-N distances.

The compounds (Me₃CCH₂)₂GaNH(t-Bu) and (PhMe₂CCH₂)₂GaNH(t-Bu) were also characterized by ¹H NMR spectroscopy. The resonances for each unique type of proton were assigned on the basis of their relative chemical shifts, coupling constants and integration data. The gallium nitrogen compounds have sharp melting points which suggests the presence of only one (trans) isomer in the solid state, as observed in the X-ray structural study. However, these compounds isomerize upon dissolution in benzene and both cis and trans isomers were observed by ¹H NMR spectroscopy. The spectra of the trans isomers of both compounds exhibited two doublets (²J = 13.6 Hz) due to geminal coupling between the methylene protons of the organic groups bonded to gallium. The compound [(Me₃CCH₂)₂GaNH(H)(t-Bu)]₂ formed an equilibrium mixture (82 % cis- and 18 % trans- isomer) which was independent of the method of preparation. In contrast, a solution of [(PhMe₂CCH₂)₂GaNH(t-Bu)]₂ contained 56 % trans isomer and [(PhMe₂CCH₂)₂GaNH(n-Pr)]₂⁶ was reported to be 100 % trans. The compound [(PhMe₂CCH₂)₂GaNHPh]₂⁵ was 93 % trans when prepared by the C₁₀H₁₀ elimination reaction and 100 % trans when prepared by the elimination of C₆H₅CMe₃ at 140 - 150 ° C.

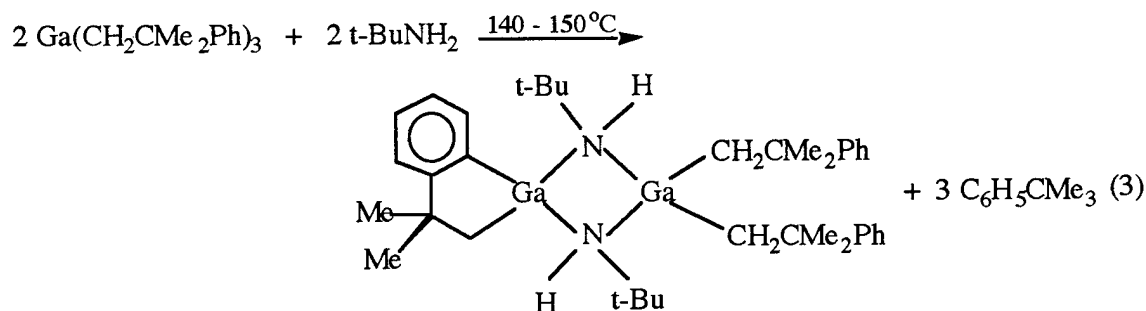
The reagents GaR₃ (R = CH₂CMe₃, CH₂CMe₂Ph) and t-BuNH₂ were investigated

for their potential to undergo the typical elimination reaction³ to form organogallium amide dimers. However, even though both sets of reagents appeared to undergo chemical change at 140 - 150 °C, only the neopentyl derivative provided a route to $[\text{R}_2\text{GaNH}(\text{t-Bu})]_2$ (eq 2).

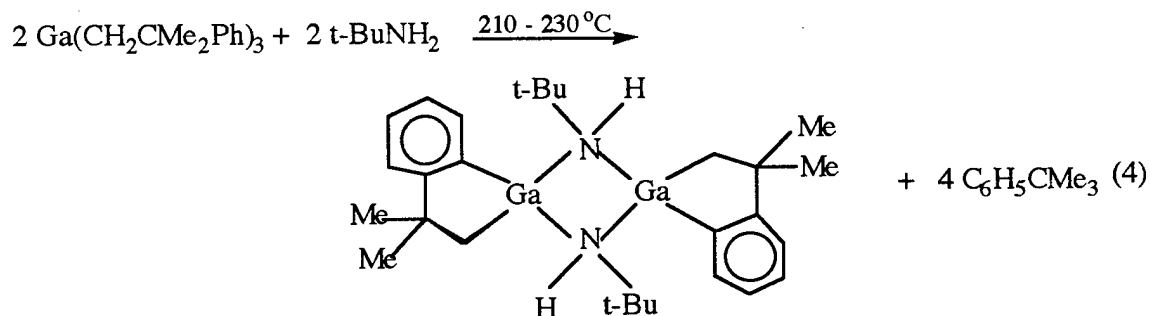


In the case of the reaction between $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ and t-BuNH_2 (eq 3), the isolated product was an organogallium(III) amide with one GaC_4 metallocyclic ring,

$[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$. The formation of this compound is



accompanied by the elimination of one molecule of *t*-butylbenzene by an orthometallation reaction. When the temperature was increased from to 210 - 230 °C (eq 4), a second



orthometallation reaction took place and the resulting organogallium amide now had two

gallium-carbon metallocyclic rings $(\text{H}_4\text{C}_6\text{Me}_2\text{CCH}_2)\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)$.

The isolation and characterization of the stoichiometric amounts of $\text{C}_6\text{H}_5\text{CMe}_3$ confirmed the reactions shown by eq 3 and 4. The orthometallated gallium nitrogen products were characterized by elemental analyses, melting point, ^1H NMR and IR spectroscopy, solubility properties, cryoscopic molecular weight, and X-ray structural studies, as appropriate.

The X-ray structural study of $[(\text{H}_4\text{C}_6\text{Me}_2\text{CCH}_2)\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ confirmed the identity of a gallium(III) amide containing one gallium-carbon metallocyclic ring. This molecule is illustrated in Figure 2. Interatomic distances and angles are collected in Table 2. The molecule has no symmetry other than C_1 . The Ga_2N_2 core of the molecule adopts a puckered or "butterfly" conformation. The angle of distortion about $\text{Ga}(1)\cdots\text{Ga}(2)$ axis is 21.9° [as determined from the dihedral angle between the $\text{Ga}(1)\text{-N}(3)\text{-Ga}(2)$ and $\text{Ga}(1)\text{-N}(4)\text{-Ga}(2)$ planes], while the distortion measured about the $\text{N}(3)\cdots\text{N}(4)$ axis is 19.6° . This portion of the molecule is shown in Figure 3.

Atom $\text{Ga}(1)$ is in a fairly normal environment with gallium(III) - neophyl bond lengths of $\text{Ga}(1)\text{-C}(00) = 1.991(5) \text{ \AA}$ and $\text{Ga}(1)\text{-C}(10) = 1.982(5) \text{ \AA}$ [$\text{Ga-C(aver)} = 1.987(7) \text{ \AA}$, slightly shorter than for the previous compound]. The interligand angle about $\text{Ga}(1)$ of $\text{C}(00)\text{-Ga}(1)\text{-C}(10) = 118.0(2)^\circ$ is indistinguishable from that in the previous compound. The average $\text{Ga}(1)\text{-N}$ distance is $2.046 \text{ \AA}$. Atom $\text{Ga}(2)$ is in a rather unusual coordination environment. There are two rather short $\text{Ga}(2)$ -amide linkages with $\text{Ga}(2)\text{-N(aver)} = 2.000 \text{ \AA}$. The two (chemically inequivalent) Ga-C bonds are a $\text{Ga-C(sp}^3\text{)}$ linkage [$\text{Ga}(2)\text{-C}(20) = 1.961(6) \text{ \AA}$] and a $\text{Ga-C(sp}^2\text{)}$ linkage [$\text{Ga}(2)\text{-C}(29) = 1.977(5) \text{ \AA}$]. It is rather surprising that the first of these is the shorter of the two. Orthometallation of the phenyl ring appears to result in no abnormal bond lengths. The six-membered ring is associated with C-C bond lengths of $1.361(13) \text{ \AA}$ - $1.400(8) \text{ \AA}$; the three longest ($1.395(9) \text{ \AA} \rightarrow 1.400(8) \text{ \AA}$) are in contact with, or a component of, the GaC_4 ring; however, these are only slightly longer than the other three aromatic C-C distances

(1.361(13) $\rightarrow$ 1.383(9) Å) and the differences may well be an artifact of our treatment of the atomic vibration ellipsoids.

