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102.72(2)°, V = 1904.5(8)$Å^3$ and Z = 8 (monomeric units). The structure consists of polymeric chains of $[Ga\text{-}C_5H_5]_\infty$ in which each gallium(III) center is linked to two ethyl ligands and is in contact with one carbon atom from each of two bridging C_5H_5 ligands. The other compound $[EtGa(C_5H_5)_2]_\infty$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (No. 19) with a = 8.213(5), b = 9.131(4), c = 14.277(10)Å, V = 1070.7(11) and Z = 4 (monomeric units). The structure was refined to R = 7.01% for those 846 reflections above 6σ. This structure is also polymeric with $[Ga\text{-}C_5H_5]_\infty$ chains. Each gallium(III) center is also bonded to an ethyl ligand and a terminal $\eta^1\text{-}C_5H_5$ ligand. When the compounds are dissolved in either benzene, toluene, cyclohexane, $CHCl_3$ or THF, ligand redistribution reactions occur to form equilibrium mixtures of species. However, when $[Et_2Ga(C_5H_5)]_\infty$ is melted, ^1H NMR spectral studies suggest the existence of only $Et_2Ga(C_5H_5)$ whereas when $[EtGa(C_5H_5)_2]_\infty$ is melted, a single compound does not exist but a mixture of $EtGa(C_5H_5)_2$, $Et_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$ are formed. Mass spectral studies of $Et_2Ga(C_5H_5)$ are consistent with the presence of $Et_2Ga(C_5H_5)$ in the gas phase, but when $[Et_2Ga(C_5H_5)]_\infty$ is heated and vaporized, uncertainty regarding the identities of the species in the gas phase arises due to the occurrence of the ligand redistribution reactions in the melt.

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by

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Abstract

The compounds $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$ have been prepared by ligand redistribution reactions in pentane solution between appropriate quantities of $GaEt_3$ and $Ga(C_5H_5)_3$. Both compounds have been fully characterized by elemental analyses, X-ray structural studies, cryoscopic molecular weight studies in benzene solution, mass spectroscopic studies, ^{1}H NMR studies of solutions and ^{1}H NMR studies of the melts. Both compounds exist as pure single compounds in the solid state. The compound $[Et_2Ga(C_5H_5)]_\infty$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with $a = 7.803(2)$, $b = 15.839(4)$, $c = 16.318(4)$Å, $\alpha = 101.98(2)$, $\beta = 95.23(2)$, $\gamma = 102.72(2)°$, $V = 1904.5(8)$Å^3 and $Z = 8$ (monomeric units). The structure consists of polymeric chains of $[Ga\text{-}C_5H_5]_\infty$ in which each gallium(III) center is linked to two ethyl ligands and is in contact with one carbon atom from each of two bridging C_5H_5 ligands. The other compound $[EtGa(C_5H_5)_2]_\infty$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 8.213(5)$, $b =$

9.131(4), c = 14.277(10)Å, V = 1070.7(11) and Z = 4 (monomeric units). The structure was refined to R = 7.01% for those 846 reflections above 6σ. This structure is also polymeric with $[Ga\text{-}C_5H_5]_\infty$ chains. Each gallium(III) center is also bonded to an ethyl ligand and a terminal η^1-C_5H_5 ligand. When the compounds are dissolved in either benzene, toluene, cyclohexane, $CHCl_3$ or THF, ligand redistribution reactions occur to form equilibrium mixtures of species. However, when $[Et_2Ga(C_5H_5)]_\infty$ is melted, ^{1}H NMR spectral studies suggest the existence of only $Et_2Ga(C_5H_5)$ whereas when $[EtGa(C_5H_5)_2]_\infty$ is melted, a single compound does not exist but a mixture of $EtGa(C_5H_5)_2$, $Et_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$ are formed. Mass spectral studies of $Et_2Ga(C_5H_5)$ are consistent with the presence of $Et_2Ga(C_5H_5)$ in the gas phase, but when $[Et_2Ga(C_5H_5)]_\infty$ is heated and vaporized, uncertainty regarding the identities of the species in the gas phase arises due to the occurrence of the ligand redistribution reactions in the melt.

Heteroleptic organometallic compounds of the heavier group 13 elements have the potential to be novel precursors for the formation of semiconducting materials if different types of organic ligands in a given molecule have different propensities for selective elimination. However, these types of compounds tend to undergo ligand redistribution reactions to form symmetrized products[1,2] if and when an appropriate reaction pathway is available. Since a typical reaction pathway for ligand exchange utilizes a vacant coordination site on the group 13 element[3], the isolable mixed ligand compounds are associated and have four coordinate group 13 atoms. However, since the degree of association can change as the phase of the compound changes, it is necessary to characterize a compound as fully and completely as possible in order to prove the existence of a single compound in the solid, liquid and gas phases and in solution. However, no compound with different organic ligands to our knowledge has been sufficiently characterized to demonstrate its existence in all phases. Only two gallium compounds, $[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$[4] and $[Me_2Ga(C{\equiv}CPh)]_2$[5-7] and six indium compounds including $\{In[CH(SiMe_3)_2](i\text{-Pr})Cl\}_2$,[8] $[In(CH_2SiMe_3)(CH_2CMe_3)Cl]_2$,[2] $[(Me)(Me_3SiCH_2)InAs(SiMe_3)_2]_2$,[9] $[(Me)(Me_3SiCH_2)InP(SiMe_3)_2]_2$,[9] $[(Me)(Me_3CCH_2)InP(SiMe_3)_2]_2$[10] and $[(Me_2In(C{\equiv}CMe)]_2$[11] have been proven to exist in the solid phase and in benzene solution. However, of these compounds only $[Me_2Ga(C{\equiv}CPh)]_2$ exists as the identical species in the solid and in solution. The other compounds isomerize or change degree of association upon dissolution. The *trans* isomer in the solid state is converted to a *cis/trans* isomer mixture in solution. Even though only two gallium compounds with two organic substituents have been sufficiently characterized to prove their existence in both the solid and solution phases, other heteroleptic organogallium compounds including $Me_2Ga(C_5H_5)$,[1,12-14]

$Et_2Ga(C_5H_5)$,[12,13] $Me_2Ga(C{\equiv}CMe)$,[11] $Me_2Ga(C{\equiv}CSiMe_3)$,[6] $(t\text{-}Bu)_2Ga(C{\equiv}CPh)$,[4] $Me_2Ga(CH{=}CH_2)$,[15] $Me_2Ga(t\text{-}Bu)$[16] and $MeGa(t\text{-}Bu)_2$[16] have been reported in the literature.

