Organometallics **1985**, *4*, 1675–1680

Syntheses, Characterizations, and Crystal and Molecular Structures of (Pentamethylcyclopentadienyl)gallium Chlorine Compounds $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$

O. T. Beachley, Jr.,*[1a] R. B. Hallock,[1a] H. M. Zhang,[1b] and J. L. Atwood[1b]

Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and University of Alabama, University, Alabama 35486

Received January 7, 1985

The first (pentamethylcyclopentadienyl)gallium compounds $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$ have been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements, IR and ^1H NMR data, Lewis acid–base studies, and X-ray structural studies. The derivative $Ga(C_5Me_5)_2Cl$ can be readily prepared from $GaCl_3$ and LiC_5Me_5 in diethyl ether. When the stoichiometry of the reagents $LiC_5Me_5/GaCl_3$ was 3.2 or 2.2, the only gallium-containing product was $Ga(C_5Me_5)_2Cl$. The identical product was isolated when the solvent was THF or the reaction mixture was refluxed. An X-ray structural study of a colorless crystal of bis(pentamethylcyclopentadienyl)gallium chloride demonstrates that the crystal consists of discrete isolated dimeric molecules of $[Ga(C_5Me_5)_2Cl]_2$. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.825$ (3) Å, $b = 14.341$ (4) Å, $c = 23.853$ (6) Å, $\alpha = 79.20$ (3)°, $\beta = 86.28$ (3)°, $\gamma = 84.93$ (3)°, and $d_{calcd} = 1.28$ g cm^{-3} for $Z = 3$. Full-matrix leas-squares refinement led to a final R value of 0.061 for 2007 observed reflections. The dimeric molecules have chlorine bridges, and the planar pentamethylcyclopentadienyl rings exhibit η^1 coordination. In benzene solution, the dimeric molecule dissociates and only monomers are observed according to the concentration independent cryoscopic molecular weight data. The dichloro derivative $Ga(C_5Me_5)Cl_2$ is readily prepared from $Ga(C_5Me_5)_2Cl$ and $GaCl_3$ by a standard ligand redistribution reaction. An X-ray structural study of a light yellow crystal of $[Ga(C_5Me_5)Cl_2]_2$ demonstrates that the compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.804$ (4) Å, $b = 8.337$ (4) Å, $c = 17.086$ (5) Å, $\beta = 94.59$ (5)°, and $d_{calcd} = 1.465$ g cm^{-3} for $Z = 2$. Full-matrix least-squares refinement led to a final R value of 0.052 for 1009 observed reflections. This dimeric molecule also contains chlorine bridges with planar η^1-pentamethylcyclopentadienyl rings. Consequently, these new compounds have provided the first structural studies of organogallium halides and permit useful comparisons with the structural data for $[GaCl_3]_2$.

Introduction

The synthesis and structural characterization of group 3 compounds containing cyclopentadienyl ligands can play an important role in the development of main-group organometallic chemistry. However, relatively little is known about this specific class of compounds. The only typical +3 oxidation state homoleptic derivatives for which the details of their syntheses, properties, and structures have been described are $Ga(C_5H_5)_3$, a simple three-coordinate gallium compound,[2] and $In(C_5H_5)_3$, a compound with one bridging and two terminal cyclopentadienyl groups.[3,4] Tricyclopentadienylgallium[2] is readily prepared from $GaCl_3$ and a slight stoichiometric excess of LiC_5H_5 in diethyl ether solution, provided the reaction temperature is maintained below room temperature. If the preparative reaction occurs at 25 °C, $[Ga(C_5H_5)_2OEt]_2$ is reported as the product.[5] The only reported cyclopentadienyl group 3 halogen derivatives are $(C_5H_5)_2InI$ and $(C_5H_5)InI_2$, but no structural data are available to explain the unusual properties of these compounds.[6] This paucity of data also extends to the pentamethylcyclopentadienyl series of compounds. No simple homoleptic or halogen derivatives have been described for any group 3 element. The only reported pentamethylcyclopentadienyl group 3 compounds are $[(C_5Me_5)Al(Cl)R]_2$ (R = Me, Et, and *i*-Bu) and $[(\eta^5\text{-}C_5Me_5)BI]^+CF_3SO_3^-$. These unusual aluminum compounds[7] were the products of reactions of alkylaluminum halides $[R_2AlCl]_2$ with LiC_5Me_5 or C_5Me_5MgCl in toluene at 25 °C. It is of interest that structural studies of $[(C_5Me_5)Al(Cl)(i\text{-}Bu)]_2$ and $[(C_5Me_5)Al(Cl)(Me)]_2$ reveal unusual planar η^3-C_5Me_5 and intermediate η^2–η^3-C_5Me_5 ring attachments to the central Al_2Cl_2 units, respectively. The boron compound[8] has an η^5-C_5Me_5–boron structure.