Distances within the GaC₄ ring appear normal but interior angles are rather irregular and range from 91.5(2) through 121.0(5)°. The formation of this ring causes bond angles about Ga(2) to show a larger range than those about the more typical Ga(1). Finally, we note that the atoms of the five-membered GaC₄ ring have an average deviation of 0.0314 Å from their least-squares plane and that this plane defines an angle of 98.7° with the N(3)-Ga(2)-N(4) plane.

The compound $[(\text{H}_4\text{C}_6\text{Me}_2\text{CCH}_2)_2\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ exists as a single isomer in the solid state, but multiple geometrical isomers are present in a benzene solution according to its ¹H NMR spectrum. Similarly, a mixture of isomers was observed for a benzene solution of the bimetallocyclic compound. The ¹H NMR spectral lines observed for the compounds with orthometallated rings were assigned by comparing their spectra with that of $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. When the geometrical isomers which arise from orientations of both the t-butyl groups bonded to nitrogen and the orthometallated phenyl rings for the bimetallic gallium amide are considered, five isomers (Figure 4) are possible. However, only two of these isomers (a and b, Figure 4) were observed in significant abundance in benzene solution. Both of these isomers have the phenyl groups oriented trans to each other but one has trans t-butyl groups on nitrogen whereas the other has cis t-butyl groups. Molecular models suggest that steric interactions are minimized when the phenyl groups are trans to one another. The ¹H NMR signal of the methylene group protons of the trans isomer exhibited geminal coupling (²J = 14.8 Hz). The monometallic gallium amide can exist as three isomers. One has the t-butyl groups on nitrogen trans to one another. The other two isomers have cis t-butyl groups. For one the phenyl ring which is a part of the metallocyclic ring can be on the same side as the N-H protons and on the side of the t-butyl groups on the other. It is also noteworthy that each compound is readily distinguishable by its melting point

$[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (116.2 - 121.0 °C),
 $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$ (139.3 - 142.0 °C) and $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}[\text{CH}_2\text{CMe}_2(\text{C}_6\text{H}_4)]$ (202.2 - 205.5 °C).

Orthometallation reactions of amino-alanes^{7,8} and -gallanes^{9, 10} have been reported previously. However, in all of these examples the metallated aromatic ring was bonded to nitrogen. Thus, the alkyl group which was originally bonded to the group 13 element and a proton which was bonded to the aromatic ring were eliminated and a heterocyclic ring of carbon, nitrogen and the group 13 element was formed. The cyclometallation reaction in the present cases is different because both substituents involved in the elimination were originally bonded to gallium and a heterocyclic ring consisting of only gallium and carbon is most unusual. This metallocyclic ring apparently is stabilized from undergoing ligand redistribution reactions^{11, 12} because the gallium(III) atom completes its stable four coordinate geometry by formation of the Ga_2N_2 ring.

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 a purified argon atmosphere in a Vacuum Atmospheres drybox equipped with a Dry Train. The starting compounds $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ ¹³, $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ ⁶, $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ ¹³ and $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}$ ⁶ were prepared by using literature methods. 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 δ (ppm) and are referenced to tetramethylsilane (TMS) as $\delta = 0.00$ ppm and benzene as $\delta = 7.15$ ppm. Melting points were observed with 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 Drezdson.¹⁴

Synthesis of $(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ from $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{-CMe}_2\text{Ph})_2\text{Cl}]_2\}$ and t-BuNH_2 . A solution of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}]_2\}$ which had been prepared from 0.115 g of Na (5.01 mmol), 0.643 g of C_{10}H_8 (5.01 mmol) and 1.86 g of $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}$ (5.00 mmol) in 40-50 mL of THF at -78°C was reacted with 0.435 g of t-BuNH_2 (5.95 mmol) as described previously.^{1, 4} The resulting solution was stirred at ambient temperature for 6-8 h and the color changed from bright yellow to colorless. After an additional 12 h at 20°C , the volatile materials ($\text{C}_{10}\text{H}_{10}$ and THF) were removed by vacuum distillation. The remaining nonvolatile material was separated by extraction with pentane into insoluble (0.286 g of NaCl, 4.93 mmol, 98.6% recovered based on Na) and soluble components. The nonvolatile, soluble material was recrystallized from pentane at -78°C and identified as $(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ (1.96 g, 4.80 mmol, 96.0% yield based on $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}$). Crystallographic quality crystals were grown by slowly cooling a heated saturated benzene solution to ambient temperature. Crystals were mounted directly from the benzene solution without removal of solvent.

$[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. Mp: $139.3\text{-}142.0^\circ\text{C}$. ^1H NMR (C_6D_6 , δ) (400 MHz): 7.48 (d, 4.0 H, *o*-Ar (cis Ph), $^3J_{\text{CCH}} = 6.80$ Hz), 7.44 (d, 6.0 H, *o*-Ar (trans Ph), $^3J_{\text{CCH}} = 8.00$ Hz), 7.33 (d, 4.0 H, *o*-Ar (cis Ph), $^3J_{\text{CCH}} = 7.60$ Hz), 7.22 (m, 14.0 H, *m*-Ar (trans Ph) + *m*-Ar (cis Ph) + *m*-Ar (cis Ph)), 7.05 (m, 6.5 H, *p*-Ar (trans Ph) + *p*-Ar (cis Ph) + *p*-Ar (cis Ph)), 1.49 (s, 9.0 H, CMe_2 (trans)), 1.48 (s, 12.0 H, CMe_2 (cis)), 1.47 (s, 3.6 H, NH (trans + cis)), 1.42 (s, 9.6 H, CMe_2 (trans)), 1.40 (s, 12.0 H, CMe_2 (cis)), 1.32 (d, 3.2 H, CH_2 (trans), $^2J_{\text{CH}} = 14.8$ Hz), 1.18 (d, 3.2 H, CH_2 (trans), $^2J_{\text{CH}} = 13.6$ Hz), 1.12 (s, 1.8 H, CH_2 (cis)), 0.97 (s, 2.3 H, CH_2 (cis)), 0.93 (s, 18.1 H, CMe_3 (cis t-Bu)), 0.89 (s, 4.0 H, CH_2 (cis)), 0.86 (s, 13.4 H, CMe_3 (trans t-Bu)). The ^1H NMR spectrum indicated 44% cis and 56% trans ($\pm 5\%$). The 300 MHz ^1H NMR spectrum (C_6D_6) confirmed the assignment of the geminal coupling constant for CH_2 for

the neophyl group in the trans isomer. IR (Nujol, cm^{-1}): 3290 (m), 3240 (m), 3081 (m), 3055 (s), 3015 (s), 2720 (m), 1941 (w), 1880 (w), 1866 (w), 1801 (w), 1740 (w), 1596 (m), 1577 (m), 1491 (s), 1278 (m), 1228 (m), 1195 (s), 1174 (s), 1139 (w), 1100 (w), 1075 (sh, m), 1069 (m), 1029 (m), 1020 (w), 972 (w), 960 (w), 945 (w), 931 (m), 915 (m), 901 (m), 898 (sh, m), 890 (m), 872 (s), 759 (vs), 712 (m), 645 (vs), 631 (m), 620 (m), 605 (m), 598 (m), 581 (m), 552 (m), 541 (m), 500 (vw), 498 (vw), 470 (w), 455 (w), 445 (w), 392 (w), 275 (w), 239 (w). Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{GaN}$: C, 70.61; H, 8.89. Found: C, 70.40; H, 9.07. Cryoscopic molecular weight, benzene solution, formula weight 408.27 (observed molality, observed mol wt, association): 0.0786, 799, 1.96; 0.0636, 800, 1.96; 0.0467, 827, 2.03. Solubility: soluble in THF, benzene, and toluene; slightly soluble in pentane.

