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# Monomeric Organogallium−Nitrogen Compounds. Chemistry of $Et_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ with Decomposition to the Metallacycle $\{Et\overline{GaNH[C_6H_2(4,6\text{-}t\text{-}Bu)_2CMe_2C}H_2\text{-}2]\}_2$ and of $EtGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$

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Two monomeric gallium−nitrogen compounds, $Et_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ and $EtGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$, have been prepared by metathetical reactions between either $Et_2GaCl$ or $EtGaCl_2$, as appropriate, and $LiNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ and have been characterized fully. Cryoscopic molecular weight studies demonstrated both compounds to be monomeric in benzene solution, whereas an X-ray structural study of the latter identified a monomer. The compound $Et_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ decomposes at room temperature to form a new metallacyclic derivative $\{Et\overline{GaNH[C_6H_2(4,6\text{-}t\text{-}Bu)_2(CMe_2C}H_2\text{-}2)]\}_2$, $GaEt_3$, and $H_2N[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$. A $^1H$ NMR spectral study and an X-ray structural study were used to elucidate its structure. The compound $EtGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$ does not decompose to the metallacycle, but it reacts readily with $GaEt_3$ to form $Et_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$.

## Introduction

Compounds with the simplest formula $R_2GaER'_2$ (E = N, P, As) are usually associated, mostly as dimers but sometimes as trimers.[1] However, monomers have been observed when sterically demanding ligands are incorporated into the molecule. The first fully characterized monomer was $(C_5Me_5)_2GaAs(SiMe_3)_2$,[2] whereas the second was $(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$.[3] It is of interest that of the monomeric gallium−nitrogen compounds of which we are aware $[C_6H_2(2,4,6\text{-}i\text{-}Pr)_3]_2GaNH[C_6H_3(2,6\text{-}i\text{-}Pr)_2]$,[4] $[C_6H_2(2,4,6\text{-}i\text{-}Pr)_3]_2GaNPh_2$,[4] $[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]_2GaN(H)Ph$,[5] $(t\text{-}Bu)_2GaN(t\text{-}Bu)(SiPh_3)$,[4] and $(t\text{-}Bu)_2GaN(1\text{-}adamantyl)(SiPh_3)$,[4] there is no compound that has two simple alkyl groups on gallium and one sterically demanding group on nitrogen. The derivative $Me_2GaNH[C_6H_3(2,6\text{-}i\text{-}Pr)_2]$ is a dimer.[6] We now report the synthesis, characterization, and reaction chemistry of two new monomeric compounds, $Et_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ and $EtGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$.

## Results and Discussion

The monomeric amide $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ was synthesized in high yield by a metathetical reaction between $Et_2GaCl$ and $LiNH[C_6H_2(t\text{-}Bu)_3]$ in pentane at 0 °C. Extraction with pentane gave a soluble, mobile liquid whose $^1H$ NMR spectrum indicated the presence of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ with the free amine $H_2N[C_6H_2(t\text{-}Bu)_3]$ as an impurity. The quantity of amine in the product from 10 independent preparations of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ varied from 1.6 to 16%, but there was no correlation between the level of amine and any known experimental variable. Extensive studies confirmed that the amine was not an impurity in $LiNH[C_6H_2(t\text{-}Bu)_3]$. Rigorously purified reagents and solvents, specially cleaned, handled, and dried glassware, and use of a drybox dedicated to this study and monitored for oxygen and water contamination suggested that the amine was not a product of accidental hydrolysis, and the provenance of the amine remains unknown. It should be noted that the properties of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$, which will be described later, prevented removal of the amine.

A cryoscopic molecular weight study of a sample of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ with less than 5% amine impurity demonstrated the compound to be monomeric in benzene solution. There was no dependence of the observed molecular weight on concentration over the range 0.073−0.047 M. The $^1H$ NMR spectrum of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ in $C_6D_6$ revealed only one set of resonances for the two ethyl groups on gallium at the

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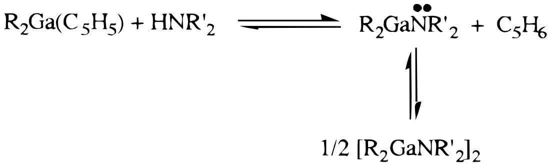
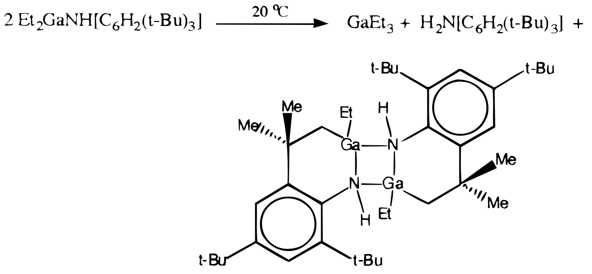
**Scheme 1. Cyclopentadiene Elimination Reaction Sequence**



normal operating temperature of the instrument. Thus, the $C_6H_2(t\text{-}Bu)_3$ substituent is not sufficiently bulky to restrict rotation about the gallium−nitrogen bond and make the two ethyl groups magnetically distinguishable.