In this paper we report the synthesis of $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$. The new compound $Ga(C_5Me_5)_2Cl$ can be isolated as the only gallium-containing product from a reaction designed to yield $Ga(C_5Me_5)_3$. The dichloroderivative $Ga(C_5Me_5)Cl_2$ was prepared from $Ga(C_5Me_5)_2Cl$ and $GaCl_3$ by a ligand redistribution reaction. Both new compounds have been fully characterized by elemental analyses, cryoscopic molecular weight data, spectroscopic data, Lewis acid–base studies, and X-ray structural studies. These two studies have also produced the first structures of neutral organogallium halides.

Experimental Section

General Data. All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in standard vacuum line or a purified argon atmosphere. Gallium(III) chloride was purified by sublimation under high vacuum at 70–80 °C immediately prior to use. Pentamethycyclopentadiene was purchased from Sterm Chemicals, Inc. Lithium pentamethylcyclopentadienide was prepared from freshly

---

[1] (a) State University of New York at Buffalo. (b) University of Alabama.

[2] Beachley, O. T. Jr.; Getman, T. D.; Kirss, R. U.; Hallock, R. B.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 751.

[3] Poland, J. S.; Tuck, D. G. *J. Organomet. Chem.* **1972**, *42*, 307.

[4] Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *Inorg. Chem.* **1972**, *11*, 2832.

[5] Cowley, A. H.; Mehrotra, S. K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1985**, *4*, 1115.

[6] Contreras, J. G.; Tuck, D. G. *J. Organomet. Chem.* **1974**, *66*, 405.

[7] (a) Schonberg, P. R.; Paine, R. T.; Campana, C. F.; Duesler, E. N. *Organometallics* **1982**, *1*, 799. (b) Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *101*, 7726.

[8] Kohl, F.; Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 56.

0276-7333/85/2304-1675$01.50/0

Table I. Crystal Data for $[Ga(C_5Me_5)_2Cl]_2$ and $[Ga(C_5Me_5)Cl_2]_2$

compd	$Ga_2C_{40}H_{60}Cl_2$	$Ga_2C_{20}H_{30}Cl_4$
mol wt	751.22	551.68
space group	$P1$	$P2_1/c$
cell const		
a, Å	7.825 (3)	8.804 (2)
b, Å	14.341 (4)	8.337 (4)
c, Å	23.853 (6)	17.086 (5)
α, deg	79.20 (3)	90.00
β, deg	86.28 (3)	94.59 (5)
γ, deg	84.93 (3)	90.00
cell vol, Å^3	2916	1250
molecules/unit cell (Z)	3	2
ρ(calcd), g cm^{-3}	1.28	1.465
μ(calcd), cm^{-1}	16.21	26.97
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.40 × 0.20 × 0.15	0.25 × 0.30 × 0.20
scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
std reflctns	400, 050, 006	200, 020, 004
decay of stds	±2%	±2%
reflctns measd	5444	1889
2θ range, deg	2–40	2–46
obsd reflctns ($I \geq 3\sigma(I)$)	2007	1009
no. of parameters varied	295	118
GOF	1.31	0.91
R	0.061	0.052
R_w	0.065	0.057

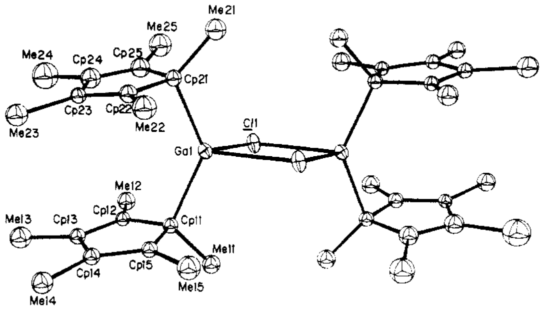

Figure 1. Labeling of atoms in $[Ga(C_5Me_5)_2Cl]_2$ (molecule A). ORTEP-II diagram showing 30% probability contours of the thermal vibration ellipsoids of non-hydrogen atoms.