Synthesis of $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$. Reaction of $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$ with t-BuNH_2 . The yellow gallium(III) dihydronaphthalene derivative $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$ was prepared in THF¹ at -78°C by using 0.117 g (5.09 mmol) Na, 0.655 g (5.11 mmol) C_{10}H_8 , 1.26 g (5.10 mmol) $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ and 40-50 mL of THF at -78°C in a Solv-Seal reaction flask and then t-BuNH_2 (0.550 g, 7.52 mmol) was added by vacuum distillation. As the solution was warmed from -196 to -78°C , a large amount of colorless precipitate formed and the solution became bright golden yellow. Then the solution was stirred for 5 d at ambient temperature. The resulting product mixture was very light brown. The THF and volatile materials were removed by vacuum distillation and then the remaining material was subjected to dynamic vacuum for 24 h. The material less volatile than the bulk THF (2.20 g) was collected in a small weighed trap and identified by ^1H NMR spectroscopy¹³ as $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ (0.66 mmol, 13% based on $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$), C_{10}H_8 (2.4 mmol, 96% recovered based on 1/2 initial C_{10}H_8) and $\text{C}_{10}\text{H}_{10}$ (1.2 mmol, 46% based on 1/2 initial C_{10}H_8). Extraction of the nonvolatile material through a glass frit with pentane separated NaCl (0.262 g, 4.48 mmol, 87.8% yield based on Na) from a pentane soluble, slightly

brown solid. This soluble material was recrystallized twice from pentane at -78°C to yield a colorless solid which was identified as $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ (0.765 g, 2.69 mmol, 52.7% based on $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$). The soluble brown product which did not crystallize is $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ ¹ (See Results and Discussion). The total amount of gallium recovered as $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$, $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$, and $[\text{Ga}(\text{CH}_2\text{CMe}_3)]_n$ (4.01 mmol) accounted for ~80% of the initial gallium.

$[(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. Mp: 203.4-205.1 $^{\circ}\text{C}$. ^1H NMR (C_6D_6 , δ) (400 MHz): 1.44 (s-br, 2.0 H, -NH (cis)), 1.31 (s-br, 0.50 H, -NH (trans)), 1.27 (s, 18.0 H, -CMe₃ (cis-neopentyl)), 1.24 (s, 7.7 H, -CMe₃ (trans neopentyl)), 1.21 (s, 18.0 H, -CMe₃ (cis neopentyl)), 1.19 (s, 21.5 H, -CMe₃ (cis and trans -N(t-Bu))), 1.14 (s, 4.0 H, -CH₂- (cis)), 1.11 (d, 0.9 H, -CH₂- (trans), $^2J_{\text{CH}} = 13.6$ Hz), 1.00 (d, 0.9 H, -CH₂- (trans), $^2J_{\text{CH}} = 13.6$ Hz), 0.90 (s, 4.0 H, -CH₂- (cis)). The ^1H NMR spectrum indicated 82% cis and 18% trans ($\pm 5\%$). A 300 MHz ^1H NMR spectrum confirmed the geminal coupling constant for the -CH₂- protons of the neopentyl group in the trans isomer. ^1H NMR (CD_2Cl_2 , δ) (400 MHz): 1.40 (s-br, 2.0 H, -NH (cis)), 1.35 (s-br, 0.43 H, -NH (trans)), 1.31 (s, 18.0 H, -CMe₃ (cis-neopentyl)), 1.27 (s, 4.0 H, -CMe₃ (trans neopentyl)), 1.10 (s, 26.7 H, -CMe₃ (trans neopentyl) + -CMe₃ (cis and trans -N(t-Bu))), 1.06 (s, 18.0 H, -CMe₃ (cis neopentyl)), 0.96 (d, 0.86 H, -CH₂- (trans), $^2J_{\text{CH}} = 13.2$ Hz), 0.92 (s, 4.0 H, -CH₂- (cis)), 0.86 (d, 0.86 H, -CH₂- (trans), $^2J_{\text{CH}} = 13.2$ Hz), 0.73 (s, 4.0 H, -CH₂- (cis)). The ^1H NMR spectrum indicated 81% cis and 19% trans ($\pm 5\%$). IR (Nujol, cm^{-1}): 3460 (m), 3390 (m), 2730 (m), 2701 (m), 2380 (w), 2280 (w), 1841 (w), 1662 (w), 1590 (s), 1342 (s), 1222 (vs), 1191 (vs), 1179 (vs), 1165 (vs), 1140 (s), 1129 (s), 1111 (s), 1104 (m), 1029 (m), 1012 (m), 1001 (s), 929 (s), 900 (vs), 855 (vs), 744 (vs), 718 (m), 695 (vs), 665 (m), 603 (s), 579 (vs), 542 (m), 528 (w), 488 (w), 467 (m), 449 (w), 388 (m), 285 (m), 259 (m), 268, 238 (m). Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{GaN}$: C, 59.18; H, 11.35. Found: C, 59.09; H, 11.31. Cryoscopic molecular weight, benzene solution, formula

weight 284.13 (observed molality, observed mol wt, association): 0.0262, 609, 2.14; 0.0219, 618, 2.17; 0.0168, 563, 1.98.

Synthesis of $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ from $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ and t-BuNH_2 . A break-seal reaction tube which was charged with $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ (1.34 g, 4.72 mmol) and t-BuNH_2 (0.345 g, 4.72 mmol) was evacuated, sealed and heated for 1 d at 140 - 150 °C. The initial solid, presumably the adduct, melted and then resolidified with heating. Noncondensable gas was not observed after the tube was opened. Neopentane CMe_4 (0.317 g, 4.40 mmol, 93.2% yield) was removed from the tube by vacuum distillation at ambient temperature and identified by ^1NMR spectroscopy. The colorless solid in the reaction tube was sublimed under vacuum at 90-110 °C to the upper part of tube and then purified by two recrystallizations from pentane at -78 °C. The final recrystallized, colorless solid was identified as $(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})$ (1.02 g, 3.60 mmol, 76.4% yield). Characterization data for this product were identical within normal experimental error with the data for the compound prepared from $\text{Na}_2\{\text{C}_{10}\text{H}_8[\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2\}$ and t-BuNH_2 .

$[(\text{Me}_3\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. Mp: 204.1-207.5 °C. The ^1H NMR spectrum in C_6D_6 indicated 79% cis and 21% trans ($\pm 5\%$). Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{GaN}$: C, 59.18; H, 11.35. Found: C, 59.32; H, 11.40.