The two compounds $Me_2Ga(C_5H_5)$[1,12-14] and $MeGa(C_5H_5)_2$,[1] which are closely related to the ethyl derivatives described in this paper, have been extensively investigated. The compound $Me_2Ga(C_5H_5)$ exists in the solid state as a polymer.[14] The gallium atom is four coordinate with two terminal methyl groups and cyclopentadienide groups which bridge the gallium atoms through the 1 and 3 positions. The liquid and gaseous phases were not fully characterized. When $[Me_2Ga(C_5H_5)]_\infty$ was dissolved in benzene, CCl_4 and THF, ligand redistribution reactions[1] occurred to form $MeGa(C_5H_5)_2$ and $GaMe_3$ which, in turn, underwent methyl and cyclopentadienide group exchange reactions. Thus, the occurrence of these reactions prevented the direct observation of the ^1H NMR lines of all three individual species. When an attempt was made to prepare $MeGa(C_5H_5)_2$,[1] $Me_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$ were isolated due to the occurrence of ligand redistribution reactions. Thus, $MeGa(C_5H_5)_2$ could not be isolated as a single compound and characterized.

The level of understanding of organogallium compounds which contain only organic substituents but of two different types has increased significantly with the syntheses and complete characterizations of $Et_2Ga(C_5H_5)$ and of $EtGa(C_5H_5)_2$, a new compound. Both compounds have been prepared by ligand redistribution reactions between appropriate quantities of $GaEt_3$ and $Ga(C_5H_5)_3$ and have been found to exist as single compounds in the solid state as demonstrated by X-structural studies. In the liquid and gaseous states, $Et_2Ga(C_5H_5)$ exists as a single compound according to NMR and mass spectral studies whereas $EtGa(C_5H_5)_2$ is in equilibrium with $Et_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$ in the melt. However, the situation is very different in solution as both compounds undergo ligand redistribution reactions (Equations 1 and 2) in benzene, toluene, THF, cyclohexane and $CHCl_3$ (all solvents that were studied), to form symmetrized

$$2\ Et_2Ga(C_5H_5) \rightleftharpoons GaEt_3 + EtGa(C_5H_5)_2 \qquad (1)$$

$$2\ EtGa(C_5H_5)_2 \rightleftharpoons Et_2Ga(C_5H_5) + Ga(C_5H_5)_3 \qquad (2)$$

products. In addition, ligand exchange reactions involving ethyl groups and cyclopentadienide groups also occur but the rates are all typically slower than for the corresponding methyl derivatives. The equilibrium constants for the ligand redistribution reactions and the rates of the exchange reactions are dependent on solvent.

The synthesis of $Et_2Ga(C_5H_5)$ by a ligand redistribution reaction between $GaEt_3$ and $Ga(C_5H_5)_3$ in a two to one mol ratio, respectively, in pentane according to equation 3 was

$$2\ GaEt_3 + Ga(C_5H_5)_3 \xrightarrow[25\,^{\circ}C]{C_5H_{12}} 3\ Et_2Ga(C_5H_5) \qquad (3)$$

straight forward and provided a near quantitative yield of the desired compound. The product had excellent elemental analyses for C and H and a sharp melting point. In contrast, the original metathesis reaction[12,13] between Et_2GaCl and NaC_5H_5 gave a relatively low yield (45%) of a product with poor elemental analyses. However, when $GaEt_3$ and $Ga(C_5H_5)_3$ were combined in pentane in a 1 to 2.00 mol ratio, respectively, in an attempt to prepare $EtGa(C_5H_5)_2$ according to equation 4, the isolated product had unacceptable elemental analyses. The percent carbon was

$$GaEt_3 + 2\ Ga(C_5H_5)_3 \xrightarrow[25\,^{\circ}C]{C_5H_{12}} 3\ EtGa(C_5H_5)_2 \qquad (4)$$

low, for example -4.54, -2.01 and -1.59% by difference for three independent samples from three different preparations. These data suggested to us that an equilibrium mixture of species had been formed by a ligand redistribution reaction of $EtGa(C_5H_5)_2$ (Equation 2). Sublimation of the product at 25 °C would lead to the isolation of $EtGa(C_5H_5)_2$ contaminated with $Et_2Ga(C_5H_5)$, if these two compounds had similar volatilities and if $Ga(C_5H_5)_3$ was nonvolatile. In order to test this hypothesis, $GaEt_3$ and $Ga(C_5H_5)_3$ were mixed in a 1 to 2.24 mol ratio, respectively, in pentane in order to shift the equilibrium (Equation 2) and minimize the formation of $Et_2Ga(C_5H_5)$. The crystalline product isolated by sublimation at 25 °C had excellent carbon, hydrogen and gallium analytical data. Thus, the successful synthesis of $EtGa(C_5H_5)_2$ provides the first example of an isolable heteroleptic organogallium compound which contains two cyclopentadienide groups and one simple alkyl substituent. The closely related compound $MeGa(C_5H_5)_2$ could not be isolated[1] and was observed to decompose to $Me_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$ at room temperature. The only other example of a similar group 13 compound is $MeAl(C_5H_5)_2$.[17] The aluminum was found to be η^2 bound to each of the two cyclopentadienide rings.

The structure of $Et_2Ga(C_5H_5)$ in the solid state is a linear polymer as depicted in Figure 1, which also shows the atomic labelling scheme. The crystallographic asymmetric unit consists of a chain of four $Et_2Ga(C_5H_5)$ moieties which extends by the translation $\pm(\vec{a} + \vec{b})$ to form an infinite linear polymer of $[Et_2Ga(C_5H_5)]_\infty$. Interatomic distances are collected in Table 1. It should be noted that one ethyl group (that whose α-carbon is C(33)) is disordered, with the two sites for the β-carbon being defined by C(34) and C(34′).

The eight independent gallium(III)-ethyl bond lengths range from Ga(4)-C(41) = 1.945(9)Å to Ga(1)-C(11) = 1.979(9)Å, the mean value being 1.963Å. Each gallium(III) center is also in contact with one carbon atom from each of two cyclopentadienide ligands. Thus Ga(1)-

C(112) = 2.245(6)Å and Ga(1)-C(214) = 2.286(6)Å; Ga(2)-C(212) = 2.272(6)Å and Ga(2)-C(315) = 2.268(6)Å; Ga(3)-C(312) = 2.277(6)Å and Ga(3)-C(415) = 2.294(7)Å; and Ga(4)-C(412) = 2.294(7) and Ga(4)-X(114) = 2.262(6)Å. [Here, X(114) = C(114) translated by $(\vec{a} + \vec{b})$.] All other Ga-C(Cp) distances are greater than 2.72Å. The average Ga-C(Cp) contact distance is 2.275Å, *i.e.*, 0.312Å greater than the σ-bonding Ga-Et distances. Clearly these Ga-C(Cp) interactions are weak. The molecular structure bears a close resemblance and the crystal structure bears a superficial resemblance to that of $Me_2Ga(C_5H_5)$.[14] However, polymerization of this methyl analogue occurs by association along the 2_1-axis (in space group $P2_1/c$); Ga-Me bond lengths are 1.962(1)-1.972(1)Å, while the two independent Ga-C(Cp) bonding interactions are 2.215(2) and 2.314(2)Å.

The Et-Ga-Et angles (Table 2) are all slightly larger than the ideal trigonal value of 120° (*i.e.*, values of 123.9(3)°-126.3(3)°, with an average value of 125.0°). The Cp-Ga-Cp contacts lie in a plane normal to the appropriate Et-Ga-Et plane with C-Ga-C angles of 98.7(2)°-100.0(2)°, averaging 99.2°. Although each Ga(III) center appears to be in a typical distorted tetrahedral environment (*i.e.*, sp^3 hybridized around gallium), the distances and angles above suggest another possibility. Each Ga(III) atom has two normal σ-bonds to the ethyl groups and a two-electron three-centered bond across the C(Cp)-Ga-C(Cp) system as shown in the following canonical structure. Distances within each C_5H_5 system show the appropriate systematic pattern.