distilled C_5Me_5H and Li-n-Bu in a hexane–pentane mixture. The solvents and other reagents were purified by conventional means and were vacuum distilled immediately prior to 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 Model 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 $SiMe_4$ as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum. The molecular weights were measured cryoscopically in benzene using an instrument similar to that described by Shriver.[9]

Synthesis of $Ga(C_5Me_5)_2Cl$. In a typical synthetic reaction, freshly sublimed $GaCl_3$ (2.19 g, 12.4 mmol) was added as a solution in 50 mL of Et_2O to a slurry of LiC_5Me_5 (3.88 g, 27.3 mmol) in 100 mL of Et_2O at room temperature with stirring. After the mixture was stirred overnight, a white precipitate was present beneath a yellow solution. The solvent was then removed by vacuum distillation and the entire apparatus was evacuated overnight at room temperature in order to ensure complete removal of Et_2O. The resulting pasty, yellow solid was extracted repeatedly with 50 mL of pentane. The light yellow, pentane-soluble solid was finally washed several times with 5 mL of cold (about −78 °C) pentane, leaving the product $Ga(C_5Me_5)_2Cl$ (3.41 g, 9.08 mmol, 73.2% yield based on $GaCl_3$) as a colorless solid. The identical product $Ga(C_5Me_5)_2Cl$ was formed when the reactant ratio of $LiC_5Me_5/GaCl_3$ was 3.2/1 or 2.2/1, when the reaction solvent was THF or Et_2O or when the reaction mixture was maintained at 0 °C or refluxed.

$Ga(C_5Me_5)_2Cl$: mp 138–142 °C melts to a yellow liquid; a colorless solid is reformed upon cooling which then remelts at 140–142 °C; ^1H NMR (benzene) δ 1.75 (s); IR (Nujol mull, cm^{-1}) 2730 (w), 1630 (m), 1618 (m), 1253 (m), 1220 (vs), 1130 (m, br), 1065 (m), 1007 (vw), 943 (vw), 838 (vw), 811 (vw), 789 (w), 717 (w), 690 (m), 596 (m), 562 (m), 434 (w), 403 (w), 290 (vs). Cryoscopic molecular weight, formula weight $Ga(C_5Me_5)_2Cl$ 376 (obsd mol wt, obsd molality, association): 405, 0.0969, 1.08; 402, 0.0698, 1.07; 393, 0.0608, 1.05. Solubility: soluble in benzene, pentane, Et_2O, and THF. No stable adducts were formed with Et_2O or THF. Anal. Calcd: C, 63.94; H, 8.05; Cl, 9.45. Found: C, 64.56; H, 8.26; Cl, 9.75. Crystals suitable for the X-ray structural study were obtained by slow sublimation of a sample in a sealed, evacuated tube heated to 100–105 °C.

Synthesis of $Ga(C_5Me_5)Cl_2$. A pentane solution of $Ga(C_5Me_5)_2Cl$ (0.520 g, 1.38 mmol) contained in a side-arm dumper was added to a pentane solution of $GaCl_3$ (0.244 g, 1.38 mmol) at room temperature. The resulting solution was then stirred overnight. After removal of pentane by vacuum distillation, a light yellow solid remained. The product was then recrystallized from a pentane solution at −78 °C to yield $Ga(C_5Me_5)Cl_2$ as a very light yellow solid (0.360 g, 1.31 mmol, 47.1% yield).

$Ga(C_5Me_5)Cl_2$: mp 90–110 °C, decomposes to a purple liquid; ^1H NMR (benzene) δ 1.76 (s); IR (Nujol mull, cm^{-1}) 2730 (w), 1605 (w), 1318 (s), 1138 (m), 1048 (m), 943 (m), 799 (w), 784 (w), 717 (w), 680 (m), 642 (vw, sh), 582 (m), 560 (vw, sh), 532 (vw), 460 (s), 390 (vs), 335 (vw), 308 (vw, sh), 275 (m, sh), 264 (vs), 225 (vs). Cryoscopic molecular weight, formula weight $Ga(C_5Me_5)Cl_2$ 276 (obsd mol wt, obsd molality, association): 479, 0.0962, 1.74; 466, 0.0611, 1.69; 473, 0.0418, 1.71. Solubility: soluble in benzene and pentane. Anal. Calcd: C, 43.68; H, 5.60. Found: C, 43.44; H, 5.61. Crystallographic quality crystals were obtained from a pentane solution cooled to 0 °C for 17 h.