Synthesis of $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ from $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ and t-BuNH_2 at 140-150 °C. A break-seal reaction tube was charged with $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ (1.88 g, 4.00 mmol) and t-BuNH_2 (0.295 g, 4.03 mmol) and heated for 4 d at 140-145 °C. No noncondensable gas was formed. The product volatile at ambient temperature was isolated by vacuum distillation and identified by ^1H NMR spectroscopy as $\text{C}_6\text{H}_5\text{CMe}_3$ (0.749 g, 5.58 mmol, 93.0% based on eq 3). After the nonvolatile, colorless solid remaining in the reaction tube was combined with ~ 50 mL benzene, the resulting solution was filtered through a medium glass frit. Subsequent

recrystallization from pentane at -78°C led to the isolation of colorless crystals which became opaque when pentane was removed. The recrystallized, colorless solid was identified as $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (1.36 g, 1.99 mmol, 99.5% yield based on eq 3). Crystallographic quality crystals were obtained by slowly cooling a heated toluene solution to ambient temperature. Crystals were mounted directly from the solution without removing solvent.

$[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$. Mp: $116.2\text{--}121.0^{\circ}\text{C}$.

^1H NMR (C_6D_6 , δ) (400 MHz): 7.82 (d) + 7.80 (m) (*o*-Ar (cis and trans C_6H_4), 7.50 (m, *o*-Ar (cis and trans C_6H_5)), 7.45 (d, *p*-Ar (cis and trans C_6H_4)), 7.34 (m), 7.22 (br-m), 7.10 (br-m), 7.04 (d), 6.97 (br-m, part of br-m of *p*-Ar + *m*-Ar for cis and trans C_6H_4 and C_6H_5), 1.61 (s), 1.59 (s, cis and trans NH), 1.56 (s), 1.55 (s), 1.54 (s), 1.48 (s, cis and trans CMe_2 for $\text{CH}_2\text{CMe}_2\text{Ph}$ and cyclo- $\text{GaCH}_2\text{CMe}_2\text{C}_6\text{H}_4$), 1.47 (s), 1.43 (s, cis and trans NH), 1.41 (s), 1.37 (s), 1.33 (s), 1.32 (s, cis and trans CMe_2 and CH_2 for $\text{CH}_2\text{CMe}_2\text{Ph}$ and cyclo- $\text{GaCH}_2\text{CMe}_2\text{C}_6\text{H}_4$), 1.21 (s), 1.20 (s), 1.11 (s), 1.07 (s), 1.04 (s), 1.01 (s), 0.97 (s, cis and trans CH_2 for $\text{CH}_2\text{CMe}_2\text{Ph}$ and cyclo- $\text{GaCH}_2\text{CMe}_2\text{C}_6\text{H}_4$), 0.92 (s, cis or trans CMe_3), 0.87 (s), 0.86 (s, cis and trans CH_2 for $\text{CH}_2\text{CMe}_2\text{Ph}$ and cyclo- $\text{GaCH}_2\text{CMe}_2\text{C}_6\text{H}_4$), 0.83 (s) + 0.82 (s, cis or trans CMe_3), 0.78 (s), 0.75 (s), 0.61 (s, cis and trans CH_2 for $\text{CH}_2\text{CMe}_2\text{Ph}$ and cyclo- $\text{Ga}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)$). The ratio of cis and trans isomers could not be determined (See Results and Discussion). IR (Nujol, cm^{-1}): 3252 (s), 3229 (s), 3220 (s), 3105 (s), 3082 (s), 3059 (s), 3030 (s), 3019 (vs), 2721 (m), 1942 (m), 1904 (m), 1884 (m), 1865 (m), 1840 (m), 1802 (m), 1744 (m), 1663 (m), 1599 (m), 1578 (m), 1490 (s), 1389 (s), 1278 (m), 1260 (m), 1230 (m), 1205 (sh, s), 1192 (vs), 1175 (vs), 1151 (m), 1139 (m), 1130 (m), 1119 (m), 1097 (m), 1075 (m), 1068 (s), 1045 (m), 1038 (m), 1026 (s), 1015 (m), 998 (w), 975 (w), 961 (w), 942 (m), 926 (s), 907 (s), 902 (sh, s), 895 (s), 872 (vs), 860 (s), 855 (sh, s), 839 (w), 830 (w), 760 (vs), 750 (m), 722 (s), 712 (s), 698 (vs), 680 (sh, m), 670 (m), 655 (m), 629 (m), 618 (m), 594 (s), 580 (m), 566 (m), 555 (s), 540 (m), 498 (w), 469 (m), 451 (w), 435 (w), 392 (m), 358 (w),

318 (w), 290 (w), 275 (w), 269 (m), 240 (m). Anal. Calcd for $C_{38}H_{58}Ga_2N_2$: C, 66.89; H, 8.57. Found: C, 66.77; H, 8.79. Cryoscopic molecular weight, benzene solution, formula weight 682.33 (observed molality, observed mol wt, association): 0.0914, 665, 0.98; 0.0745, 673, 0.99; 0.0544, 680, 1.00.

Synthesis of $[(H_4C_6)Me_2CCH_2]Ga[NH(t-Bu)]_2Ga[CH_2CMe_2(C_6H_4)]$ from $Ga(CH_2CMe_2Ph)_3$ and $t-BuNH_2$ at 210-240 °C. A break-seal reaction tube, which had been charged with $Ga(CH_2CMe_2Ph)_3$ (2.14 g, 4.55 mmol) and $t-BuNH_2$ (0.333 g, 4.55 mmol) and sealed, was heated for 4 d at 210-230 °C in a tube furnace. The tube was then cooled to -196 °C and opened. Noncondensable gas was not observed. The volatile product was isolated by vacuum distillation and identified by 1H NMR spectroscopy as $C_6H_5CMe_3$ (1.07 g, 7.94 mmol, 87.3% based on eq4). The remaining nonvolatile, colorless solid was removed from the reaction tube with ~ 50 mL benzene, purified by recrystallization from toluene at -78 °C and identified as $[(H_4C_6)Me_2CCH_2]Ga[NH(t-Bu)]_2Ga[CH_2CMe_2(C_6H_4)]$ (0.660 g, 1.20 mmol, 56.1% yield based on eq 4). Removal of toluene caused the recrystallized, colorless crystals to become opaque. Thus, crystals were mounted directly from a toluene solution but the structure could not be solved.