The shortest C-C distance in each ring (*i.e.*, C(115)-C(111) = 1.363(10), C(215)-C(211) = 1.337(10), C(313)-C(314) = 1.345(10) and C(413)-C(414) = 1.352(10)Å) is for that carbon-carbon bond in which neither of the carbon atoms interact closely with a gallium(III) center. Other C-C(Cp) distances for the four distinct rings lie in the ranges 1.392(9)-1.432(9), 1.398(9)-1.436(9), 1.390(10)-1.429(10) and 1.401(9)-1.431(10)Å, respectively.

The polymeric nature of $EtGa(C_5H_5)_2$ is shown in Figure 2, which also shows the atomic labelling scheme. Association occurs by interaction of units along that 2_1-axis which runs along **b**. [A similar feature is found in $Me_2Ga(C_5H_5)$, but in a different space group ($P2_1/c$, rather than the present $P2_12_12_1$).] Figure 3 illustrates the crystallographic packing, viewed down '**b**' and shows clearly that the structure consists of linear chains of $[EtGa(C_5H_5)_2]_\infty$ which are <u>not</u> cross-connected. Interatomic distances and angles are collected in Tables 3 and 4. This structural study is of lower accuracy than that for $Et_2Ga(C_5H_5)$, but, nevertheless, some valuable information may be gleaned from it.

The gallium(III) center forms simple σ-bonds to an ethyl group (Ga(1)-C(1) = 1.960(13)Å) and to an η^1-cyclopentadienide ligand (Ga(1)-C(11) = 2.032(15)Å). The second C_5H_5 ligand is bridged by two gallium atoms as in $[Et_2Ga(C_5H_5)]_\infty$. Each gallium atom, in turn, is in contact with two cyclopentadienide ligands, therefore forming the $[Ga\text{-}C_5H_5]_\infty$ backbone of the polymer. The important contacts are Ga(1)-C(21) = 2.232(12) and Ga(1)-C(23b) = 2.187(15)Å. The average Ga-C(Cp) distance of 2.210Å is slightly shorter than the 2.275Å in $Et_2Ga(C_5H_5)$, but is still substantially longer than the $Ga\text{-}C_5H_5$ σ-bonded distance of 2.032(15)Å. The C(1)-Ga(1)-C(11) angle is 119.7(6)° as compared to the C(21)-Ga(1)-C(23b) angle of 98.5(5)°.

Distances within the terminal η^1-C_5H_5 ligand are as expected, with two short bonds (C(12)-C(13) = 1.349(21) and C(14)-C(15) = 1.330(26)Å) and three longer bonds (1.419(23)-1.447(23)Å). The pattern in the bridging C_5H_5 ligand is not clear cut, with all five C-C bonds lying in the range 1.370(18)-1.423(19)Å. Even though $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$ exist as polymers in the solid state, cryoscopic molecular weight studies in benezene solution indicate the presence of only monomeric species. Thus, the polymers are broken during solvation by benzene.

Proton NMR spectral data (Table 5 and 6) demonstrate clearly that both $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)$ undergo ligand redistribution reactions to form the equilibrium mixtures of species as indicated by equations 1 and 2 in all solvents studied (benzene, toluene, cyclohexane, chloroform and THF). A comparison of the chemical shifts (Tables 1 and 2) and the relative intensities of the lines for all species formed after a given compound was dissolved in a specific solvent confirm the identities of all species. The data also indicate that $Et_2Ga(C_5H_5)$ is more stable to a ligand redistribution reaction in a given solvent than is $EtGa(C_5H_5)_2$. When different solvents are compared for the same compound, the extent of reaction is different. Thus, the equilibrium constant for redistribution of $Et_2Ga(C_5H_5)$ decreases in the order $C_4D_8O > C_6D_6 > C_7D_8 > C_6D_{12} \sim CDCl_3$ whereas for $EtGa(C_5H_5)_2$ K decreases in the order $C_7H_8 > C_6D_{12} \sim CDCl_3 \sim C_4D_8O \sim C_6D_6$. Thus, solvation effects appear to be very important. The data in Tables 5 and 6 also show that the relative rates of ligand exchange depend on the compound dissolved and the solvent. The rate of exchange of C_5H_5 groups between the different species in all solvents except THF is rapid on the NMR time scale as only one line for the C_5H_5 protons is observed in any given spectrum. In contrast, the rate of exchange of ethyl groups is more dependent on solvent. Coupling between the ethyl group protons of all species was observed for only THF solutions of

$Et_2Ga(C_5H_5)$ but for all solutions of $EtGa(C_5H_5)_2$. For benzene solutions of $Et_2Ga(C_5H_5)$, ethyl group coupling was not observed for $GaEt_3$ only, whereas for toluene, cyclohexane and $CDCl_3$ solutions, ethyl coupling was observed for lines for only $Et_2Ga(C_5H_5)$.

The last remaining question concerns the nature of $Et_2Ga(C_5H_5)$ and of $EtGa(C_5H_5)_2$ in the melt. Does a single compound or does an equilibrium mixture of species exist in the liquid phase? In order to answer these questions, the ^1H NMR spectra of the melts were recorded. The reference for both spectra was C_6D_6 which had been sealed in a capillary tube and inserted into the NMR tube. The spectrum of the melt of $Et_2Ga(C_5H_5)$ at 45°C was composed of one triplet, one quartet and one singlet for methylene, methyl and cyclopentadienide protons, respectively. In contrast, the spectrum of $EtGa(C_5H_5)_2$ exhibited five broad, poorly defined resonances. There were two resonances for methylene protons, two resonances for methyl protons and one for cyclopentadienide protons. The chemical shifts of the less intense set of methylene and methyl resonances were the same as those observed for the melt of $Et_2Ga(C_5H_5)$ whereas the others must be due to the ethyl protons of $EtGa(C_5H_5)_2$. The C_5H_5 protons were averaged to give a single line. Thus, $Et_2Ga(C_5H_5)$ melts at 35-36°C whereas $EtGa(C_5H_5)_2$ decomposes at 39.0-39.4°C. All data are consistent with the conclusion that $EtGa(C_5H_5)_2$ has a greater tendency to undergo ligand redistribution reactions to form mixtures of species and that cyclopentadienide groups exchange faster than do ethyl groups between gallium compounds.