Crystallographic Studies. Single crystals of the two title compounds were sealed under an N_2 atmosphere in thin-walled glass capillaries. The crystals were mounted and data were collected on a Enraf-Nonius CAD-4 diffractometer by the $\omega/2\theta$ scan technique. The reflection data were corrected for Lorentz and polarization effects but not for absorption effects. A summary of the data collection parameters and final lattice parameters as

---

[9] Shriver, D. F. "The Manipulations of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969, p 159.

Table II. Final Fractional Coordinates for $[Ga(C_5Me_5)_2Cl]_2$

atom	*x/a*	*y/b*	*z/c*
Ga(1)	0.6055 (4)	0.3879 (2)	0.4867 (1)
Ga(2)	0.6176 (3)	0.0316 (2)	0.1775 (1)
Ga(3)	0.8339 (3)	−0.1937 (2)	0.1615 (1)
Cl(1)	0.3408 (7)	0.4570 (5)	0.4882 (3)
Cl(2)	0.5683 (6)	−0.1308 (4)	0.1677 (3)
Cl(3)	0.8842 (6)	−0.0321 (4)	0.1702 (3)
Cp(11)	0.632 (2)	0.292 (1)	0.5604 (9)
Cp(12)	0.803 (2)	0.263 (2)	0.5641 (9)
Cp(13)	0.821 (2)	0.166 (2)	0.5653 (9)
Cp(14)	0.668 (2)	0.131 (2)	0.5625 (9)
Cp(15)	0.556 (2)	0.203 (1)	0.5569 (9)
Me(11)	0.564 (3)	0.336 (2)	0.611 (1)
Me(12)	0.924 (3)	0.330 (2)	0.569 (1)
Me(13)	0.970 (3)	0.102 (2)	0.570 (1)
Me(14)	0.651 (3)	0.025 (2)	0.561 (1)
Me(15)	0.387 (3)	0.200 (2)	0.554 (1)
Cp(21)	0.668 (3)	0.378 (2)	0.407 (1)
Cp(22)	0.661 (3)	0.273 (2)	0.407 (1)
Cp(23)	0.804 (3)	0.232 (2)	0.4120 (9)
Cp(24)	0.914 (3)	0.304 (2)	0.412 (1)
Cp(25)	0.837 (3)	0.387 (2)	0.405 (1)
Me(21)	0.586 (3)	0.449 (2)	0.359 (1)
Me(22)	0.510 (3)	0.231 (2)	0.403 (1)
Me(23)	0.852 (3)	0.123 (2)	0.421 (1)
Me(24)	1.090 (4)	0.277 (2)	0.417 (1)
Me(25)	0.918 (3)	0.480 (2)	0.398 (1)
Cp(31)	0.582 (3)	0.053 (2)	0.257 (1)
Cp(32)	0.593 (3)	0.157 (2)	0.2495 (9)
Cp(33)	0.453 (3)	0.203 (2)	0.249 (1)
Cp(34)	0.339 (3)	0.134 (2)	0.261 (1)
Cp(35)	0.408 (3)	0.043 (2)	0.266 (1)
Me(31)	0.681 (3)	−0.007 (2)	0.304 (1)
Me(32)	0.755 (3)	0.203 (2)	0.241 (1)
Me(33)	0.421 (3)	0.314 (2)	0.237 (1)
Me(34)	0.160 (4)	0.161 (2)	0.262 (1)
Me(35)	0.343 (3)	−0.053 (2)	0.285 (1)
Cp(41)	0.553 (2)	0.111 (2)	0.1048 (9)
Cp(42)	0.622 (2)	0.206 (2)	0.0944 (9)
Cp(43)	0.502 (2)	0.277 (1)	0.0940 (9)
Cp(44)	0.355 (3)	0.232 (2)	0.101 (1)
Cp(45)	0.381 (3)	0.141 (2)	0.1107 (9)
Me(41)	0.598 (3)	0.061 (2)	0.053 (1)
Me(42)	0.795 (3)	0.219 (2)	0.083 (1)
Me(43)	0.524 (3)	0.384 (2)	0.079 (1)
Me(44)	0.202 (3)	0.292 (2)	0.102 (1)
Me(45)	0.264 (3)	0.066 (2)	0.120 (1)
Cp(51)	0.910 (3)	−0.204 (2)	0.080 (1)
Cp(52)	1.066 (3)	−0.251 (2)	0.088 (1)
Cp(53)	1.068 (3)	−0.344 (2)	0.088 (1)
Cp(54)	0.917 (3)	−0.365 (2)	0.076 (1)
Cp(55)	0.820 (2)	−0.284 (2)	0.0713 (9)
Me(51)	0.887 (3)	−0.114 (2)	0.034 (1)
Me(52)	1.201 (3)	−0.191 (2)	0.096 (1)
Me(53)	1.207 (3)	−0.415 (2)	0.095 (1)
Me(54)	0.877 (4)	−0.467 (2)	0.072 (1)
Me(55)	0.654 (3)	−0.274 (2)	0.054 (1)
Cp(61)	0.864 (3)	−0.285 (2)	0.233 (1)
Cp(62)	1.028 (3)	−0.307 (2)	0.246 (1)
Cp(63)	1.074 (3)	−0.397 (2)	0.245 (1)
Cp(64)	0.945 (3)	−0.445 (2)	0.230 (1)
Cp(65)	0.825 (3)	−0.382 (2)	0.224 (1)
Me(61)	0.772 (3)	−0.251 (2)	0.287 (1)
Me(62)	1.132 (3)	−0.229 (2)	0.259 (1)
Me(63)	1.239 (3)	−0.449 (2)	0.261 (1)
Me(64)	0.952 (3)	−0.551 (2)	0.232 (1)
Me(65)	0.651 (3)	−0.397 (2)	0.217 (1)