$[(H_4C_6)Me_2CCH_2]Ga[NH(t-Bu)]_2Ga[CH_2CMe_2(C_6H_4)]$. Mp: 202.2 - 205.5 °C. 1H NMR (C_6D_6 , δ) (400 MHz): 7.80 (d, 2.9 H, *o*-Ar (trans t-Bu) + *o*-Ar (cis t-Bu)), $^3J_{CCH} = 7.60$ Hz), 7.54 (d, 2.9 H, *p*-Ar (trans t-Bu) + *p*-Ar (cis t-Bu)), $^3J_{CCH} = 6.80$ Hz), 7.32 (m, 5.8 H, *m*-Ar (trans t-Bu) + *m*-Ar (cis t-Bu)), 1.85 (s, 0.8 H, NH (cis t-Bu)), 1.70 (s, 2.0 H, NH (trans t-Bu)), 1.57 (s, 6.0 H, CMe_2 (trans t-Bu)), 1.56 (s, 2.6 H, CMe_2 (cis)), 1.55 (s, 8.7 H, CMe_2 (trans t-Bu) + CMe_2 (cis t-Bu)), 1.09 (s, 0.80 H, CH_2 (cis t-Bu)), 1.07 (d, 2.0 H, CH_2 (trans t-Bu)), $^2J_{CH} = 14.8$ Hz), 0.93 (s, 0.8 H, CH_2 (cis t-Bu)), 0.91 (s, 7.6 H, CMe_3 (cis t-Bu)), 0.88 (s, 18.0 H, CMe_3 (trans t-Bu)), 0.83 (d, 2.0 H, CH_2 (trans t-Bu)), $^2J_{CH} = 14.8$ Hz). The 1H NMR spectrum was consistent with species which had C_6H_4 groups trans to each other and with

t-Bu groups on nitrogen oriented to give a mixture of isomers, 19% cis and 81% trans ($\pm$ 5%). See Results and Discussion. The 300 MHz ^1H NMR spectrum was identical to the 400 MHz spectrum. IR (Nujol, cm^{-1}): 3250 (m), 3110 (m), 3060 (m), 3035 (s), 2720 (m), 1951 (w), 1920 (w), 1845 (w), 1815 (w), 1750 (w), 1580 (w), 1412 (m), 1392 (m), 1350 (s), 1342 (s), 1308 (m), 1275 (m), 1261 (m), 1230 (m), 1220 (m), 1198 (s), 1172 (m), 1155 (m), 1118 (w), 1100 (m), 1079 (m), 1045 (m), 1038 (m), 1030 (m), 1019 (w), 1000 (w), 972 (w), 948 (w), 928 (s), 909 (s), 871 (vs), 845 (m), 830 (w), 762 (vs), 750 (m), 728 (s), 718 (m), 710 (m), 649 (s), 594 (s), 563 (m), 550 (w), 465 (m), 437 (m), 393 (m), 352 (w), 325 (m), 288 (m). Anal. Calcd for $\text{C}_{28}\text{H}_{44}\text{Ga}_2\text{N}_2$: C, 61.36; H, 8.09. Found: C, 61.13; H, 8.20. The compound had insufficient solubility in benzene for a cryoscopic molecular weight study.

Collection of X-Ray Diffraction Data for $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. A well-defined crystal of approximate orthogonal dimensions $0.25 \times 0.25 \times 0.20$ 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.¹⁵ The Laue symmetry (C_{2h}) indicated the monoclinic system; the systematic absences ($h0\ell$ for $\ell = 2n+1$ and $0k0$ for $k = 2n+1$) uniquely define the ubiquitous centrosymmetric monoclinic space group $\text{P}2_1/\text{c}$ (No. 14).^{16a} A total of 8320 reflections (representing two equivalent forms) were collected, corrected for absorption and merged to yield 2922 independent reflections with $R(\text{int}) = 1.71\%$. Details appear in Table 3.

Determination of Crystal Structure of $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$. 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.¹⁷ The analytical scattering factors for neutral atoms^{18a} were corrected for the $\Delta f'$ and $i\Delta f''$ components of

anomalous dispersion.^{18b} The structure was solved via a combination of Patterson synthesis, difference-Fourier syntheses and least-squares refinement. All non-hydrogen atoms were refined anisotropically. The positional and anisotropic thermal parameters for the hydrogen atom attached to nitrogen (in the μ -NH(t-Bu) ligand) were also refined. All other hydrogen atoms were placed in calculated positions based upon $d(\text{C-H}) = 0.96 \text{ \AA}$.¹⁹ Refinement converged with $R = 2.75 \%$ for those data with $|F_o| > 6.0\sigma(F_o)$.

Collection of X-Ray Diffraction Data for $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$. A well-defined crystal of approximate orthogonal dimensions $0.65 \times 0.25 \times 0.20 \text{ mm}$ was sealed into a thin-walled glass capillary as described above. The crystal was mounted with its extended direction close-to-colinear with the Φ -axis of a Siemens R3m/V automated four-circle diffractometer. The Laue symmetry (C_{2h}) indicated the monoclinic system. The systematic absences (hkl for $h+k = 2n+1$ and $h0\ell$ for $\ell = 2n+1$) indicated the possible space groups $C2/c$ or Cc . Intensity statistics favored the common centrosymmetric space group $C2/c$ (No. 15).^{16b} This choice was verified by the successful solution and refinement of the structure. A total of 14247 reflections (representing two equivalent forms) were collected, corrected for absorption and merged ($R(\text{int}) = 1.45 \%$) to yield 3495 independent non-zero reflections. Reflections were collected via the ω -scan technique because of the potential problems that might be caused by overlap of adjacent reflections when carrying out the more customary 2θ - θ scans along the $40 \text{ \AA}$ a -axis. Details are provided in Table 3.

Determination of Crystal Structure of $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$. This structure was solved as described for the previous structure. Refinement converged with $R = 3.20 \%$ for those data with $|F_o| > 6\sigma(F_o)$.

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Supporting Information Available. 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.

References

1. Beachley, O. T., Jr.; Pazik, J. C.; Noble, M. J. *Organometallics* **1994**, *13*, 2885.
2. Noble, M. J.; State University of New York at Buffalo; Ph. D. Thesis; 1994.
3. (a) Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol.1, p 588 and references therein. (b) Coates, G. E.; Green, M. L. H.; Wade, K., Eds. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1, p 177 and references therein. (c) Cowley, A. H.; Jones, R. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. (d) Schauer, S. J.; Lake, C. H.; Watkins, C. L.; Krannich, L. K.; Powell, D. H. *J. Organomet. Chem.* **1997**, *549*, 31 and references therein.
4. Beachley, O. T., Jr.; Pazik, J. C.; Noble, M. J. *Organometallics* **1998**, *17*, 2121.
5. Beachley, O. T., Jr.; Noble, M. J.; Churchill, M. R.; Lake, C. H. *Organometallics* **1998**, *17*, (In press)..
6. Beachley, O. T., Jr.; Noble, M. J.; Churchill, M. R.; Lake, C. H. *Organometallics* **1992**, *11*, 1051.
7. Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 245.
8. Dillingham, M. D. B.; Hill, J. B.; Lee, B.; Schauer, S. J.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1993**, *28*, 337.

9. Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.
10. Schauer, S. J.; Lake, C. H.; Watkins, C. L.; Krannich, L. K. *Organometallics* **1996**, *15*, 5641.
11. Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R. *J. Organomet. Chem.* **1992**, *434*, 11.
12. Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Toomey, L. M. *Organometallics* **1996**, *15*, 3653.
13. Beachley, O. T., Jr.; Pazik, J. C. *Organometallics* **1988**, *7*, 1516.
14. Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986; p 38.
15. Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.
16. *International Tables for X-Ray Crystallography*, Volume 1 (2nd edition), Kynoch Press, Birmingham, England, **1965**, (a) p 99; (b) p 101.
17. Sheldrick, G. M. SHELXTL PLUS, Release 4.11 (VMS), Siemens Analytical Instrument Corp., Madison, WI, **1989**.
18. *International Tables for X-Ray Crystallography*, Volume 4 Kynoch Press, Birmingham, England, **1974** (a) pp 99-101; (b) pp 149-150.
19. Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table 1
Selected Bond Distances (Å) and Angles (deg) for
 $[(\text{PhMe}_2\text{CCH}_2)\text{GaNH}(\text{t-Bu})]_2$.