In conclusion, the compounds $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$ exist as pure, single compounds in the solid state. Upon melting, the integrity of $Et_2Ga(C_5H_5)$ is maintained whereas $EtGa(C_5H_5)_2$ undergoes ligand redistribution reactions to form $Ga(C_5H_5)_3$ and $Et_2Ga(C_5H_5)$. Dissolution causes all compounds to undergo ligand redistribution reactions and form new compounds. The hypothesis that the ligand redistribution reactions are prevented when the gallium is four coordinate is supported by the X-ray structural studies. Both $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$ are polymers with four-coordinate gallium atoms in the solid state. The compounds undergo redistribution upon dissolution when monomers are formed. The cryoscopic molecular weight studies of both $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$ in benzene solution are consistent with the presence of monomeric species. Thus, if these hypotheses are used, $Et_2Ga(C_5H_5)$ exists as a single compound in the melt if the polymeric structure is maintained. In contrast, the decomposition of $EtGa(C_5H_5)_2$ in the melt to form $Ga(C_5H_5)_3$ and $Et_2Ga(C_5H_5)$ suggests the presence of monomeric $EtGa(C_5H_5)_2$ in the liquid phase. The compound $Ga(C_5H_5)_3$ is monomeric in the solid state.[18]

Experimental

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting material $Ga(C_5H_5)_3$ was prepared and purified by the literature method[18] whereas $GaEt_3$ was purchased from Strem Chemicals and purified by vacuum distillation. Solvents were dried by conventional procedures. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer Model 683 spectrometer. Absorption intensities are reported with abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). Mass spectra were obtained by electron impact by using a VG Model 70-SE high resolution mass spectrometer. 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 VXR-400 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at 0.00 ppm. The following abbreviations were used to report the multiplicities of the lines, s (singlet), d (doublet), t (triplet), br (broad). All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries filled with purified argon and are uncorrected. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdon.[19]

Synthesis of $Et_2Ga(C_5H_5)$. A 1.20g (4.53 mmol) sample of $Ga(C_5H_5)_3$ was added to a flask which was connected to a 100 ml Schlenk flask by means of a glass elbow. Approximately 50 ml of pentane was condensed onto the $Ga(C_5H_5)_3$ at -196°C. Then, 1.42g (9.07 mmol) of $GaEt_3$ was vacuum distilled onto the pentane. Upon warming, a colorless solution formed. After 12 hours at room temperature, the solvent was removed by vacuum distillation. The crude product was sublimed at 25°C into the 100 ml Schlenk flask at -196°C to yield 2.44g (12.6 mmol, 92.9%) of $Et_2Ga(C_5H_5)$ as a colorless solid. **$Et_2Ga(C_5H_5)$.** Mp 35-36°C. IR (Nujol mull, cm^{-1}): 3077(m), 2897(vs), 2803(w), 2720(w), 1410(m), 1228(w), 1185(w), 1106(w), 1070(w), 997(m), 980(s), 956(w), 932(w), 831(m), 813(s), 792(vs), 747(vs), 645(m), 612(s), 594(m), 555(m), 500(m), 320(m). Mass Spectrum (m/e, relative intensity): 163 ($EtGa(C_5H_5)^+$), 39; 127 (Et_2Ga^+), 63; 69 (Ga^+), 100. Anal. Calcd for $C_9H_{15}Ga$: C, 56.03; H, 7.84. Found: C, 55.97; H, 7.74. Cryoscopic molecular weight, benzene solution, formula weight 192.9 (observed molality, observed mol. wt., association): 0.0781, 224, 1.16; 0.0606, 262, 1.36; 0.0494, 237, 1.23; 0.0406, 251, 1.30; 0.0248, 248, 1.28.

Synthesis of $EtGa(C_5H_5)_2$. The compound $EtGa(C_5H_5)_2$ was synthesized by a ligand redistribution reaction between $Ga(C_5H_5)_3$ and $GaEt_3$ by using the above procedure. After 0.62g (2.33 mmol) $Ga(C_5H_5)_3$ and 0.16g (1.04 mmol) $GaEt_3$ were allowed to react in pentane solution, the pentane was removed by vacuum distillation to leave a colorless solid. Sublimation at 25°C provided 0.603g (2.63 mmol, 84.7% based on $GaEt_3$) of pure $EtGa(C_5H_5)_2$. **$EtGa(C_5H_5)_2$.** Mp 39.0-39.4°C dec. IR (Nujol mull, cm^{-1}): 3085(w), 2713(w), 1928(vw), 1790(vw), 1412(w), 1300(w), 1234(vw), 1165(vw), 1150(vw), 1103(w), 1072(w), 1000(w), 975(m), 890(w), 875(w), 845(m), 819(m), 790(m), 746(vs), 657(w), 635(m), 540(w), 389(w), 361(w), 330(w). Mass Spectrum (m/e, relative intensity): 199 ($Ga(C_5H_5)_2^+$), 13; 163 ($EtGa(C_5H_5)^+$), 33; 69 (Ga^+), 100. Anal. Calcd for $C_{12}H_{15}Ga$: C, 62.95; H, 6.60; Ga, 30.45. Found: C, 62.70; H, 6.71; Ga, 30.14. Cryoscopic molecular weight, benzene solution, formula weight 229.0 (observed molality, observed mol. wt., association): 0.0860, 221, 0.97; 0.0646, 221, 0.96; 0.0429, 225, 0.98.

Collection of X-Ray Diffraction Data. In each case crystals were sealed (under very strict air- and moisture-free conditions) into thin-walled glass capillaries. The crystals were inspected under a binocular polarizing microscope to ensure that they were single; they were then accurately centered in a eucentric goniometer on an upgraded Syntex $P2_1$/Siemens P3 automated four-circle diffractometer. Determination of the Laue symmetry and unit cell parameters were carried out as described in detail previously.[20] Intensity data (Mo, Kα, $\lambda = 0.710730$Å) were collected at room temperature (24 ± 2°C) using graphite-monochromatized radiation. Data were corrected for absorption and for Lorentz and polarization effects. Details are given in Table 7.

$Et_2Ga(C_5H_5)$. The crystal was of dimensions 0.2 × 0.2 × 0.3 mm and was mounted along its extended direction. The cell dimensions and diffraction symmetry ($\bar{1}$ only) indicated the triclinic crystal group. Possible space groups are the non-centrosymmetric space group P1 (No. 1) and the centrosymmetric space group $P\bar{1}$ (No. 2). The far more common, centrosymmetric $P\bar{1}$ was assumed; this was confirmed by the successful solution of the structure in this higher space group.

$EtGa(C_5H_5)_2$. The crystal was rather larger than would normally be preferred (approximately 0.27 × 0.33 × 0.8 mm) and not of high quality. However, no better crystal could be obtained. The cell parameters and diffraction symmetry (D_{2h}) indicated the orthorhombic crystal system. The systematic absences h00 for h = 2n+1, 0k0 for k = 2n+1, and 00l for l = 2n+1 uniquely define the non-centrosymmetric space group $P2_12_12_1$ (No. 19).

Determination of the Crystal Structures. All crystallographic calculations were carried out on a VAXstation 3100 computer system with use of the Siemens SHELXTL PLUS program package.[21] The analytical form of the scattering factors for neutral atoms was used with both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion included in the calculations.[22] Structures were solved by direct methods and difference-Fourier syntheses. All non-hydrogen atoms were located and the positional and anisotropic thermal parameters were refined. Hydrogen atoms were not located directly, but were included in calculated positions with d(C-H) = 0.95Å.[23] Refinement was continued until convergence was reached. Each structure was checked by means of a final difference-Fourier synthesis. Specific details are listed in Table 7 or are outlined below.

