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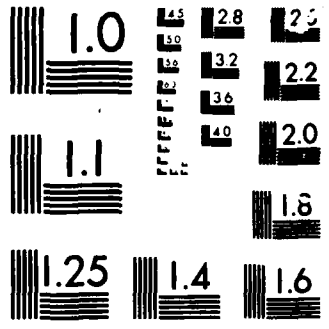
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TECHNICAL REPORT NO. 14

Synthesis, Characterization, and Crystal and Molecular

Structure of Trimesitylgallium(III)

by

O. T. Beachley, Jr., Melvyn Rowen Churchill,

John C. Pazik and Joseph W. Ziller

Prepared for Publication

in

Organometallics

State University of New York at Buffalo
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Buffalo, New York 14214

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Contribution from the Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Synthesis, Characterization, and Crystal and Molecular Structure of
Trimesitylgallium(III)

by

O. T. Beachley, Jr.^{*}, Melvyn Rowen Churchill, John C. Pazik and
Joseph W. Ziller

Abstract

The compound trimesitylgallium(III) (GaMes_3) has been prepared and fully characterized by elemental analysis, IR and ^1H NMR data, Lewis acid-base studies and an X-ray structural study. Trimesitylgallium(III) crystallizes in the centrosymmetric trigonal space group $P\bar{3}$ (No. 147) with $a=13.415(4)\text{\AA}$, $c=7.628(2)\text{\AA}$ and $\rho(\text{calc'd}) = 1.19 \text{ g cm}^{-3}$ for mol. wt. 427.3 and $Z=2$. Single crystal X-ray diffraction data (Mo $K\alpha$, $2\theta= 4.0-40.0^\circ$) were collected with a Syntex P2, automated four-circle diffractometer. All atoms (including hydrogen atoms) were located and the structure was refined to

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Introduction

Bulky substituents have been used in main-group chemistry to stabilize a variety of unusual compounds. Of the possible groups with large steric demands, aromatic rings with alkyl groups in the 2 and 6 positions have been frequently employed. Mesityl (Mes) groups have been used to stabilize Si_2Mes_4 , the first fully characterized compound with a silicon-silicon double bond.¹ The 2,6-diethylphenyl substituent stabilized a compound with a germanium-germanium double bond² whereas the 2,6-diisopropylphenyl group provided sufficient steric effects to provide a tin-tin derivative³. The 2,4,6-tri(t-butyl)phenyl substituent was used as a substituent in compounds with phosphorus-phosphorus⁴ and arsenic-arsenic double bonds.⁵

In group 13 chemistry in general and gallium chemistry in particular, very few typical compounds with bulky substituents are known. The derivative $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, a pyrophoric liquid at room temperature, has been fully characterized.⁶ In contrast, trimesitylgallium(III) (GaMes_3) has been reported but no characterization data were given.⁷ The compound was prepared in very low yield (8%) from gallium metal and dimesitylmercury in refluxing benzene. In this paper we report the facile synthesis of GaMes_3 in high yield from GaCl_3 and the mesityl Grignard reagent in Et_2O . The new compound has been fully characterized by elemental analyses, IR and ^1H NMR spectroscopic data, and an X-ray structural study.

Experimental Section

General Data: All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or a purified argon atmosphere. Gallium(III) chloride was purified by sublimation under high vacuum at 70-80° immediately prior to use. Bromomesitylene was purchased from Aldrich Chemicals and was used as received. The Grignard reagent was prepared in refluxing Et₂O using standard procedures. All solvents were purified before use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with abbreviations w(weak), m(medium), s(strong), vs(very strong) and sh(shoulder). The ¹H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe₄ as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum.

Synthesis of GaMes₃. In a typical synthetic experiment, the Grignard reagent MesMgBr prepared from 5.80g (0.239 mol) magnesium, 44.2g(0.222 mol) MesBr and 90mL of Et₂O was added slowly over a period of 45 min. to 8.70g (0.0494 mol) GaCl₃ dissolved in 250 mL of Et₂O. After the addition was complete, the reaction mixture was refluxed for 16 h. The ether was then removed by vacuum distillation. The resulting solid was extracted with 175 mL of pentane eight times. The yellowish pentane soluble solid was then recrystallized from pentane to provide 15.1g (35.4 mmol, 71.6% yield based on GaCl₃) of crude GaMes₃. The product was further purified by vacuum sublimation at 160-175°C and additional recrystallizations from pentane. GaMes₃: mp 186-187.8°C; ¹H NMR (C₆D₆) δ 2.14 (p-Me,3H), 2.33 (O-Me,6H),