(a) Gallium-Ligand bond lengths

Ga(1)–N(1)	2.028(3)	Ga(1)–C(00)	2.007(4)
Ga(1)–N(1A)	2.073(3)	Ga(1)–C(10)	2.003(4)
Ga(1)•••Ga(1A)	3.044(1)		

(b) Distances involving the nitrogen atoms

N(1)–C(21)	1.502(4)	N(1)–Ga(1)	2.028(3)
N(1)–H(1)	0.856(24)	N(1)–Ga(1A)	2.073(3)
N(1)•••N(1A)	2.748(2)		

(c) Angles around gallium

N(1)–Ga(1)–N(1A)	84.2(1)	C(00)–Ga(1)–C(10)	117.9(1)
N(1)–Ga(1)–C(00)	116.0(1)	C(00)–Ga(1)–N(1A)	98.3(1)
N(1)–Ga(1)–C(10)	117.5(1)	C(10)–Ga(1)–N(1A)	116.1(1)

(d) Angles around Nitrogen

Ga(1)–N(1)–Ga(1A)	95.8(1)	Ga(1)–N(1)–H(1)	102.0
Ga(1)–N(1)–C(21)	127.3(2)	Ga(1A)–N(1)–H(1)	99.0
Ga(1A)–N(1)–C(21)	125.6(2)	C(21)–N(1)–H(1)	101.6

Table 1 (Continued)(e) Ga-C(α)-C(β) angles

Ga(1)-C(00)-C(01) 124.6(2)

Ga(1)-C(10)-C(11) 128.9(2)

Table 2

Selected Bond Distances (Å) and Angles (deg) for
 $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$.

(a) Gallium-Ligand bond lengths

Ga(1)—N(3)	2.056(5)	Ga(2)—N(3)	1.993(4)
Ga(1)—N(4)	2.036(3)	Ga(2)—N(4)	2.006(5)
Ga(1)—C(00)	1.991(5)	Ga(2)—C(20)	1.961(6)
Ga(1)—C(10)	1.982(5)	Ga(2)—C(29)	1.977(5)
Ga(1)•••Ga(2)	2.990(1)		

(b) Distances involving the nitrogen atoms

N(3)—C(31)	1.480(9)	N(4)—C(41)	1.502(8)
N(3)•••N(4)	2.671(7)		

(c) C—C Distances within GaC₄ ring

C(20)—C(21)	1.537(8)	C(24)—C(29)	1.397(8)
C(21)—C(24)	1.522(9)		

Table 2 (Continued)**(d) C—C Distances within orthometallated phenyl system**

C(24)—C(25)	1.395(9)	C(27)—C(28)	1.383(9)
C(25)—C(26)	1.361(13)	C(28)—C(29)	1.400(8)
C(26)—C(27)	1.367(12)	C(29)—C(24)	1.397(8)

(e) Angles around gallium atoms

N(3)—Ga(1)—N(4)	81.8(2)	N(3)—Ga(2)—N(4)	84.1(2)
N(3)—Ga(1)—C(00)	106.1(2)	N(3)—Ga(2)—C(20)	127.6(2)
N(3)—Ga(1)—C(10)	116.8(3)	N(3)—Ga(2)—C(29)	117.5(2)
N(4)—Ga(1)—C(00)	114.8(2)	N(4)—Ga(2)—C(20)	115.1(2)
N(4)—Ga(1)—C(10)	113.9(2)	N(4)—Ga(2)—C(29)	125.0(2)
C(00)—Ga(1)—C(10)	118.0(2)	C(20)—Ga(2)—C(29)	91.5(2)

(f) Angles around nitrogen atoms

Ga(1)—N(3)—Ga(2)	95.2(2)	Ga(1)—N(4)—Ga(2)	95.4(2)
Ga(1)—N(3)—C(31)	130.1(3)	Ga(1)—N(4)—C(41)	126.0(3)
Ga(2)—N(3)—C(31)	125.1(3)	Ga(2)—N(4)—C(41)	120.0(3)

(g) Angles within the GaC₄ ring

Ga(2)—C(20)—C(21)	107.7(4)	C(21)—C(24)—C(29)	121.0(5)
C(20)—C(21)—C(24)	111.8(5)	C(24)—C(29)—Ga(2)	107.6(4)

Table 2 (Continued)

(h) Angles within orthometallated phenyl system

C(29)–C(24)–C(25)	119.5(6)	C(26)–C(27)–C(28)	119.6(7)
C(24)–C(25)–C(26)	121.5(6)	C(27)–C(28)–C(29)	121.8(6)
C(25)–C(26)–C(27)	120.0(7)	C(28)–C(29)–C(24)	117.5(5)

(i) Gallium–C(α)–C(β) angles

Ga(1)–C(00)–C(01)	122.8(4)	Ga(2)–C(29)–C(24)	107.6(4)
Ga(1)–C(10)–C(11)	125.8(3)	Ga(2)–C(29)–C(28)	134.9(4)
Ga(2)–C(20)–C(21)	107.7(4)		

Table 3.

Data for the X-Ray Crystallographic Studies of
 $[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$ and
 $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$.

Compound	$[(\text{PhMe}_2\text{CCH}_2)_2\text{GaNH}(\text{t-Bu})]_2$	$[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$
Molec. Formula	$\text{C}_{48}\text{H}_{72}\text{Ga}_2\text{N}_2$	$\text{C}_{38}\text{H}_{58}\text{Ga}_2\text{N}_2$
Crystal System	Monoclinic	Monoclinic
Space Group	$\text{P2}_1/\text{c}$ (No. 14)	$\text{C2}/\text{c}$ (No.15)
a, Å	10.349(3)	40.536(9)
b, Å	13.594(2)	9.4592(14)
c, Å	16.518(4)	21.826(5)
β , °	107.17(2)	116.777(13)
V, Å ³	2220.2(8)	7471.5(23)
Z	2	8
molec wt	816.5	682.4
D, g/cm ³	1.221	1.213
$\mu(\text{Mo K}\alpha)$, mm ⁻¹	1.240	1.462
T, max/min	0.7408/0.8358	0.6185/0.7365
F(000)	872	2896
2 θ range, deg	5 - 45	5 - 40
h	0 to +11	0 to 38
k	-14 to +14	-9 to +9
l	-17 to +16	-20 to +18
Reflections Collected	8320	14247

Table 3 (Cont.)

Independent Reflections	2922 ($R_{\text{int}} = 1.71\%$)	3495 ($R_{\text{int}} = 1.43\%$)
Reflections above 6σ	1978	2261
Weighting Scheme, w^{-1}	$\sigma^2(F) + 0.0003F^2$	$\sigma^2(F) + 0.0003F^2$
χ (secondary extinction)	0.00009(6)	0.000000(7)
Number of parameters refined	236	380
Final R indices (all data)	$R = 5.60\%$ $wR = 3.77\%$	$R = 6.21\%$ $wR = 3.95\%$
R Indices (6σ data)	$R = 2.75\%$ $wR = 2.62\%$	$R = 3.20\%$ $wR = 3.01\%$
Goodness-of-Fit	1.04	1.14
Largest and Mean $\Delta\sigma$	0.007, 0.001	0.002, 0.001
Data-to-Parameter Ratio	12.4:1	9.2:1
Largest Difference Peak, $\text{e}\text{\AA}^{-3}$	0.36	0.39
Largest Difference Hole, $\text{e}\text{\AA}^{-3}$	-0.35	-0.33

Captions to Figures

Figure 1. Molecular geometry and atomic labeling for $[(\text{PhMe}_2\text{CCH}_2)\text{GaNH}(\text{t-Bu})]_2$. [ORTEP2 diagram showing 30 % probability ellipsoids and with hydrogen atoms artificially reduced.]