$Et_2Ga(C_5H_5)$. Atomic coordinates are collected in Table 8. The crystallographic asymmetric unit contains four formula units; these are linked together and extended to form an infinite polymer. Final discrepancy indices are R = 3.53% for those 3226 data with $F_o > 6\sigma(F_o)$ and R = 6.41% for all 5024 unique reflections.

$EtGa(C_5H_5)_2$. Atomic coordinates are collected in Table 9. The crystallographic asymmetric unit is the monomeric formula unit. An infinite polymer is created by linkages involving the 2_1 axis along '**b**'. Transmission factors were rather low (0.0883-0.1829) due to the larger-than-usual crystal that was used. Final discrepancy indices are, as expected, higher than for the previous structure, with R = 7.01% for those 694 reflections with $F_o > 6\sigma(F_o)$ and R = 7.76% for all 846 reflections. The absolute configuration of the crystal was determined by η-refinement, yielding the value η = +0.4(2); although this value is not ideal, it confirms that we have chosen the correct enantiomeric crystal form.

^1H NMR Spectral Studies of $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)$ in Different Solvents. In a typical experiment, a small quantity (~10mg) of the desired compound was placed in an NMR tube. Next, approximately 0.6ml of the appropriate solvent was vacuum distilled into the NMR tube at -196°C. The ^{1}H NMR spectrum (400 MHz) of the resulting solution was recorded upon warming of the solution to room temperature. The coupling constant for all triplets and quartets from ethyl groups was 8 Hz in all spectra. The NMR spectral data are provided in Tables 5 and 6.

^{1}H NMR Spectra of Molten $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$. A 3mm diameter glass capillary was filled with approximately 0.5 ml C_6D_6 and sealed under vacuum. This tube was then placed in an NMR tube which contained approximately 0.5g of the appropriate compound. The NMR tube was then sealed by fusion. The NMR spectrum (400 MHz) of each compound was recorded at 45°C. **$Et_2Ga(C_5H_5)$.** ^{1}H NMR: -0.11 (q, $(CH_3\mathit{CH_2})_2Ga(C_5H_5)$, relative intensity 1.0); 0.84 (t, $(\mathit{CH_3}CH_2)_2Ga(C_5H_5)$, relative intensity 1.6); 6.06 (s, $(CH_3CH_2)_2Ga(\mathit{C_5H_5})$, relative intensity 1.4). **$EtGa(C_5H_5)_2$.** ^{1}H NMR: -0.40 (broad, $(CH_3\mathit{CH_2})Ga(C_5H_5)_2$, relative intensity 2.1); 0.03 (broad, $(CH_3\mathit{CH_2})_2Ga(C_5H_5)$, relative intensity 1.0); 0.60 (broad, $(\mathit{CH_3}CH_2)Ga(C_5H_5)_2$, relative intensity 2.8); 0.83 (broad, $(\mathit{CH_3}CH_2)_2Ga(C_5H_5)$, relative intensity 1.1); 6.00 (broad singlet, (C_5H_5), relative intensity 9.9).

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Supplementary Material Available. Complete tables of interatomic distances and angles, anisotropic thermal parameters and calculated positions for hydrogen atoms (__ pp). For ordering information see any current masthead page.

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Table 1

Interatomic distances (in Å) for $Et_2Ga(C_5H_5)$

Atoms	dist.	Atoms	dist.
(A) Ga-C(Cp) distances			
Ga(1)···C(111)	2.817(6)	Ga(1)···C(211)	3.504(7)
Ga(1)-C(112)	2.245(6)	Ga(1)···C(212)	3.512(7)
Ga(1)···C(113)	2.791(6)	Ga(1)···C(213)	2.805(6)
Ga(1)···C(114)	3.501(7)	Ga(1)-C(214)	2.286(6)
Ga(1)···C(115)	3.467(7)	Ga(1)···C(215)	2.887(6)
Ga(2)···C(211)	2.792(6)	Ga(2)···C(311)	2.843(6)
Ga(2)-C(212)	2.272(6)	Ga(2)···C(312)	3.524(7)
Ga(2)···C(213)	2.844(6)	Ga(2)···C(313)	3.464(7)
Ga(2)···C(214)	3.514(7)	Ga(2)···C(314)	2.810(6)
Ga(2)···C(215)	3.444(7)	Ga(2)-C(315)	2.268(6)
Ga(3)···C(311)	2.813(6)	Ga(3)···C(411)	2.904(7)
Ga(3)-C(312)	2.277(6)	Ga(3)···C(412)	3.521(7)
Ga(3)···C(313)	2.849(6)	Ga(3)···C(413)	3.384(7)
Ga(3)···C(314)	3.493(7)	Ga(3)···C(414)	2.728(7)
Ga(3)···C(315)	3.510(7)	Ga(3)-C(415)	2.294(7)
Ga(4)···X(111)[a]	3.498(7)	Ga(4)···C(411)	2.804(7)
Ga(4)···X(112)[a]	3.504(7)	Ga(4)-C(412)	2.294(7)

Table 1 (cont.)

	Atoms	dist.	Atoms	dist.
	Ga(4)···X(113)[a]	2.775(6)	Ga(4)···C(413)	2.888(7)
	Ga(4)-X(114)[a]	2.262(6)	Ga(4)···C(414)	3.496(7)
	Ga(4)···X(115)[a]	2.868(6)	Ga(4)···C(415)	3.510(7)
(B)	Ga-C_2H_5 distances			
	Ga(1)-C(11)	1.979(9)	Ga(3)-C(31)	1.975(5)
	Ga(1)-C(13)	1.963(8)	Ga(3)-C(33)	1.958(9)
	Ga(2)-C(21)	1.959(7)	Ga(4)-C(41)	1.945(9)
	Ga(2)-C(23)	1.969(7)	Ga(4)-C(43)	1.955(5)
(C)	C-C(ethyl) distances			
	C(11)-C(12)	1.437(12)	C(33)-C(34)	1.350(29)
	C(13)-C(14)	1.475(12)	C(33)-C(34′)	1.391(21)
	C(21)-C(22)	1.508(10)	C(34)···C(34′)	1.486(33)
	C(23)-C(24)	1.509(10)	C(41)-C(42)	1.502(12)
	C(31)-C(32)	1.528(9)	C(43)-C(44)	1.529(9)
(D)	C-C(Cp) distances			
	C(111)-C(112)	1.432(9)	C(311)-C(312)	1.393(8)
	C(112)-C(113)	1.392(9)	C(312)-C(313)	1.429(10)

Table 1 (cont.)

Atoms	dist.	Atoms	dist.
C(113)-C(114)	1.399(7)	C(313)-C(314)	1.345(10)
C(114)-C(115)	1.421(10)	C(314)-C(315)	1.419(8)
C(115)-C(111)	1.363(10)	C(315)-C(311)	1.390(10)
C(211)-C(212)	1.410(9)	C(411)-C(412)	1.401(9)
C(212)-C(213)	1.398(9)	C(412)-C(413)	1.431(10)
C(213)-C(214)	1.420(9)	C(413)-C(414)	1.352(10)
C(214)-C(215)	1.436(9)	C(414)-C(415)	1.428(10)
C(215)-C(211)	1.337(10)	C(415)-C(411)	1.410(10)

[a] X(111) → X(115) are symmetry related to C(111) → C(115) by the translation ($\vec{a}+\vec{b}$).