6.70 (m^{-1} , 2H); IR(Nujol mull, cm^{-1}) 2725(w), 1775(w), 1737(w), 1597(s), 1547(s), 1282(w), 1258(vw), 1231(w), 1166(vw), 1047(w), 1027(m), 1008(sh), 938(vw), 918(vw), 883(w), 843(vs), 829(w), 795(vw), 705(w) 681(vw), 580(m), 558(m), 540(s), 512(vw), 480(w), 338(vs), 300(w), 243(m). Solubility: soluble in benzene, Et_2O and THF; slightly soluble in pentane. No stable adducts were formed with Et_2O or THF. Anal. Calcd: C, 75.90; H, 7.78. Found: C, 75.73; H, 7.86. Crystals suitable for the X-ray structural study were obtained by recrystallization of a sample from pentane at $-10^\circ C$.

Collection of X-Ray Diffraction Data.

A glasslike, transparent, colorless crystal of trimesitylgallium(III) of approximate orthogonal dimensions $0.20 \times 0.28 \times 0.33 \text{ mm}^3$ was inserted into a thin-walled glass capillary under an inert atmosphere (Ar) and was aligned on our Syntex P2₁ automated four-circle diffractometer. Determination of the crystal's orientation matrix and unit cell parameters were carried out as described previously.⁸ A full shell of intensity data with $2\theta=4.0-40.0^\circ$ were collected using the $2\theta-\theta$ scan technique; details appear in Table 1. The observed $\bar{3} (S_6)$ Laue symmetry indicated a trigonal space group based upon the point groups $3 (C_3)$ or $\bar{3} (S_6)$. There were no systematic absences. Possible space groups are $P3 (C_3^1; \text{No. } 143)$ or $\bar{P}3 (C_{3i}^1; \text{No. } 147)$.⁹ The latter centrosymmetric alternative was later found to be the correct space group. All data were corrected for the effects of absorption ($\mu=12.3 \text{ cm}^{-1}$) and the six symmetry-equivalent forms for each reflection were averaged ($R(I) = 1.36\%$ and $R_w(I) = 2.41\%$). Lorentz and polarization corrections were now applied and the data were reduced to unscaled $|F_0|$ values. Any datum with $I(\text{net}) < 0$ was assigned the value

$|F_0| = 0$. A Wilson plot was used to place data on an approximately absolute scale.

Solution and Refinement of the Structure of Trimesitylgallium(III)

All crystallographic calculations were performed using the SUNY-Buffalo modification of the Syntex XTL interactive crystallographic program package. Calculated structure factors were based upon the analytical forms of the neutral atoms' scattering factors; both the real ($\Delta f'$) and the imaginary ($\Delta f''$) components of anomalous dispersion were included for all atoms.¹⁰ The function minimized during least-squares refinement was $\sum w(|F_0| - |F_C|)^2$, where $1/w = \{[\sigma(|F_0|)]^2 + [0.015|F_0|]^2\}$.

The position of the gallium atom was determined from a Patterson map. A difference-Fourier synthesis phased by this atom ($R_F = 40.4\%$)¹¹ revealed the locations of all carbon atoms. Refinement of all appropriate positional and anisotropic thermal parameters led to convergence with $R_F = 7.7\%$, $R_{WF} = 6.8\%$ and $GOF = 3.83$ for 85 variables refined against all 743 reflections. A difference - Fourier synthesis now revealed the positions of all hydrogen atoms in the structure (peak heights ranging from $0.26e^-/A^3$ down to $0.17e^-/A^3$). These were included in the model and their positional and isotropic thermal parameters were refined. Convergence was reached with $R_F = 3.9\%$, $R_{WF} = 3.3\%$ and $GOF = 1.12$ for 129 variables refined against all 743 unique reflections ($R_F = 3.0\%$, $R_{WF} = 3.1\%$ for those 655 reflections with $|F_0| > 3\sigma(|F_0|)$).

A final difference-Fourier map showed no significant features; the structure is both correct and complete. Final atomic parameters are collected in Table 2.