The reagents $Et_2Ga(C_5H_5)$[7] and $H_2N[C_6H_2(t\text{-}Bu)_3]$ have the potential to undergo the cyclopentadiene elimination reaction[8−10] to form $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$, but no gallium−nitrogen products could be isolated when this reaction was attempted. In contrast, $Et_2Ga(C_5H_5)$ reacts with many other amines and phosphines at room temperature to form compounds of the type $(Et_2GaER'_2)_n$ in high purity and in high yield.[8] The reagent $Me_2Ga(C_5H_5)$[11] reacts similarily.[9] To reconcile these apparently conflicting observations, a $^1H$ NMR spectroscopic investigation of a reaction mixture of $Et_2Ga(C_5H_5)$ and $D_2N[C_6H_2(t\text{-}Bu)_3]$ in a 1:1 mol ratio in $C_6D_6$ was carried out. Three closely spaced lines rather than the typical intense singlet were observed for the cyclopentadienide protons. These multiple lines are consistent with the presence of a mixture of $Et_2Ga(C_5H_5)$, $Et_2Ga(C_5H_4D)$, $Et_2Ga(C_5H_3D_2)$, etc., and confirm the occurrence of the cyclopentadiene elimination reaction. The intensity of the N−H resonance for the amine increased also, but its broadness prevented meaningful integration. This system was monitored for 17 days by recording repeated $^1H$ NMR spectra, but no change was observed after the initial spectrum. These data suggest that the cyclopentadiene elimination reaction occurs, and the two equilibria shown in Scheme 1 must be used to describe this system. The NMR data suggest that the initial equilibrium shown in Scheme 1 is achieved rapidly, but the equilibrium constant is small. Thus, when $Et_2Ga(C_5H_5)$ reacts with $H_2N[C_6H_2(t\text{-}Bu)_3]$, the gallium−nitrogen product is a monomer which reacts with cyclopentadiene, a weak protonic acid, to reform the reactants. However, when the initially formed gallium−nitrogen product dimerizes, the electron pair on nitrogen is used in bonding and the initial equilibrium in Scheme 1 is shifted to the right to favor formation of the associated organometallic product. Removal of cyclopentadiene by distillation or dimerization also minimizes the possibility of the back reaction and favors the formation of the organogallium−nitrogen product. These observations suggest that the absence of an isolable product from the cyclopentadiene elimination reaction enables one to predict which gallium compounds will be monomeric. Additional research to test this hypothesis is in progress.

The compound $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ decomposes at room temperature to form a metallacyclic compound $\{EtGaNH[C_6H_2(t\text{-}Bu)_2(CMe_2CH_2)]\}_2$, $GaEt_3$, and $H_2N[C_6H_2(t\text{-}Bu)_3]$ as summarized by eq 1. Since this reaction involved the conversion of a mobile liquid to a solid, the rate of decomposition was readily observed. For unknown reasons some samples of the monomeric gallium amide remained mobile liquids for many hours or even days, whereas others decomposed in less than 1 h at room temperature. Even though these experimental observations would suggest that the reaction might involve a catalytic path, we were not able to identify a reagent including $H_2N[C_6H_2(t\text{-}Bu)_3]$, $GaEt_3$, or Li(n-Bu) that influenced the rate of formation of the metallacycle. The decomposition reaction itself was also considered as a potential source of the amine impurity in $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$. However, the $^1H$ NMR spectra of solutions of freshly prepared $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$, which had resonances for the amine, did not exhibit resonances assignable to the metallacycle. The balanced equation for decomposition (eq 1) requires the formation of equimolar amounts of amine and metallacycle (monomer).



(1)

The metallacyclic product $\{EtGaNH[C_6H_2(t\text{-}Bu)_2(CMe_2CH_2)]\}_2$ has been fully characterized and found to be dimeric in benzene solution by a cryoscopic molecular weight study and in the solid state by an X-ray structural study. This species crystallizes in the space group $C2/c$, with $Z = 4$. The dimeric molecule lies about a crystallographic inversion center at (3/4, 3/4, 1/2) and has precise $C_i$ ($\bar{1}$) symmetry. The basic crystallographic asymmetric unit is numbered normally; atoms in the "other half" of the molecule are related to the basic unit by the transformation $[3/2-x, 3/2-y, 1-z]$ and are identified with the suffix "a", as illustrated in Figure 1. The molecule consists of a symmetrical set of five fused rings: a six-membered arene ring, a six-membered metallacycle, a four-membered $Ga_2N_2$ ring, a second six-membered metallacycle, and a final arene ring. The ethyl groups bonded to gallium and the $GaNC_4$ metallacyclic rings are on opposite sides of the molecule and thus have trans orientation. Important interatomic bond distances and angles are collected in Table 1. The central $Ga_2N_2$ portion of the molecule is required to be strictly planar but has only $C_i$ (rather than the possible $D_{2h}$) symmetry because the Ga−N distances show some alternation (Ga(1)−N(1) = Ga(1A)−N(1A) = 2.068(6) Å versus Ga(1)−N(1A) = Ga(1A)−N(1) = 2.021(6) Å, $\Delta = 0.047(8)$ Å). The Ga(1)···Ga(1A) distance of 2.971(2) Å is nonbonding. The angle at Ga(1) is acute (N(1)−Ga(1)−N(1A) = 86.8(2)°), while the supplementary angle at N(1) is obtuse (Ga(1)−N(1)−Ga(1A) = 93.2(2)°).

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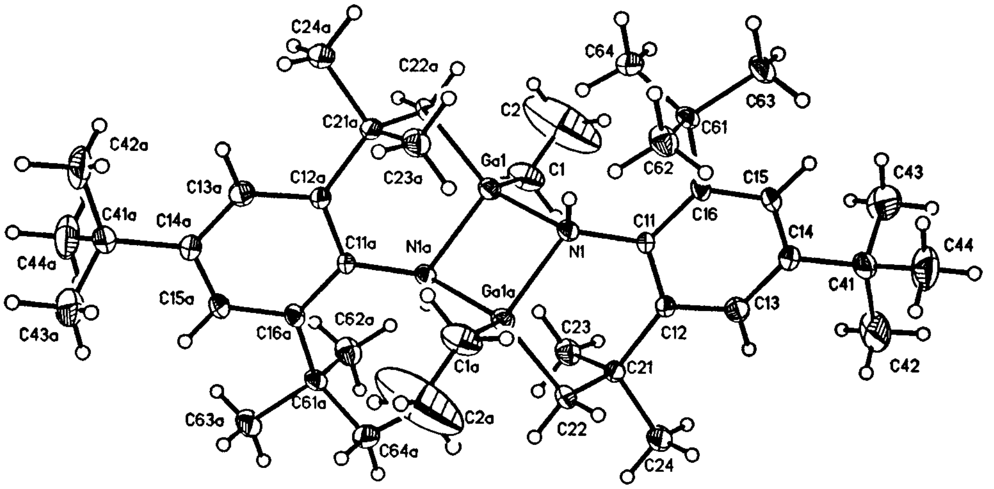