Table III. Final Fractional Coordinates for $[Ga(C_5Me_5)Cl_2]_2$

atom	*x/a*	*y/b*	*z/c*
Ga	0.3598 (1)	0.5213 (2)	0.42710 (7)
Cl(1)	0.3785 (3)	0.5390 (4)	0.5662 (1)
Cl(2)	0.2500 (4)	0.2976 (4)	0.4038 (2)
Cp(1)	0.309 (1)	0.731 (2)	0.3794 (7)
Cp(2)	0.335 (1)	0.691 (1)	0.2977 (6)
Cp(3)	0.199 (1)	0.642 (1)	0.2604 (6)
Cp(4)	0.079 (1)	0.649 (2)	0.3141 (6)
Cp(5)	0.141 (1)	0.715 (2)	0.3833 (7)
Me(1)	0.392 (2)	0.869 (2)	0.4186 (8)
Me(2)	0.484 (1)	0.706 (2)	0.2621 (8)
Me(3)	0.170 (2)	0.586 (2)	0.1765 (7)
Me(4)	−0.084 (1)	0.608 (2)	0.2959 (8)
Me(5)	0.059 (2)	0.761 (2)	0.4534 (7)

Table IV. Bond Lengths (Å) and Bond Angles (deg) for $[Ga(C_5Me_5)_2Cl]_2$

	Bond Distances		
Ga(1)–Cl(1)	2.432 (7)	Ga(1)–Cl(1)′	2.499 (8)
Ga(1)–Cp(11)	2.03 (2)	Ga(1)–Cp(21)	1.96 (2)
Ga(2)–Ga(3)	3.665 (4)	Ga(2)–Cl(2)	2.462 (6)
Ga(2)–Cl(3)	3.431 (7)	Ga(2)–Cp(31)	1.98 (2)
Ga(2)–Cp(41)	1.97 (2)	Ga(3)–Cl(2)	2.417 (7)
Ga(3)–Cl(3)	2.446 (7)	Ga(3)–Cp(51)	2.04 (2)
Ga(3)–Cp(31)	1.96 (2)		
	Bond Angles		
Cl(1)–Ga(1)–Cl(1)′	82.6 (2)	Cl(1)–Ga(1)–Cp(11)	107.4 (6)
Cl(1)–Ga(1)–Cp(21)	107.9 (7)	Cp(11)–Ga(1)–Cp(21)	130.3 (9)
Cl(2)–Ga(2)–Cl(3)	82.3 (2)	Cl(2)–Ga(2)–Cp(31)	112.4 (7)
Cl(3)–Ga(2)–Cp(31)	105.6 (7)	Cl(2)–Ga(2)–Cp(41)	104.1 (3)
Cl(3)–Ga(2)–Cp(41)	111.6 (7)	Cp(31)–Ga(2)–Cp(41)	130.5 (9)
Cl(2)–Ga(3)–Cl(3)	82.8 (2)	Cl(2)–Ga(3)–Cp(51)	112.8 (7)
Cl(3)–Ga(3)–Cp(51)	104.1 (7)	Cl(2)–Ga(3)–Cp(61)	105.2 (7)
Cl(3)–Ga(3)–Cp(61)	112.3 (7)	Cp(51)Ga(3)–Cp(61)	129.3 (9)
Ga(1)–Cl(1)–Ga(1)′	97.2 (3)	Ga(2)–Cl(2)–Ga(3)	97.5 (2)
Ga(2)–Cl(3)–Ga(3)	97.5 (2)		