Results and Discussion

The first example of a fully characterized gallium(III) compound containing a bulky aromatic substituent is represented by trimesitylgallium(III). The compound was readily prepared in 72% yield using a typical Grignard reaction and the Et₂O solvent was easily removed by vacuum distillation. The product was partially purified by sublimation at 160-175°C under high vacuum and was recrystallized from pentane solution. Available data suggest that GaMe₃ is an exceedingly weak Lewis acid. Neither Et₂O nor THF form adducts which are stable to dissociation at room temperature. The only other reported organogallium(III) compound from which the strong base THF can be readily removed at room temperature is Ga(C₅Me₅)₂Cl.¹²

The crystal consists of discrete molecular units of formula Ga(C₆H₂Me₃)₃; there are no abnormally close intermolecular contacts. The scheme used for labelling atoms is shown in Figure 1; interatomic distances and angles are collected in Table 3 while intramolecular planes are given in Table 4. The gallium(III) atom lies on a site of crystallographic 3-fold symmetry (at 1/3, 2/3, z); the molecule thus has precise C₃ symmetry and approximate D₃ symmetry. Atoms in the basic asymmetric unit are labelled as shown in Table 2; atoms in the other two-thirds of the molecule are labelled with a prime (C₃¹ rotation from basic unit) or double prime (C₃² rotation).

The gallium(III)-carbon(aromatic) distances are equivalent, with Ga-C(1)=1.968(4)Å. The gallium atom lies 0.063Å from the C(1)···C(1')···C(1'') plane and is associated with the interligand angle C(1)-Ga-C(1')=119.93(16)°. The coordination geometry about gallium is thus close to the ideal trigonal planar case.

The aromatic rings take up a propeller-like arrangement and make a dihedral angle of 55.90° with the coordination plane. The molecule viewed in Figure 1 has a left-handed propeller (i.e., A) arrangement; however, the other molecule in the unit cell of this centrosymmetric crystal has the opposite handedness. The dihedral angle of 55.90° is not purely a twist angle. The gallium(III) atom lies $0.2137(4)\text{A}$ from the plane of the aromatic ring so there is some bending back of the aromatic ring such that the Ga-C(1)···C(4) system is no longer linear. The "bending back" can be estimated as 6.23° (from $\sin^{-1} [(\text{deviation of Ga atom})/(\text{Ga-C(1) dist})]$). It is this distortion which prevents the molecule (in the solid state) from having perfect D_3 symmetry.

Other distances lie within the expected ranges, with C-C(aromatic) = $1.365(6)$ - $1.399(6)\text{A}$, C-Me = $1.502(9)$ - $1.511(8)\text{A}$ and C-H = $0.83(6)$ - $1.06(7)\text{A}$. (The average C-H distance here of $0.95 \pm 0.06 \text{A}$ is in precise agreement with the accepted "X-ray determined value" - see ref. 13).

The average gallium-carbon bond distances in GaMe_3 ($1.968(4)\text{A}$) are comparable with other three coordinate gallium(III) compounds. For example, the corresponding distances are $1.967(2)\text{A}$ for GaMe_3 (electron diffraction data)¹⁴, 1.963A for $\text{Ga}(\text{CH}=\text{CH}_2)_3$ ¹⁵ and $2.05[3]\text{A}$ for $\text{Ga}(\text{C}_5\text{H}_5)_3$ ¹⁶. In contrast, most four coordinate gallium compounds exhibit longer gallium-carbon distances such as $1.97(1)\text{A}$ for $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ ¹², $1.99(2)\text{A}$ for $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$ ¹², $1.998[4]\text{A}$ for $\text{Me}_3\text{GaNMe}_3$ (electron diffraction data)¹⁷, $1.99[1]\text{A}$ for $[\text{Ga}(\text{CH}_2\text{SiMe}_3)_3]_2 \cdot \text{TMED}$ ¹⁸ and $2.029[14]\text{A}$ for $\text{KGa}(\text{CH}_2\text{SiMe}_3)_3\text{H}$ ¹⁹. However, $[\text{Ga}(\text{C}\equiv\text{CPh})\text{Me}_2]_2$ which has bridging $\text{C}\equiv\text{CPh}$ groups does not fit the above pattern and exhibits a surprisingly short terminal Ga-C(Me) bond distance²⁰ of $1.952(8)\text{A}$. These data suggest that the reduced Lewis acidity of GaMe_3 is probably related to the steric demands of the mesityl group.

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Supplementary Material Available: A list of observed and calculated structure factor amplitudes (5 pp).