Table 2

Selected angles (°) within $Et_2Ga(C_5H_5)$

Atoms

(A) Et-Ga-Et angles

C(11)-Ga(1)-C(13)	125.0(3)	C(31)-Ga(3)-C(33)	126.3(3)
C(21)-Ga(2)-C(23)	123.9(3)	C(41)-Ga(4)-C(43)	124.7(3)

(B) Cp-Ga-Cp angles

C(112)-Ga(1)-C(214)	98.7(2)	C(312)-Ga(3)-C(415)	99.2(2)
C(212)-Ga(2)-C(315)	99.0(2)	C(412)-Ga(4)-X(412)[a]	100.0(2)

[a] See footnote *a* to Table 1

Table 3

Interatomic distances (Å) for $EtGa(C_5H_5)_2$

(A) Distance of Ga(1) to carbon atoms of the ‘bridging’ C_5H_5 ligands

Ga(1)-C(21)	2.232(12)	Ga(1)···C(21b)[a]	3.475(17)
Ga(1)···C(22)	2.686(13)	Ga(1)···C(22b)[a]	2.688(16)
Ga(1)···C(23)	3.462(15)	Ga(1)-C(23b)[a]	2.187(15)
Ga(1)···C(24)	3.493(15)	Ga(1)···C(24b)[a]	2.921(16)
Ga(1)···C(25)	2.859(13)	Ga(1)···C(25b)[a]	3.575(17)

(B) Distance of Ga(1) to carbon atoms of the terminal C_5H_5 ligand

Ga(1)-C(11)	2.032(15)	Ga(1)···C(14)	3.573(17)
Ga(1)···C(12)	2.819(16)	Ga(1)···C(15)	2.802(16)
Ga(1)···C(13)	3.593(17)		

(C) Ga-Et bond lengths

Ga(1)-C(1)	1.960(13)	C(1)-C(2)	1.498(23)

(D) Distances within C_5H_5 Rings

C(11)-C(12)	1.432(19)	C(21)-C(22)	1.423(19)
C(12)-C(13)	1.349(21)	C(22)-C(23)	1.370(18)
C(13)-C(14)	1.419(23)	C(23)-C(24)	1.411(20)
C(14)-C(15)	1.330(26)	C(24)-C(25)	1.388(19)
C(15)-C(11)	1.447(23)	C(25)-C(21)	1.411(18)

[a] The atoms C(21b) → C(25b) are as shown in Figure 2 and are related to the atoms C(21) → C(25) by the ORTEP symmetry code 3646 (*i.e.*, 1-x, -1/2+y, 3/2+z).

Table 4

Selected angles (°) for $EtGa(C_5H_5)_2$

C(1)-Ga(1)-C(11)	119.7(6)	C(21)-Ga(1)-C(23b)[a]	98.5(5)
C(1)-Ga(1)-C(21)	114.3(5)	C(11)-Ga(1)-C(21)	100.1(5)
C(1)-Ga(1)-C(23b)[a]	115.2(5)	C(11)-Ga(1)-C(23b)[a]	106.1(5)
Ga(1)-C(11)-C(12)	107.7(10)	Ga(1)-C(21)-C(22)	91.9(7)
Ga(1)-C(11)-C(15)	106.1(11)	Ga(1)-C(21)-C(25)	101.0(9)
		Ga(1)-C(23b)-C(22b)[a]	95.4(9)
Ga(1)-C(1)-C(2)	114.6(9)	Ga(1)-C(23b)-C(24b)[a]	106.6(10)
C(15)-C(11)-C(12)	105.2(13)	C(25)-C(21)-C(22)	106.5(10)
C(11)-C(12)-C(13)	109.1(13)	C(21)-C(22)-C(23)	109.0(11)
C(12)-C(13)-C(14)	107.1(14)	C(22)-C(23)-C(24)	107.7(12)
C(13)-C(14)-C(15)	110.7(15)	C(23)-C(24)-C(25)	108.4(12)
C(14)-C(15)-C(11)	107.4(15)	C(24)-C(25)-C(21)	108.1(12)

[a] See footnote *a* to Table 3.

Table 5

^{1}H NMR SPECTRA OF $Et_2Ga(C_5H_5)$

Assignments

Solvent	Et_3Ga		$Et_2Ga(C_5H_5)$			$EtGa(C_5H_5)_2$			K_{eq}
	CH_2	CH_3	CH_2	CH_3	C_5H_5	CH_2	CH_3	C_5H_5	
Benzene	0.46	1.15	0.17	0.97	6.28	-0.30	0.75	6.28	4.1×10^{-3}
	0.44	*1.14*				*-0.29*	*0.75*	*6.13*	
Toluene	--	1.13	0.19	1.01	6.23	-0.29	0.75	6.23	1.0×10^{-3}
	0.43	*1.14*				*-0.29*	*0.76*	*6.13*	
THF	0.27	1.07	0.09	0.99	6.02	-0.18	0.85	5.97	1.3×10^{-2}
	0.29	*1.07*				*-0.16*	*0.86*	*5.93*	
C_6H_{12}	0.63	--	0.27	1.03	6.28	-0.20	0.80	6.28	(1)
	0.69	*1.17*				*-0.25*	*0.78*	*6.17*	
$CHCl_3$	0.62	1.20	0.35	1.05	6.38	-0.25	0.80	6.38	(1)
	0.65	*1.15*				*-0.23*	*0.80*	*6.30*	

Values in italics are for lines from pure compound dissolved in the appropriate solvent.

(1) Integrations had large error due to weak, broad lines for the products.

Table 6

^{1}H NMR SPECTRA OF EtGa(C_5H_5)$_2$

Assignments

Solvent	C_5H_5	EtGa(C_5H_5)$_2$			Et$_2$Ga(C_5H_5)			K_{eq}
		CH_2	CH_3	C_5H_5	CH_2	CH_3	C_5H_5	
Benzene	6.13	-0.29	0.75	6.13	0.17	0.97	6.13	3.3×10^{-2}
	5.93				*0.17*	*0.97*	*6.28*	
Toluene	6.13	-0.29	0.76	6.13	0.19	0.99	6.13	4.6×10^{-2}
					0.19	*1.01*	*6.23*	
THF	5.85	-0.16	0.86	5.93	0.11	1.02	6.00	2.4×10^{-2}
	5.82				*0.09*	*0.99*	*6.02*	
C_6H_{12}	6.17	-0.25	0.78	6.17	0.30	1.03	6.17	2.7×10^{-2}
	5.92				*0.27*	*1.03*	*6.28*	
$CHCl_3$	6.30	-0.23	0.80	6.30	0.37	1.07	6.30	3.3×10^{-2}
					0.35	*1.05*	*6.38*	

Values in italics are for lines from pure compound dissolved in the appropriate solvent.