**Figure 1.** Labeling of atoms in the $\{EtGaNH[C_6H_2(t\text{-}Bu)_2CMe_2CH_2]\}_2$ molecules (an ORTEP2 diagram).[24] The 30% probability envelopes are shown for the vibration ellipsoids of all non-hydrogen atoms, while hydrogen atoms are artificially reduced.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for $\{EtGaNH[C_6H_2(t\text{-}Bu)_2CMe_2CH_2]\}_2$**

| | | | |
|---|---|---|---|
| (a) Gallium–Ligand Bond Lengths | | | |
| Ga(1)–N(1) | 2.068(6) | Ga(1)–C(1) | 1.949(8) |
| Ga(1)–N(1A) | 2.021(6) | Ga(1)–C(22A) | 1.952(7) |
| Ga(1)···Ga(1A) | 2.971(2) | | |
| (b) Distances within Metallacyclic Ring | | | |
| N(1)–C(11) | 1.459(10) | C(21)–C(22) | 1.536(11) |
| C(11)–C(12) | 1.414(7) | C(22)–Ga(1A) | 1.952(7) |
| C(12)–C(21) | 1.556(9) | Ga(1A)–N(1) | 2.021(6) |
| (c) Distances within Carbocyclic Ring | | | |
| C(16)–C(11) | 1.412(10) | C(13)–C(14) | 1.371(11) |
| C(11)–C(12) | 1.414(7) | C(14)–C(15) | 1.371(8) |
| C(12)–C(13) | 1.400(13) | C(15)–C(16) | 1.389(13) |
| (d) Angles around Gallium | | | |
| N(1)–Ga(1)–N(1A) | 86.8(2) | C(1)–Ga(1)–C(22A) | 117.2(3) |
| N(1)–Ga(1)–C(1) | 113.6(4) | C(1)–Ga(1)–N(1A) | 122.7(3) |
| N(1)–Ga(1)–C(22A) | 114.7(2) | C(22A)–Ga(1)–N(1A) | 97.8(3) |
| (e) Angles around Nitrogen | | | |
| Ga(1)–N(1)–Ga(1A) | 93.2(2) | Ga(1A)–N(1)–C(11) | 119.6(4) |
| Ga(1)–N(1)–C(11) | 123.6(4) | | |
| (f) Angles within the Metallacyclic Ring | | | |
| Ga(1A)–N(1)–C(11) | 119.6(4) | C(12)–C(21)–C(22) | 111.9(4) |
| N(1)–C(11)–C(12) | 120.8(6) | C(21)–C(22)–Ga(1A) | 116.9(4) |
| C(11)–C(12)–C(21) | 126.1(7) | C(22)–Ga(1A)–N(1) | 97.8(3) |
| (g) Angles within the Carbocyclic Ring | | | |
| C(16)–C(11)–C(12) | 120.4(7) | C(13)–C(14)–C(15) | 116.6(9) |
| C(11)–C(12)–C(13) | 117.1(6) | C(14)–C(15)–C(16) | 124.3(7) |
| C(12)–C(13)–C(14) | 123.9(6) | C(15)–C(16)–C(11) | 117.3(5) |

The original $NH[C_6H_2(t\text{-}Bu)_3]$ ligand has suffered mono-dehydrogenation of a *tert*-butyl group in the 2-position, which results in the formation of a Ga–C(sp$^3$) $\sigma$-bond as part of a six-membered Ga–NH–C(sp$^2$)–C(sp$^2$)–CMe$_2$–CH$_2$ ring. This metallacyclic ring has a nonplanar twist-boat conformation (see Figure 2). Finally, it should be noted that the two very different gallium–carbon linkages are both Ga–C(sp$^3$) linkages and have similar bond lengths, Ga(1)–C(1) = 1.949(8) Å (to the ethyl ligand) and Ga(1)–C(22A) = 1.952(7) Å (to the metallacycle). This Ga–C(Et) distance is comparable to that observed in such other ethyl–gallium molecules as $Et_2Ga(C_5H_5)$,[7] which range from 1.945(9) to 1.979(9) Å, $EtGa(C_5H_5)_2$[7] at 1.960(13) Å, $[Et_2GaP(t\text{-}Bu)_2]_2$[10] at 1.999(6) and 1.998(6) Å, and $[Et_2GaS(SiPh_3)]_2$[10] at 1.934(14) and 1.971(11) Å.