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11. $R_F(\%) = 100 \Sigma (|F_0| - |F_C|) / \Sigma |F_0|$; $R_{WF}(\%) = 100 [\Sigma W(|F_0| - |F_C|)^2 / \Sigma W |F_0|^2]^{1/2}$; $GOF = [\Sigma W(|F_0| - |F_C|)^2 / (NO - NV)]^{1/2}$, where NO=number of observations and NV=number of variables.
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Table 1 Experimental Data for X-Ray Diffraction Study of Trimesityl gallium(III)

(A) Crystal Parameter at 19°C (292K)

crystal system: Trigonal	V=1188.9(5)Å ³
space group: $P\bar{3}(C_{3i}^1$; No. 147)	Z=2
a=13.4152(42)Å	mol wt=427.3
c=7.6284(18)Å	formula=C ₂₇ H ₃₃ Ga
	$\rho(\text{calc'd})=1.19\text{gcm}^{-3}$

(B) Data Collection

Diffractometer: Syntex P2₁

Radiation: Mo K α ($\lambda=0.710730\text{Å}$)

Monochromator: highly orientated (pyrolytic) graphite; equatorial mode; $2\theta(m)=12.160^\circ$; assumed to be 50% perfect for polarization correction.

Reflections measured: $\pm h, \pm k, \pm l$ for $2\theta=4.0^\circ-40.0^\circ$, 4444 total yielding 743 unique reflections (file name GAT2-192)

Scan type: Coupled $2\theta(\text{crystal})-\theta(\text{counter})$

Scan width: symmetrical, $[1.8 + \Delta(\alpha_1 - \alpha_2)]^\circ$

Scan speed: 4.0 deg/min (in 2θ .)

Backgrounds: stationary crystal and counter at beginning and end of 2θ scan; each for one-half of total scan time.

Standard reflections: three ($\bar{1}7\bar{1}$; $\bar{4}6\bar{2}$; $\bar{7}31$) collected after each batch of 97 reflections; no fluctuations were observed.

Absorption coefficient: $\mu=12.3\text{ cm}^{-1}$; corrected empirically by interpolation (in 2θ and ϕ) between ψ scans of close-to-axial reflections ($1, \bar{1}, 4$; $\bar{2}, 2, \bar{4}$; $0, 0, 3$)

Table 2 Final Atomic Parameters for Trimesitylgallium(III)^a

ATOM	X	Y	Z	B, Å ²
Ga	1/3	2/3	-0.16315(8)	
C(1)	0.27678(38)	0.77662(31)	-0.17020(46)	
C(2)	0.20576(31)	0.77273(34)	-0.30756(45)	
C(21)	0.16153(58)	0.67959(57)	-0.44557(74)	
C(3)	0.17647(35)	0.85894(37)	-0.31976(55)	
C(4)	0.21493(34)	0.94886(33)	-0.20359(56)	
C(41)	0.18187(59)	1.03919(51)	-0.22297(82)	
C(5)	0.20319(35)	0.94950(40)	-0.06755(60)	
C(6)	0.31364(38)	0.86513(37)	-0.04035(46)	
C(61)	0.38293(68)	0.86904(59)	0.11027(70)	
H(21A)	0.1891(45)	0.6844(42)	-0.5198(71)	12.0(17)
H(21B)	0.2271(56)	0.6991(49)	-0.5316(84)	16.0(24)
H(21C)	0.1342(33)	0.6102(36)	-0.4022(52)	7.0(13)
H(3)	0.1296(26)	0.8532(23)	-0.4150(38)	4.29(72)
H(41A)	0.1424(39)	1.0433(38)	-0.1160(64)	10.7(14)
H(41B)	0.2450(38)	1.1055(39)	-0.2371(56)	9.3(15)
H(41C)	0.1380(45)	1.0258(45)	-0.3302(74)	13.3(19)
H(5)	0.3103(20)	1.0093(32)	0.0102(48)	6.2(10)
H(61A)	0.4198(39)	0.9459(44)	0.1665(63)	11.2(15)
H(61B)	0.4366(37)	0.8563(38)	0.0896(56)	8.2(16)
H(61C)	0.3299(63)	0.7989(63)	0.1930(85)	18.2(26)

^a Anisotropic thermal parameters for all non-hydrogen atoms are collected in the Supplementary Material (q.v.)