Table 7

Data for X-Ray Structural Studies of $Et_2Ga(C_5H_5)$ and $EtGa(C_5H_5)_2$

	$Et_2Ga(C_5H_5)$	$EtGa(C_5H_5)_2$
Formula	$C_9H_{15}Ga$	$C_{12}H_{15}Ga$
Cryst. system	triclinic	orthorhombic
Space Group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a, Å	7.803(2)	8.213(5)
b, Å	15.839(4)	9.131(4)
c, Å	16.318(4)	14.277(10)
α, deg	101.98(2)	90.00
β, deg	95.23(2)	90.00
γ, deg	102.72(2)	90.00
V, $Å^3$	1904.5(8)	1070.7(11)
Z	8	4
formula wt	192.9	229.0
ρ(calc'd), g cm^{-3}	1.346	1.420
μ(Mo Kα), mm^{-1}	2.811	2.512
Transmission min/max	0.377/0.558	0.088/0.183
2θ range, deg	5.0-45.0	5.0-45.0
Index ranges	h 0→8	h 0→8
	k -17→+16	k 0→9
	ℓ -17+17	ℓ 0→15

Table 7 (cont.)

	$Et_2Ga(C_5H_5)$	$EtGa(C_5H_5)_2$
Reflections collected	5551	846
Unique reflections	5024 (R_{int} = 0.97%)	846
Reflections > 6σ	3226	694
R indices (all data)	R = 6.41%	R = 7.76%
	R_w = 6.23%	R_w = 9.01%
R indices (6σ data)	R = 3.53%	R = 7.01%
	R_w = 3.97%	R_w = 6.34%
Largest diff. peak, $e^-/Å^3$	0.54	1.65
Deepest diff. hole, $e^-/Å^3$	-0.41	-1.24

Table 8

Final Atomic Parameters (× 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

for $Et_2Ga(C_5H_5)$.

Table 9

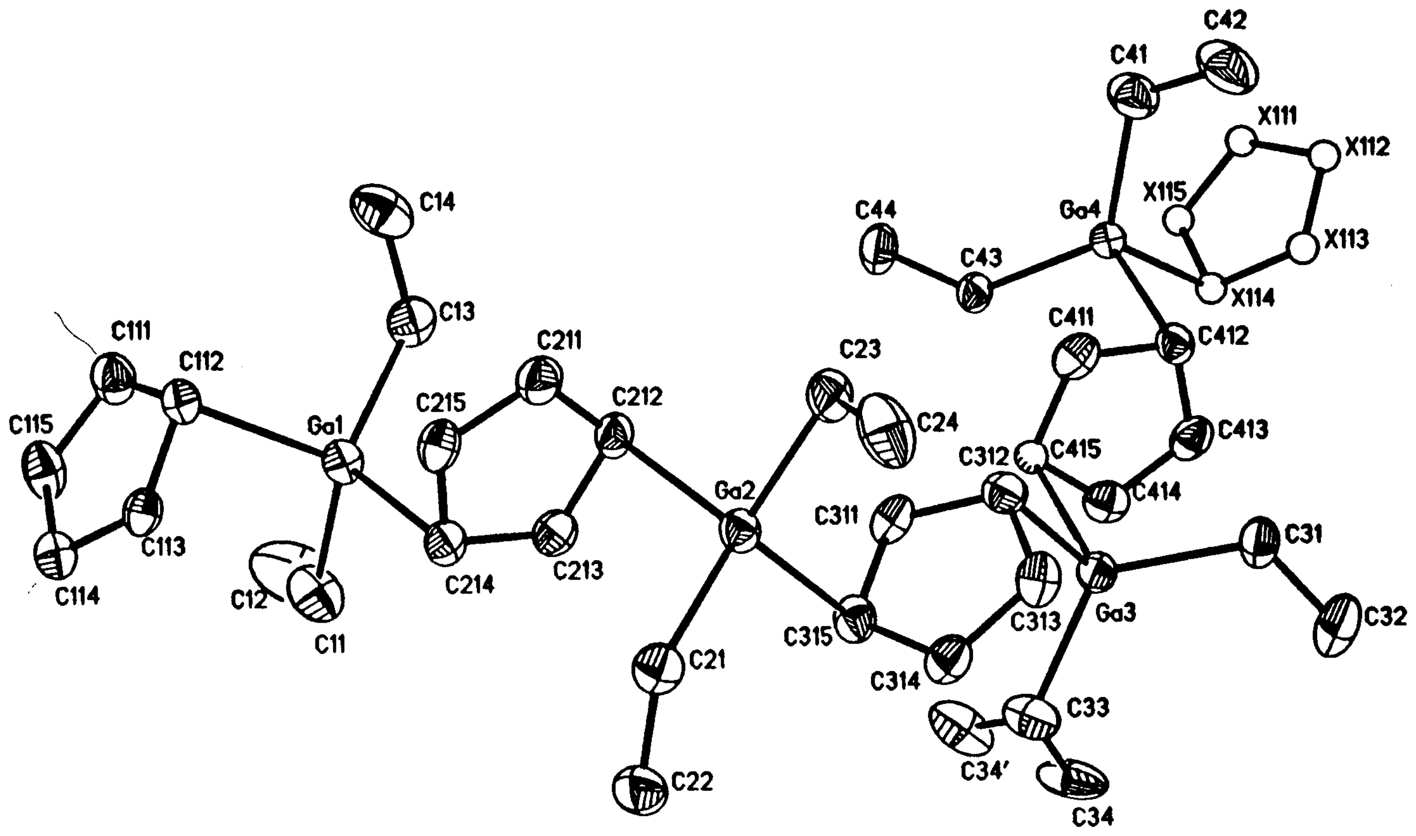
Final Atomic Parameters (× 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $EtGa(C_5H_5)_2$.

FIGURE CAPTIONS

Figure 1. Structure of $[Et_2Ga(C_5H_5)]_\infty$. The figure shows the crystallographic asymmetric unit plus one additional C_5H_5 ligand (labelled X111 → X115 and symmetry related to the ring C(111) → C(115) by the translation $(\vec{\mathbf{a}}+\vec{\mathbf{b}})$).

Figure 2. Structure of $[EtGa(C_5H_5)_2]_\infty$. The figure shows a portion of the strand of polymeric $[Ga(C_5H_5)_2(C_2H_5)]_\infty$ formed by translation of the basic asymmetric unit by the 2_1 axis along $\vec{\mathbf{b}}$.

Figure 3. Packing of $[EtGa(C_5H_5)_2]_\infty$ molecules in the crystal. Note that polymerization occurs by way of the 2_1 axis down **b** and that there is no interchain cross-linking.