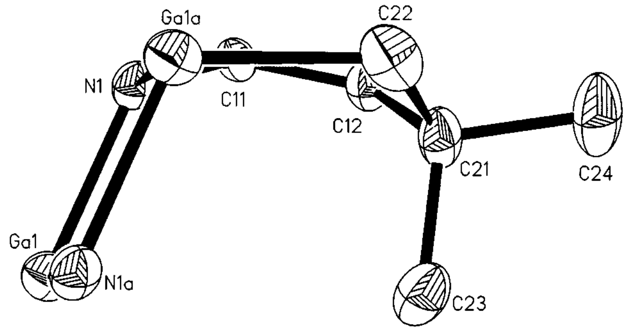
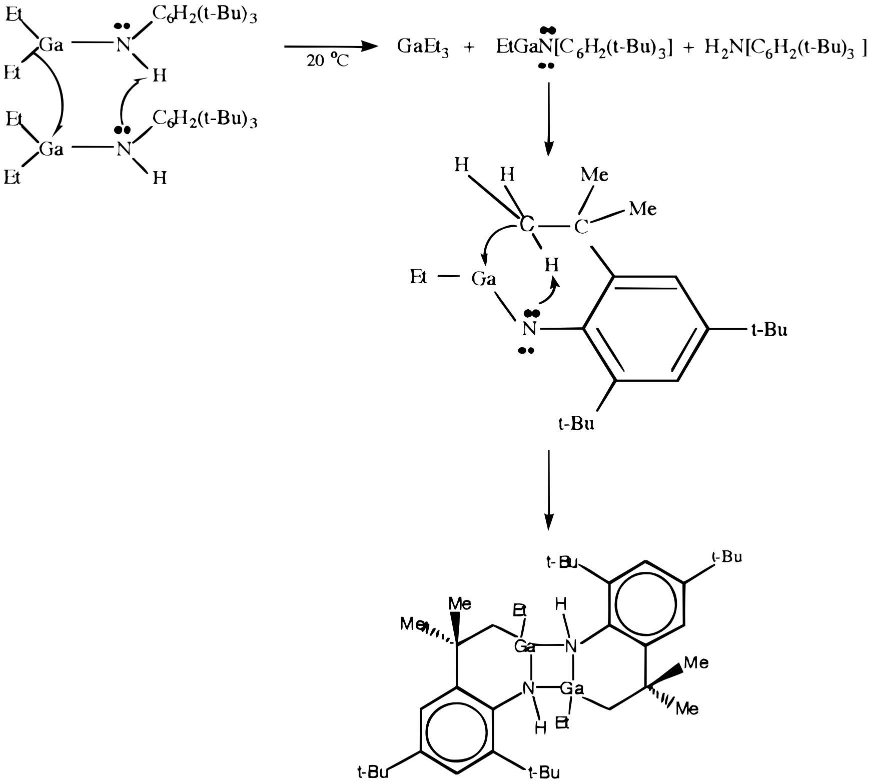


**Figure 2.** Twist-boat conformation of the six-membered metallacyclic ring N(1)–Ga(1A)–C(22)–C(21)–C(12)–C(11). Note the four-membered ring about N(1)–Ga(1A).

The $^1H$ NMR spectrum of $\{EtGaNH[C_6H_2(t\text{-}Bu)_2(CMe_2CH_2)]\}_2$ in benzene solution is consistent with the results of the structural study, as both the ethyl groups bonded to gallium and the $GaNC_4$ metallacyclic rings have trans orientation. However, the phenyl protons are nonequivalent due to the ring orientation. Thus, two sets of closely spaced lines at 7.65 and 7.42 ppm are observed. The resonance for the unique N–H protons in the metallacycle occurs at 4.76 ppm and is readily distinguished from the N–H resonance for $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ at 3.63 ppm. The $-CH_2C(CH_3)_2N$ bridge contains diastereotopic methyl groups, which results in two singlets of equal intensity at 1.76 and 1.59 ppm. Resonances for the *ortho* and *para tert*-butyl group singlets are of equal intensity and appear at 1.49 and 1.37 ppm. The bridging methylene group contains two diastereotopic protons, and thus, two singlets are observed. Since the ratio of the difference in frequency between the two lines and their coupling constant is large, a pseudoquartet appears in the range 1.00–1.20 ppm. A triplet at 0.95 ppm and a quartet at 0.46 ppm due to the ethyl group on gallium complete the spectrum of the metallacyclic compound.

Orthometalation reactions of aminoalanes[12,13] and gallanes[14,15] have been reported. When the results of the current study are compared to those in the literature, many differences including the nature of the reactants, the products, and reaction conditions are

**Scheme 2. Decomposition of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ by Initial Ligand Transfer Reactions**



noted, but the metallacyclic products are analogous. All previous examples[12−15] involved dimeric reactants with decomposition temperatures around 200 °C, whereas the current study reveals a monomer that decomposed at room temperature. The decomposition of a dimer produced a simple hydrocarbon from the organic substituent bonded to the group 13 atom and a proton from the *ortho* alkyl substituent, whereas the decomposition of monomeric $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ formed $GaEt_3$ and $H_2NC_6H_2(t\text{-}Bu)_3$. Ethane was not observed.

Two different reaction paths can be envisioned for the conversion of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ to the metallacycle, $GaEt_3$, and $H_2N[C_6H_2(t\text{-}Bu)_3]$. The pathway that is consistent with our experimental data and the literature involves formal transfer of an ethyl group and an NH proton from one monomer to another to form an acetylenic type of intermediate $EtGaN[C_6H_2(t\text{-}Bu)_3]$ as well as $GaEt_3$ and $H_2N[C_6H_2(t\text{-}Bu)_3]$, as illustrated in Scheme 2. The vacant orbital on gallium and the electron pair on nitrogen in the monomeric unit might facilitate this process. The final steps for the formation of the metallacycle from the unsaturated intermediate $EtGaN[C_6H_2(t\text{-}Bu)_3]$ include the transfer of hydrogen from the *tert*-butyl group to the imine nitrogen and then formation of a new gallium−carbon bond. Dimerization via formation of gallium−nitrogen donor−acceptor bonds gives the final observed product. An alternative pathway (Scheme 3) involves an initial ligand redistribution reaction to form $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ and $GaEt_3$. Transfer of a proton from one amide group to another in $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ would lead to the formation of the amine and the identical unsaturated intermediate as proposed in Scheme 1. Abstraction of hydrogen from a *tert*-butyl group by nitrogen, ring closure, and dimerization would give the observed product.