Table 3

Selected Distances (Å) and Angles (°) with Esd's for Trimesityl-gallium(III)

(A) Gallium-carbon distance
Ga-C(1) 1.968(4)

(B) C-C(ring) distances

C(1)-C(2)	1.399(6)	C(4)-C(5)	1.378(7)
C(2)-C(3)	1.398(6)	C(5)-C(6)	1.390(7)
C(3)-C(4)	1.365(6)	C(6)-C(1)	1.390(5)

(C) C(ring)-C(Me) distances

C(2)-C(21)	1.510(7)	C(6)-C(61)	1.511(8)
C(4)-C(41)	1.502(9)		

(D) C-H distances

C(3)-H(3)	0.94(3)	C(41)-H(41B)	0.88(5)
C(5)-H(5)	0.92(4)	C(41)-H(41C)	1.03(6)
C(21)-H(21A)	0.93(6)	C(61)-H(61A)	0.99(5)
C(21)-H(21B)	1.02(7)	C(61)-H(61B)	0.83(6)
C(21)-H(21C)	0.88(4)	C(61)-H(61C)	1.06(7)
C(41)-H(41A)	0.98(5)		

(E) C-Ga-C and Ga-C-C angles

C(1)-Ga-C(1')	119.93(16)	Ga-C(1)-C(2)	120.18(29)
		Ga-C(1)-C(6)	121.08(30)

(F) C-C-C(ring) angles

C(6)-C(1)-C(2)	118.5(4)	C(3)-C(4)-C(5)	117.3(4)
C(1)-C(2)-C(3)	119.1(4)	C(4)-C(5)-C(6)	122.1(4)
C(2)-C(3)-C(4)	122.8(4)	C(5)-C(6)-C(1)	120.1(4)

(G) C-C-Me angles

C(1)-C(2)-C(21)	122.1(4)	C(5)-C(4)-C(41)	121.8(5)
C(3)-C(2)-C(21)	118.8(4)	C(5)-C(6)-C(61)	118.8(5)
C(3)-C(4)-C(41)	120.9(5)	C(1)-C(6)-C(61)	121.0(4)

Table 4

Important Molecular Planes for Trimesitylgallium (III). ^a

Atom dev., Å Atom dev., Å

(A) Coordinations plane:

$$0.0000X + 0.0000Y - 1.0000Z - 1.2460=0$$

Ga* -0.0014(6)
C(1)* 0.0524(35)
C(1')* 0.0524(35)
C(1'')* 0.0524(35)

(B) Plane of aromatic ring

$$0.6223X + 0.5462Y - 0.5607Z - 4.7147=0$$

C(1)*	0.011(4)	Ga	0.2137(4)
C(2)*	-0.003(4)	C(21)	0.016(7)
C(3)*	-0.008(5)	C(41)	0.014(7)
C(4)*	0.009(5)	C(61)	-0.102(7)
C(5)*	0.001(5)		
C(6)	-0.011(4)		

(C) Dihedral angle

Plane A/ Plane B 55.90°

^a Atoms marked with an asterisk were used in determining the least-squares plane.

Caption to Figure

Figure 1

Labelling of atoms in the trimesitylgallium(III) molecule. The molecule is viewed approximately (but not exactly) down the crystallographic C_3 axis. [ORTEP-II diagram; 30% probability ellipsoids for non-hydrogen atoms and with hydrogen atoms artificially reduced for clarity].

Figure 2

Stereoscopic view of the trimesitylgallium(III) molecule, viewed approximately (but not exactly) down the Ga-C(1) bond and showing the propeller-like nature of the molecule.