Figure 2. Molecular geometry and atomic labeling for $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$. [ORTEP2 diagram showing 30 % probability ellipsoids and with hydrogen atoms artificially reduced.]

Figure 3. The puckered Ga_2N_2 ring and the GaC_4 metallocyclic ring in the orthometallated compound $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2$.

Figure 4. Geometrical Isomers of $[(\text{H}_4\text{C}_6)\text{Me}_2\text{CCH}_2]\text{Ga}[\text{NH}(\text{t-Bu})]_2\text{Ga}[\text{CH}_2\text{CMe}_2(\text{C}_6\text{H}_4)]$

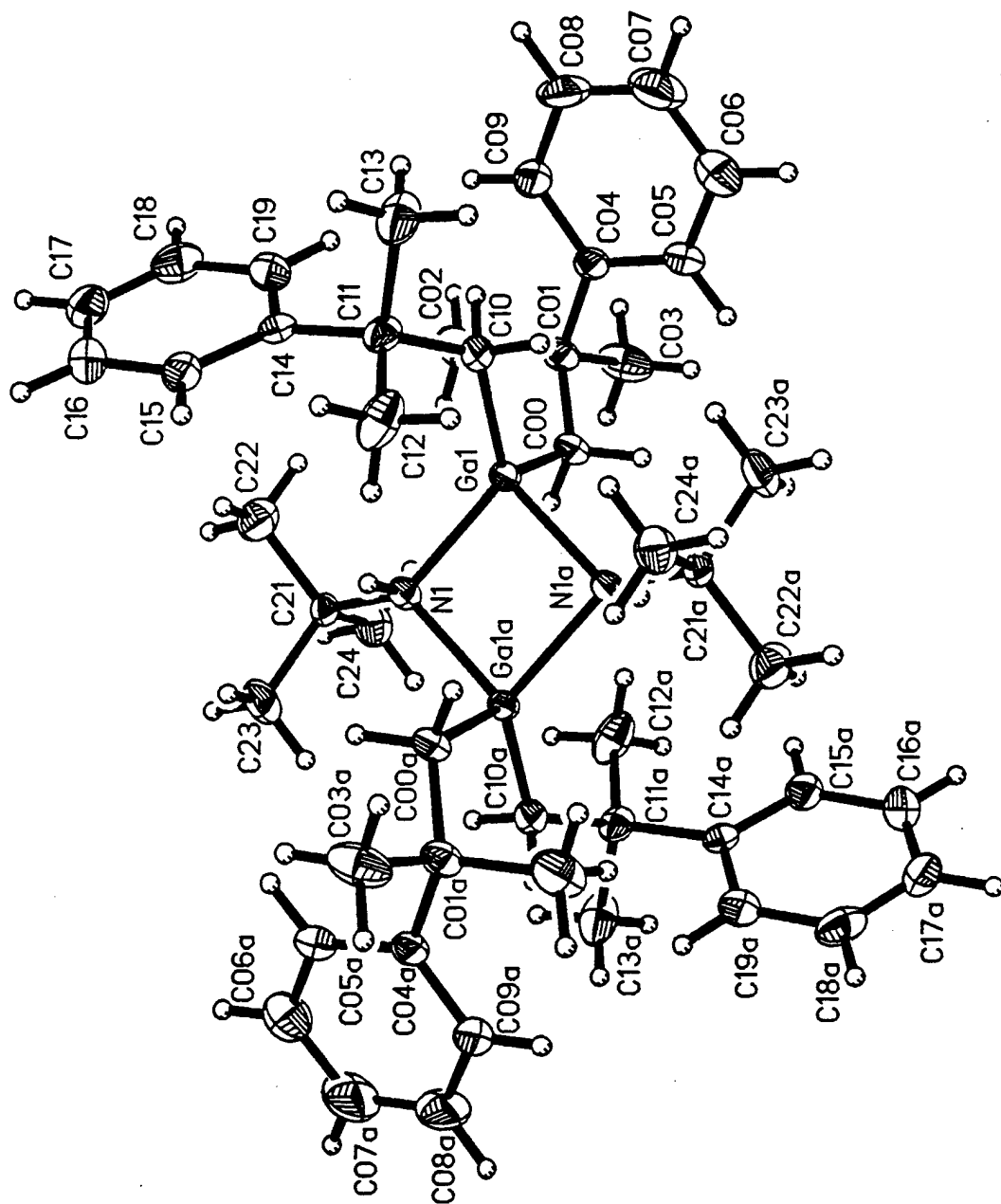