The hypotheses presented by Scheme 3 was tested by the independent synthesis and characterization of $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$. This compound was prepared by a metathetical reaction between $EtGaCl_2$ and $LiNH[C_6H_2(t\text{-}Bu)_3]$ in a 1:2 mol ratio in pentane. Even though the elemental analyses of this product for carbon and hydrogen were in good agreement with the empirical formula and the melting point range of the compound was less than two degrees, 141.7−143.1 °C, the $^1H$ NMR spectrum of the product in $C_6D_6$ indicated the presence of the amine as an impurity. The level of the amine impurity in products from different synthetic experiments ranged from 6 to 21% according to $^1H$ NMR spectral data, but the metallacycle was present in only trace amounts. Furthermore, $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ does not decompose to form the metallacycle either at room temperature or at the melting temperature of the compound. Numerous $^1H$ NMR spectra of these $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$−amine product mixtures have been recorded over the course of two years without any change in the concentration of $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$, the metallacycle, or the amine. The compound $EtGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ is monomeric in benzene solution over the concentration range 0.040−0.085 M according to a cryoscopic molecular weight study and exhibits chemistry typical of this type of compound. It reacts readily with $GaEt_3$ at room temperature to undergo a ligand redistribution reaction to form $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$.

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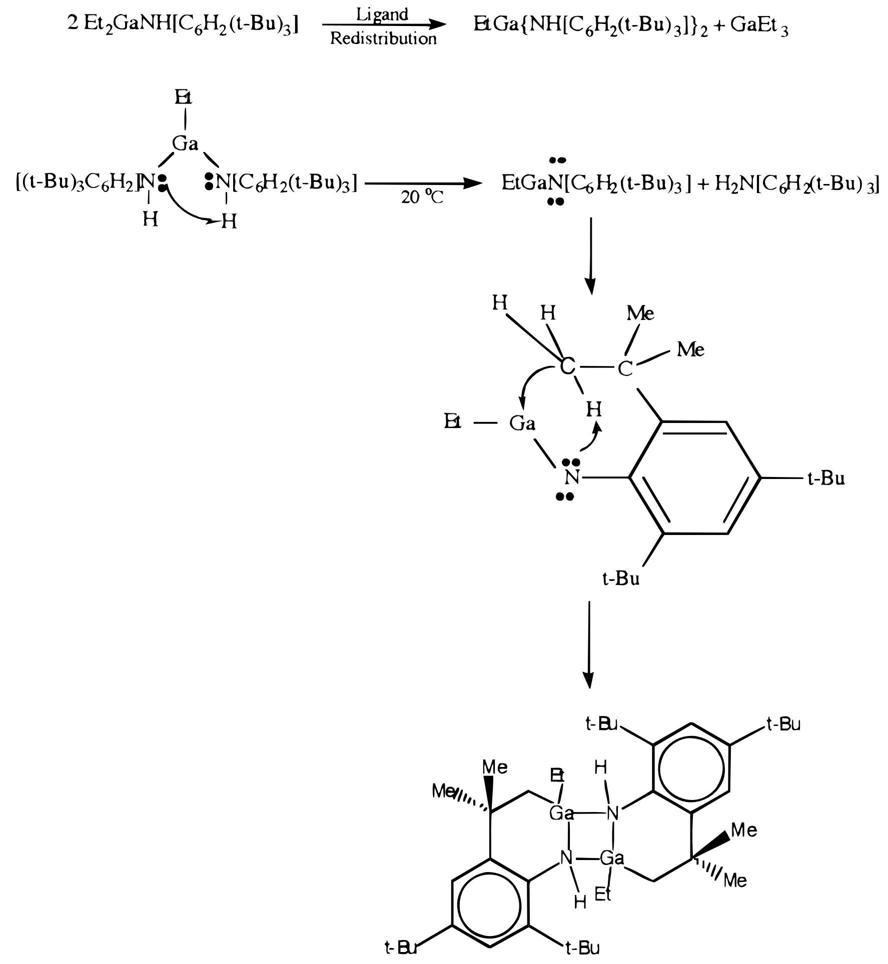
**Scheme 3. Decomposition of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ by Initial Ligand Redistribution Reaction**



## Experimental Section

All compounds were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting materials $GaEt_3$ and Li(n-Bu) were purchased from Strem Chemicals, Inc., and Aldrich Chemical Co., respectively. All solvents were dried by conventional procedures. Deuterated amine $D_2NC_6H_2(t\text{-}Bu)_3$ was prepared by an exchange reaction between $H_2NC_6H_2(t\text{-}Bu)_3$ and $D_2O$ in diethyl ether and then purified by vacuum sublimation at 65 °C. Elemental analyses were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The $^1H$ NMR spectra were recorded at 400 MHz by using a Varian Unity-Inova 400 spectrometer. Proton chemical shifts are reported in $\delta$ (ppm) units and are referenced to $SiMe_4$ at $\delta$ 0.00 ppm and benzene at $\delta$ 7.15 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectra were observed for either neat liquids or Nujol mulls, as appropriate, between KBr plates and were recorded with a Perkin-Elmer 683 spectrometer. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with purified argon and are uncorrected. Molecular weights were measured cryoscopically for benzene solutions by using an instrument similar to that described by Shriver and Drezdzon.[16]

**Preparation of $Et_2GaCl$.** This compound was prepared in essentially quantitative yield from $GaEt_3$ and freshly sublimed $GaCl_3$ in a 2:1 mol ratio in pentane solution at room temperature. (The literature[17] describes a similar reaction between the neat reagents, but elevated temperatures were required for complete reaction.) The pentane was removed by vacuum distillation while maintaining the reaction flask at 0 °C. The remaining colorless liquid was purified by vacuum distillation by using a short-path still with an oil bath temperature of 60 °C, a pressure of less than $10^{-3}$ Torr, and a receiving flask at −196 °C. $Et_2GaCl$: Colorless liquid at room temperature; bp 40−45 °C ($<10^{-3}$ Torr) (lit:[17] 60−62 °C, 2 Torr). $^1H$ NMR ($C_6D_6$, $\delta$): 1.19 (t, $GaCH_2CH_3$, 3H), 0.79 (q, $GaCH_2CH_3$, 2H). IR (Neat, $cm^{-1}$): 2724 (w), 2363 (vw), 2140 (vw), 1412 (m), 1230 (m), 1191 (w), 1000 (s), 957 (m), 938 (m), 655 (vs), 566 (s), 512 (s).