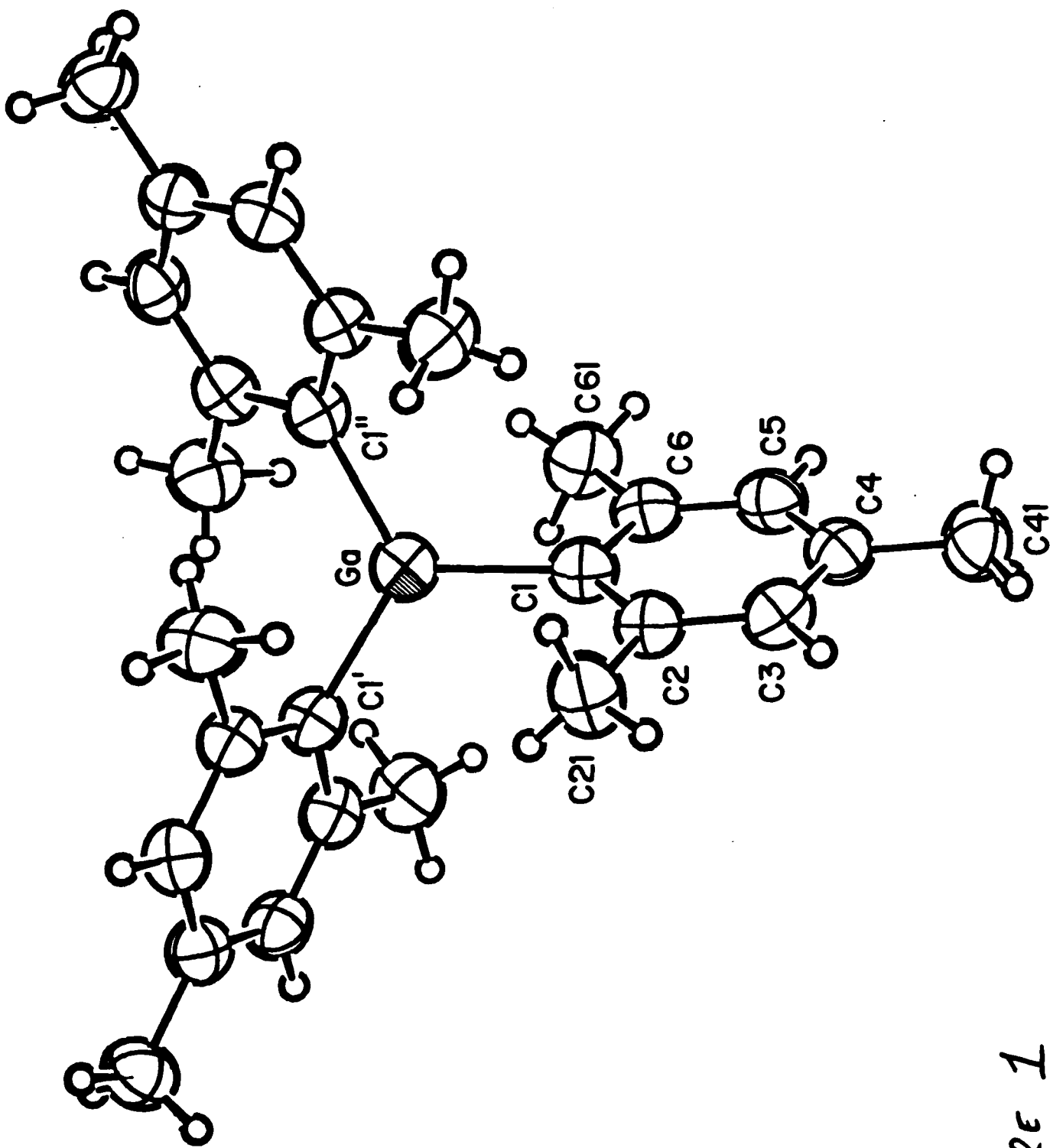


FIGURE 1

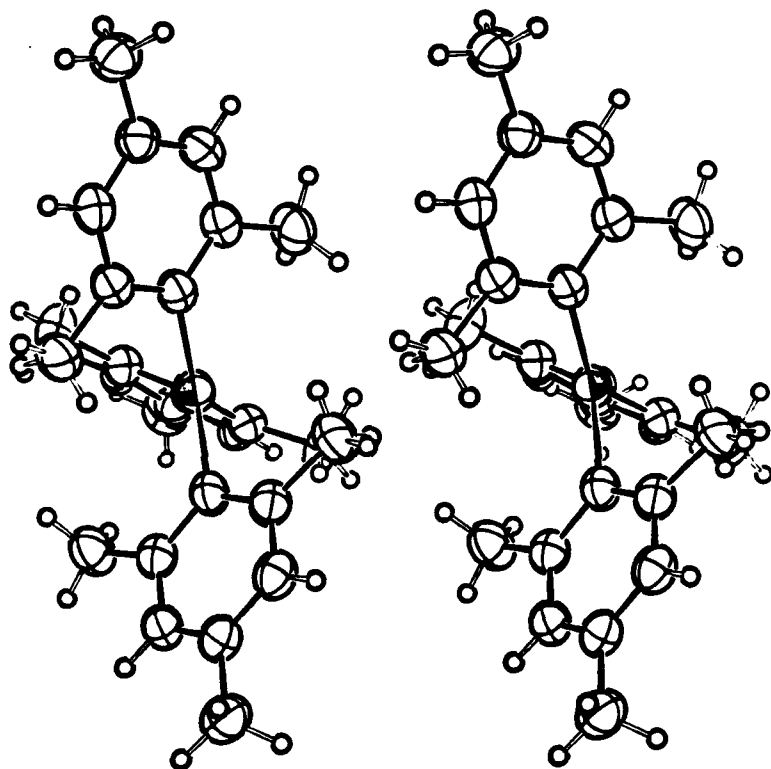


FIG. 2
CORRECT SIZE—
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