C42
C41
X111
X112
X115
C44
Ga4
X113
C43
X114
C14
C411
C412
C13
C111
C211
C23
C112
C212
C215
C24
C413
C415
C312
C115
Ga1
Ga2
C311
C414
C31
C113
C213
C313
Ga3
C12
C214
C114
C315
C32
C11
C21
C314
C33
C34'
C22
C34

FIGURE 1

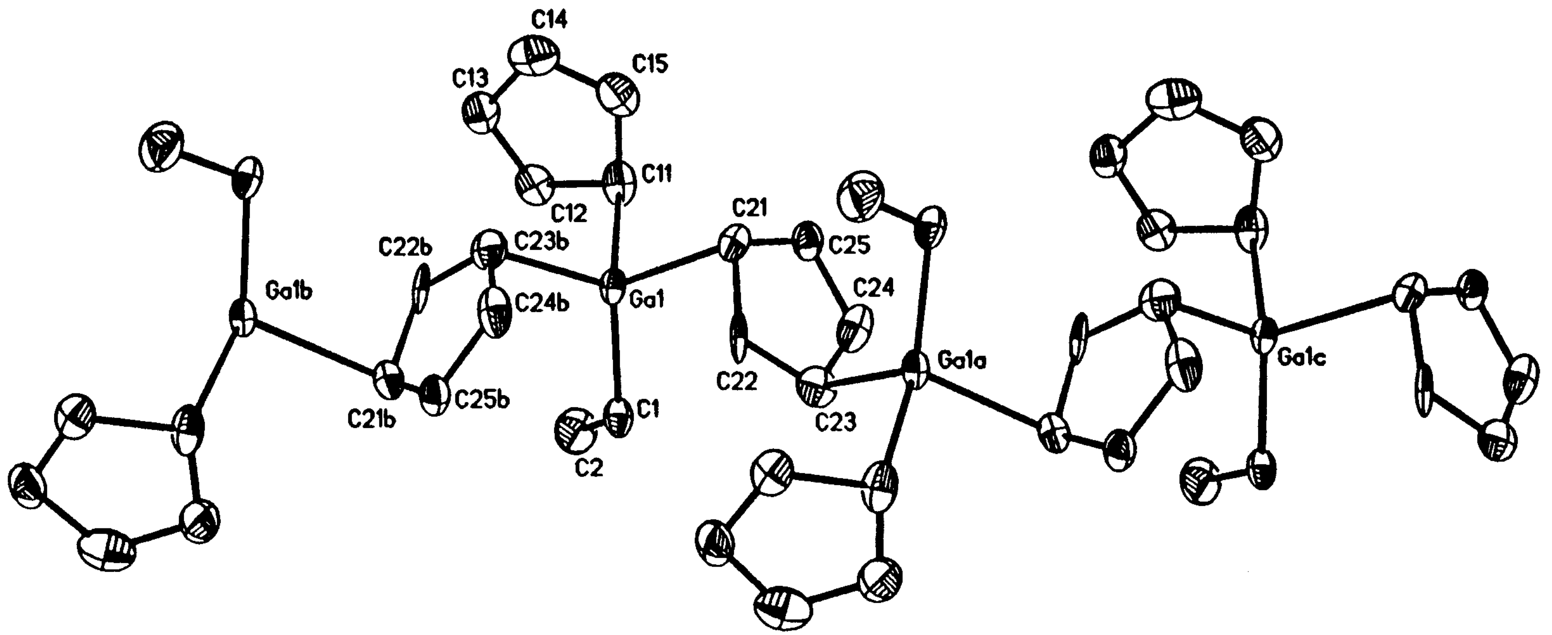

C14
C13
C15
C11
C12
C21
C22b
C23b
C25
C24
Ga1b
C24b
Ga1
Ga1a
Ga1c
C22
C21b
C25b
C1
C23
C2

FIGURE 2

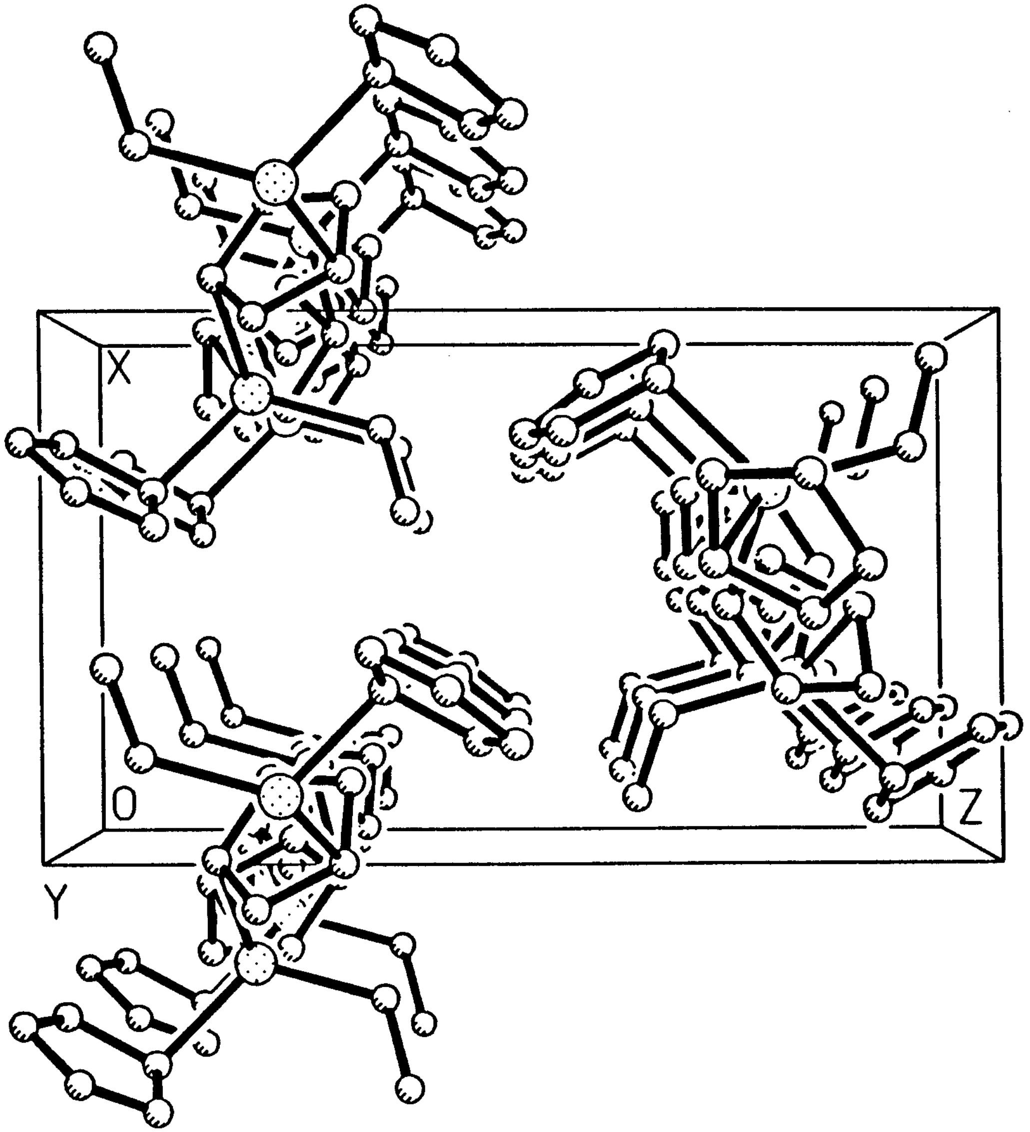


Figure 3.

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