**Preparation of $EtGaCl_2$.** A room-temperature ligand redistribution reaction between 2.489 g (14.14 mmol) of freshly sublimed $GaCl_3$ and 1.109 g (7.07 mmol) of $GaEt_3$ dissolved in approximately 50 mL of pentane was used to prepare 3.498 g of $EtGaCl_2$ (20.61 mmol, 97.3% yield) as a colorless crystalline solid. The compound was purified by sublimation at room temperature between two flasks connected by an elbow. $EtGaCl_2$: Mp 50.5−51.4 °C (lit:[18] 44−45 °C). $^1H$ NMR ($C_6D_6$, $\delta$): 0.89 (t, $GaCH_2CH_3$, 3H), 0.73 (q, $GaCH_2CH_3$, 2H). Anal. Calcd for $C_2H_5GaCl_2$: C, 14.16; H, 2.97; Cl, 41.79. Found: C, 14.20; H, 2.98; Cl, 41.91.

**Reaction of $Et_2Ga(C_5H_5)$ with $D_2NC_6H_2(t\text{-}Bu)_3$.** After an NMR tube was charged with 0.0027 g (0.014 mmol) of $Et_2Ga(C_5H_5)$,[7] 0.0037 g (0.014 mmol) of $D_2NC_6H_2(t\text{-}Bu)_3$, and 0.6 mL of $C_6D_6$ to form a colorless solution, the tube was sealed and spectra were recorded. $^1H$ NMR ($C_6D_6$, $\delta$): 7.40 [s, Ph−H, amine], 6.28 [s, $Ga(C_5H_{5-x}D_x)$], 6.25 [s, $Ga(C_5H_{5-x}D_x)$], 6.22 [s, $Ga(C_5H_{5-x}D_x)$], 3.63 [s, N−H, amine], 1.40 [s, o-(t-Bu)], 1.39 [s, p-(t-Bu)], 0.97 [t, Ga $CH_2CH_3$], 0.18 [q, Ga $CH_2CH_3$].

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[16] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986; p 38.

[17] Eisch, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 3830.

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Resonances due to the ethyl groups for $GaEt_3$ and $EtGa(C_5H_{5-x}D_x)_2$ formed by the ligand redistribution reactions of the cyclopentadienyl gallium compounds[7] were also observed.

**Preparation of $LiNH[C_6H_2(t\text{-}Bu)_3]$.** The reagent $LiNH[C_6H_2(t\text{-}Bu)_3]$ was prepared by slowly adding by using an addition funnel (20 drops/min) a solution of $H_2N[C_6H_2(t\text{-}Bu)_3]$ (5.86 g, 18.6 mmol dissolved in 30 mL of pentane) to a stirred solution of Li(n-Bu) (1.6 M in hexanes, 12 mL, 19.2 mmol, diluted with 20 mL of pentane) which had been cooled to 0 °C. A colorless precipitate was apparent after adding approximately 2 mL of amine solution ~1 min). The reaction mixture was stirred and allowed to warm to room temperature overnight. After the mixture was filtered under vacuum with a coarse frit, the remaining solid was washed three times to provide 4.58 g of $LiNH[C_6H_2(t\text{-}Bu)_3]$ (17.2 mmol, 92.1% based on $H_2N[C_6H_2(t\text{-}Bu)_3]$) as a colorless solid. When Li(n-Bu) was added to the amine, a lower yield of an impure product (which had to be washed with benzene to remove unreacted $H_2N[C_6H_2(t\text{-}Bu)_3]$) was obtained**.** $LiNH[C_6H_2(t\text{-}Bu)_3]$: $^1H$ NMR (THF-$d_8$, $\delta$) 6.78 (s, Ph−H, 2H), 3.03 (s, N−H, 1H), 1.44 (s, o-(t-Bu), 18H), 1.18 (s, p-(t-Bu), 9H).

**Preparation of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$.** A pentane solution of $Et_2GaCl$ (0.954 g, 5.83 mmol) was added with stirring to a slurry of $LiNH[C_6H_2(t\text{-}Bu)_3]$ (1.57 g, 5.87 mmol) which had been cooled to 0 °C. After it had been stirred for 2 h, the product mixture was filtered and washed twice with pentane. The solvent was removed by vacuum distillation at room temperature to leave $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ as a colorless, mobile liquid (0.989 g, 5.21 mmol, 89.3% yield based on $Et_2GaCl$). **$Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$:** Decomposes at room temperature into $GaEt_3$, $H_2N[C_6H_2(t\text{-}Bu)_3]$, and $\{EtGaNH[C_6H_2(t\text{-}Bu)_2CMe_2CH_2]\}_2$ (see Results and Discussion section). $^1H$ NMR ($C_6D_6$, $\delta$): 7.46 (s, Ph−H, 2H), 3.63 (s, N−H, 1H), 1.53 (s, o-(t-Bu), 18H), 1.36 (s, p-Ph-(t-Bu), 9H), 1.05 (t, Ga−$CH_2CH_3$, 6H), 0.55 (q, Ga−$CH_2CH_3$, 4H). (The resonances of the impurity $H_2N[C_6H_2(t\text{-}Bu)_3]$ have been omitted.) IR (neat, $cm^{-1}$): 3510 (vw), 3400 (w), 3090 (w), 2090 (vs), 2735 (vw), 1760 (vw), 1598 (w), 1460 (m), 1450 (m), 1424 (vs), 1372 (m), 1358 (s), 1349 (m), 1282 (m), 1260 (m), 1230 (vs), 1210 (m), 1192 (m), 1115 (m), 998 (m), 957 (w), 937 (w), 918 (w), 872 (m), 830 (m), 812 (w), 780 (m), 742 (m), 738 (w), 710 (w), 638 (m), 612 (m,br), 558 (m), 515 (m), 466 (w), 442 (w). Anal. Calcd for $C_{22}H_{40}GaN$: C, 68.05; H, 10.38. Found: C, 68.57; H, 10.54; C, 68.56; H, 10.50. Cryoscopic molecular weight, benzene solution, formula weight 388 (observed molality, observed molecular weight, association): 0.073, 360, 0.93; 0.047, 361, 0.93.