FIG. 1

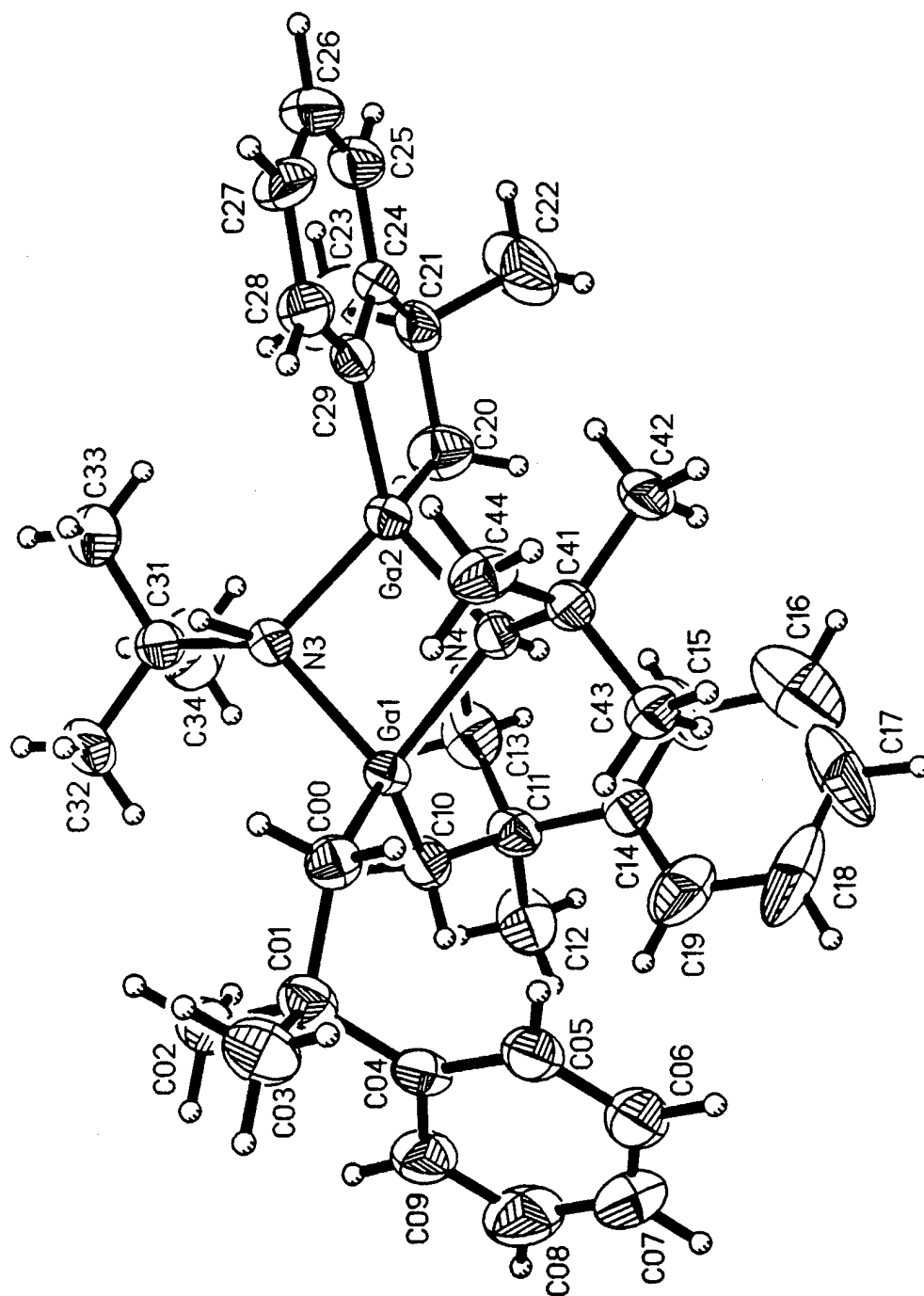


Fig 2

Fig 3

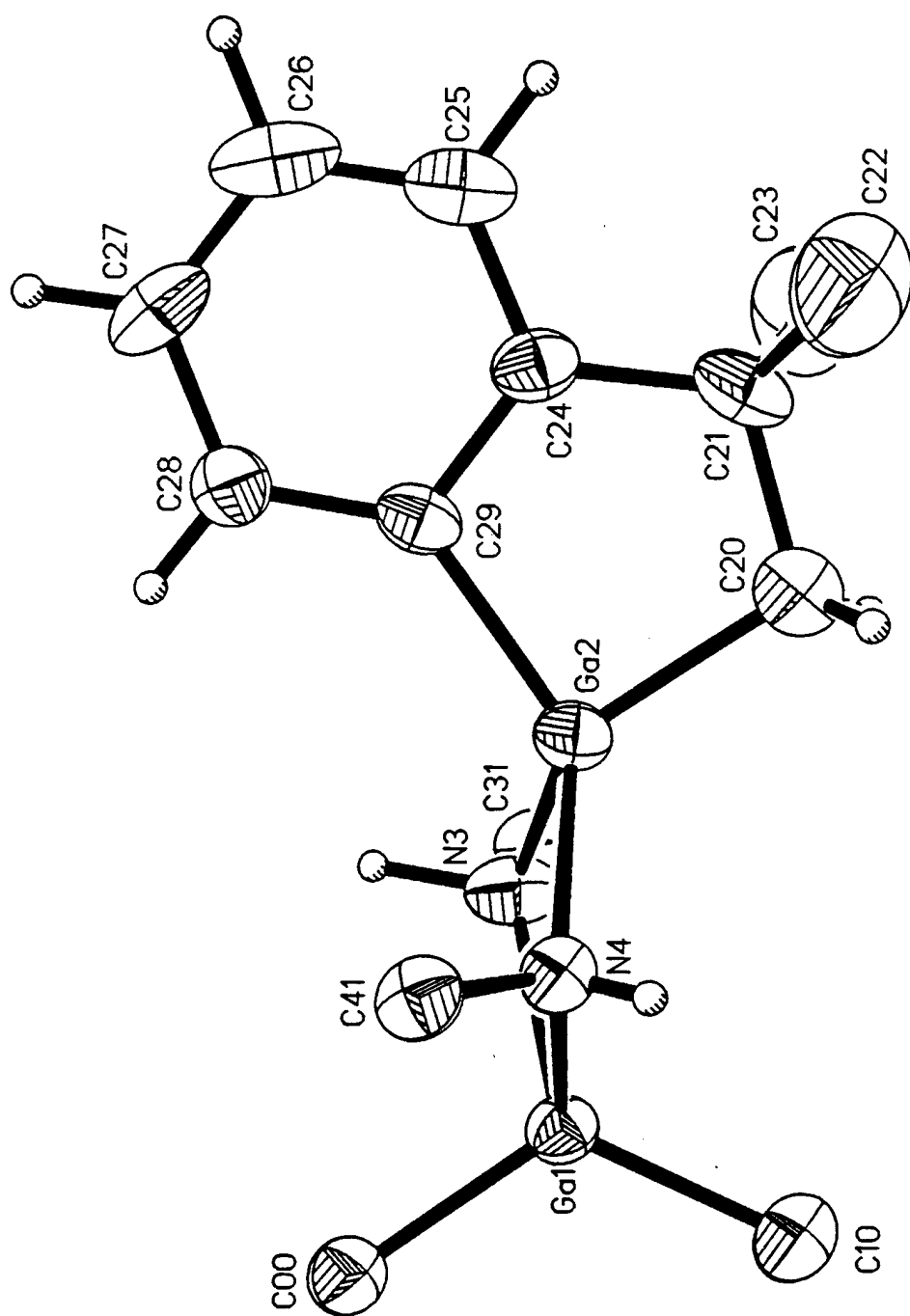
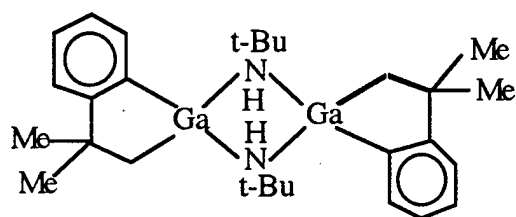
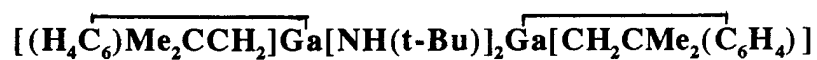
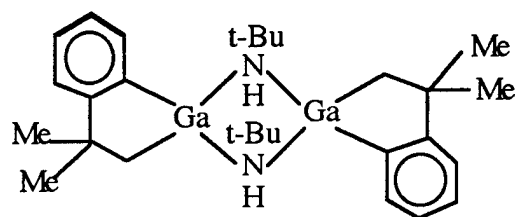


Figure 4

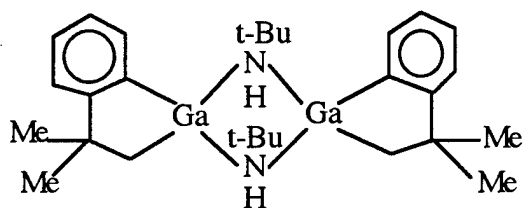
Geometrical Isomers of



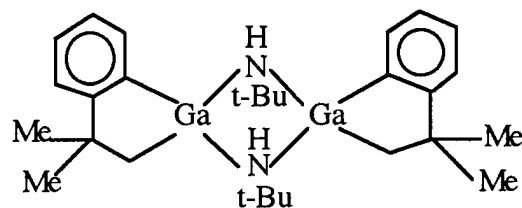
(a) trans / trans



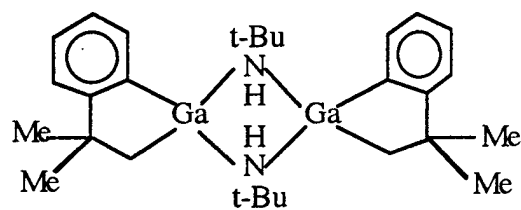
(b) trans / cis



(c) cis / cis (t-Bu groups up)



(d) cis / cis (H atoms up)



(e) cis / trans

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