**Decomposition of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$.** A 0.739 g (1.90 mmol) sample of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ was heated with a 65 °C oil bath for about 12 h to form a colorless solid and a liquid that was volatile at room temperature. The volatile material was isolated by vacuum distillation at room temperature and identified by $^1H$ NMR spectroscopy as $GaEt_3$ (0.083 g, 0.53 mmol). The remaining nonvolatile solid was heated to 80 °C, and a colorless solid sublimed onto a −78 °C coldfinger. This product was identified as $H_2N[C_6H_2(t\text{-}Bu)_3]$ (0.194 g, 0.74 mmol) by comparing its $^1H$ NMR spectrum and melting point with those of an authentic sample. The nonvolatile residue was recrystallized from pentane and identified as $\{EtGaNH[C_6H_2(t\text{-}Bu)_2CMe_2CH_2]\}_2$ (0.386 g, 0.99 mmol). X-ray quality crystals were grown by recrystallization of a pentane solution. $\{EtGaNH[C_6H_2(t\text{-}Bu)_2CMe_2CH_2]\}_2$: Mp 243.6−244.6 °C. $^1H$ NMR ($C_6D_6$, $\delta$): 7.65 (s, Ph−H, 1H), 7.42 (s, Ph−H, 1H), 4.76 (s, N−H, 1H), 1.76 (s, Ph−C($CH_3$)−Ga, 3H), 1.59 (s, Ph−C($CH_3$)−Ga, 3H), 1.49 (s, o-(t-Bu), 9H), 1.37 (s, p-(t-Bu), 9H), 1.10 (d, $J = 13.6$ Hz, Ph−C$(CH_3)_2CH_2$−Ga, 2H), 0.95 (t, $GaCH_2CH_3$, 3H), 0.46 (q, $GaCH_2CH_3$, 2H). IR (Nujol, cm-$^1$): 3380 (m), 1414 (s), 1358 (s), 1282 (m), 1260 (m), 1236 (m), 1220 (m), 1210 (m, sh), 1202 (m), 1198 (m), 1160 (m), 1140 (m), 1122 (vs), 1098 (w), 1060 (m), 996 (m), 940 (w, br), 890 (w), 877 (m), 830 (m), 820 (m), 802 (m), 777 (m), 729 (m), 707 (s), 665 (m), 612 (w), 535 (m), 470 (vw), 450 (vw), 395 (w, br). Anal. Calcd for $C_{20}H_{34}GaN$: C, 67.06; H, 9.57. Found: C, 67.25; H, 9.31. Cryoscopic molecular weight, benzene solution, formula weight 358 (observed molality, observed molecular weight, association): 0.067, 646, 1.80; 0.056, 649, 1.81; 0.037, 648, 1.81. Volatile Liquid ($GaEt_3$): $^1H$ NMR ($C_6D_6$, $\delta$) 1.17 (t, $GaCH_2CH_3$, 3H), 0.44 (q, $GaCH_2CH_3$, 2H). These resonances are identical to those observed for an authentic sample of $GaEt_3$. Volatile Solid ($H_2N[C_6H_2(t\text{-}Bu)_3]$): Mp 144.7−145.8 °C. $^1H$ NMR ($C_6D_6$, $\delta$): 7.40 (s, Ph−H, 2H), 3.63 (s, N−H, 2H), 1.40 (s, o-(t-Bu), 18H), 1.39 (s, p-(t-Bu), 9H). These resonances are identical to those observed for an authentic sample of $H_2N[C_6H_2(t\text{-}Bu)_3]$ (mp 145−146 °C).

**Preparation of $EtGa[N(H)C_6H_2(t\text{-}Bu)_3]_2$.** The reagent $EtGaCl_2$ (0.306 g, 1.80 mmol) dissolved in 25 mL of pentane and cooled to 0 °C was added to 1.02 g (3.82 mmol) of $LiNH[C_6H_2(t\text{-}Bu)_3]$ slurried in 25 mL of pentane at 0 °C. After 2 h of stirring, the mixture was filtered and the insoluble fraction was washed two additional times with pentane. Recrystallization and subsequent removal of pentane by vacuum distillation provided 0.989 g of $EtGa[N(H)C_6H_2(t\text{-}Bu)_3]_2$ (1.60 mmol, 88.6% yield based on $EtGaCl_2$) as a colorless solid. $EtGa[N(H)C_6H_2(t\text{-}Bu)_3]_2$: Mp 146.6−149.2 °C. $^1H$ NMR ($C_6D_6$, $\delta$): 7.52 (s, Ph−H, 4H), 3.30 (s, N−H, 2H), 1.64 (s, o-(t-Bu), 36H), 1.36 (s, p-(t-Bu), 18H), 0.49−0.56 (m, $GaCH_2CH_3$, 5H). (The resonances that were observed for the impurity $H_2N[C_6H_2(t\text{-}Bu)_3]$ have been omitted.) IR (Nujol, $cm^{-1}$): 3405 (m), 1592 (w, br), 1422 (vs), 1358 (vs), 1288 (m), 1265 (m, br), 1225 (s), 1195 (m), 1112 (m), 1010 (w), 963 (w), 876 (m), 840 (w), 827 (m), 812 (w), 780 (w), 750 (w), 738 (w), 720 (w), 540 (w), 470 (w). Anal. Calcd for $C_{38}H_{65}GaN_2$: C, 73.66; H, 10.57. Found: C, 73.45; H, 10.49. Cryoscopic molecular weight, benzene solution, formula weight 620 (observed molality, observed molecular weight, association): 0.085, 573, 0.92; 0.063, 583, 0.94; 0.040, 569, 0.92.

**Ligand Redistribution Reaction between $EtGa[N(H)C_6H_2(t\text{-}Bu)_3]_2$ and $GaEt_3$.** A sample of $GaEt_3$ (0.134 g, 0.854 mmol) was reacted with $EtGa[N(H)C_6H_2(t\text{-}Bu)_3]_2$ (0.528 g, 0.852 mmol) in approximately 20 mL of pentane in a Solv-seal tube. The volatile material was then removed after 2 h by vacuum distillation to leave 0.490 g of $Et_2Ga[N(H)C_6H_2(t\text{-}Bu)_3]$ (1.26 mmol, 73.7% yield) as a colorless, mobile liquid. The $^1H$ NMR spectrum of the product was identical with that observed for an authentic sample.

**Collection of X-ray Diffraction Data for $\{EtGaNH[C_6H_2(t\text{-}Bu)_2\text{-}CMe_2CH_2]\}_2$.** A well-defined transparent colorless crystal of dimensions 0.3 × 0.2 × 0.15 mm was sealed into a thin-walled glass capillary under an argon atmosphere under meticulous anaerobic and moisture-free conditions. Unit cell parameters were determined and intensity data were collected at 24 °C (297 K) on a Siemens R3m/V automated four-circle diffractometer as described previously.[19] Details are provided in Table 2. The Laue symmetry ($C_{2h}$) indicated the monoclinic system. The systematic absences ($hkl$ for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$) indicated the possible space groups $C2/c$ or $Cc$. Intensity statistics favored the common centrosymmetric space group $C2/c$ (No. 15).[20] This choice was verified by the successful solution and refinement of the structure. A total of 5335 reflections (representing two equivalent forms) were collected, corrected for absorption, and merged ($R$(int) = 1.76%) to yield 2598 independent nonzero reflections of which 1521 were considered observed under the condition $|F_o| \geq 6.0\sigma|F_o|$).

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(19) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(20) *International Tables for X-ray Crystallography,* Volume 1 (2nd ed.); Kynoch Press: Birmingham, England, 1965; p 101.

**Table 2. Data for X-ray Crystallographic Studies of {EtGaNH[$C_6H_2$(t-Bu)$_2$CMe$_2$CH$_2$]}$_2$**

| | |
|---|---|
| molecular formula | $C_{40}H_{68}Ga_2N_2$ |
| cryst syst | monoclinic |
| space group | *C*2/*c* (No. 15) |
| *a*, Å | 24.953(4) |
| *b*, Å | 10.626(1) |
| *c*, Å | 18.463(2) |
| $\beta$, deg | 126.16(1) |
| *V*, Å$^3$ | 3952.4(10) |
| *Z* | 4 |
| fw | 716.4 |
| *D*, g/cm$^3$ | 1.204 |
| $\mu$(Mo Kα), mm$^{-1}$ | 1.384 |
| *T*, max/min | 0.8191/0.9711 |
| *F*(000) | 1536 |
| 2$\theta$ range, deg | 5.0−45.0 |
| *h* | 0 to 26 |
| *k* | −11 to 11 |
| *l* | −19 to 16 |
| reflns collected | 5335 |
| ind reflns | 2598 |
| *R*(int) | 1.76% |
| obsd (>6$\sigma$) reflns | 1521 (58.5%) |
| weighting scheme | $\sigma^2(F) + 0.0003F^2$ |
| no. of params refined | 200 |
| final *R* indices (all data)[a] | *R* = 8.38%<br>*wR* = 5.18% |
| *R* indices (6$\sigma$ data)[a] | *R* = 3.98%<br>*wR* = 4.26% |
| goodness-of-fit | 1.31 |
| largest, mean $\Delta/\sigma$ | 0.001, 0.000 |
| data-to-param ratio | 7.6:1 |
| largest diff peak, e Å$^{-3}$ | 0.42 |
| largest diff hole, e Å$^{-3}$ | −0.35 |

[a] *R* indices are defined as follows: $R(\%) = 100\sum||F_o| - |F_o||/\sum|F_o|$; $wR(\%) = 100\sum w(|F_o| - |F_o|)^2/\sum w|F_o|^2$.

**Determination of Crystal Structure of {EtGaNH[$C_6H_2$-(t-Bu)$_2$CMe$_2$CH$_2$]}$_2$.** Crystallographic calculations were performed on a VAX station 3100 computer by use of the SHELXTL PLUS (Release 4.11 (VMS)) program system.[21] The analytical scattering factors for neutral atoms[22a] were corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[22b] The structure was solved by a combination of direct methods, difference Fourier syntheses, and least-squares refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions based upon $d$(C−H) = 0.96 Å.[23] Refinement converged with *R* = 3.98% for those data with $|F_o| > 6.0\sigma(F_o)$. A final difference Fourier map showed no unexpected features ($\rho = -0.35 \rightarrow 0.42$ e/Å$^3$). Diagrams were drawn by using the ORTEP2 routine.[24]

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**Supporting Information Available:** Complete tables of positional parameters, interatomic distance and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms for the compound studied. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990136+

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