Table V. Bond Lengths (Å) and Bond Angles (deg) for $[Ga(C_5Me_5)Cl_2]_2$

	Bond Distances		
Ga–Cl(1)′	2.352 (3)	Ga–Cl(1)	2.373 (3)
Ga–Cl(2)	2.124 (4)	Ga–Cp(1)	1.97 (1)
Cp(1)–Cp(2)	1.47 (2)	Cp(1)–Cp(5)	1.49 (2)
Cp(1)–Me(1)	1.49 (2)	Cp(2)–Cp(3)	1.37 (1)
Cp(2)–Me(2)	1.49 (2)	Cp(3)–Cp(4)	1.46 (2)
Cp(3)–Me(3)	1.51 (2)	Cp(4)–Cp(5)	1.35 (2)
Cp(4)–Me(4)	1.50 (2)	Cp(5)–Me(5)	1.50 (2)
	Bond Angles		
Cl(1)–Ga–Cl(1)′	88.6 (1)	Cl(1)′–Ga–Cl(2)	104.5 (1)
Cl(1)–Ga–Cl(2)	103.7 (1)	Cl(1)′–Ga–Cp(1)	113.7 (4)
Cl(1)–Ga–Cp(1)	110.8 (4)	Cl(2)–Ga–Cp(1)	128.1 (4)
Ga′–Cl(1)–Ga	91.4 (1)	Ga–Cp(1)–Cp(2)	98.2 (8)
Ga–Cp(1)–Cp(5)	95.8 (8)	Cp(2)–Cp(1)–Cp(5)	105 (1)
Ga–Cp(1)–Me(1)	114.2 (8)	Cp(2)–Cp(1)–Me(1)	119 (1)
Cp(5)–Cp(1)–Me(1)	120 (1)	Cp(1)–Cp(2)–Cp(3)	108 (1)
Cp(1)–Cp(2)–Me(2)	125 (1)	Cp(3)–Cp(2)–Me(2)	127 (1)
Cp(2)–Cp(3)–Cp(4)	109 (1)	Cp(2)–Cp(3)–Me(3)	128 (1)
Cp(4)–Cp(3)–Me(3)	123 (1)	Cp(3)–Cp(4)–Cp(5)	109 (1)
Cp(3–)Cp(4)–Me(4)	125 (1)	Cp(5)–Cp(4)–Me(4)	126 (1)
Cp(1)–Cp(5)–Cp(4)	109 (1)	Cp(1)–Cp(5)–Me(5)	124 (1)
Cp(4)–Cp(5)–Me(5)	127 (1)		

determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 25 high angle reflections ($2\theta > 26°$ for $Ga(C_5Me_5)_2Cl$ and $2\theta > 36°$ for $Ga(C_5Me_5)Cl_2$) accurately centered on the diffractometer are given in Table I.

Solution and Refinement of the Structure for $Ga(C_5Me_5)_2Cl$. The structure was solved by direct methods (MULTAN 80).[10] The gallium and chlorine atoms were located from *E* maps, and the subsequent calculation of difference Fourier maps permitted the location of all non-hydrogen atoms. Neutral atom scattering factors for Ga and Cl were taken from Cromer and Waber[11] and for H from standard sources.[12] The full-matrix least-squares refinement with isotropic temperature factors for

---

[10] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 80, a system of computer programs for the automatic solution of crystal structures from diffraction data, University of York, York, England, 1980.

[11] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

[12] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

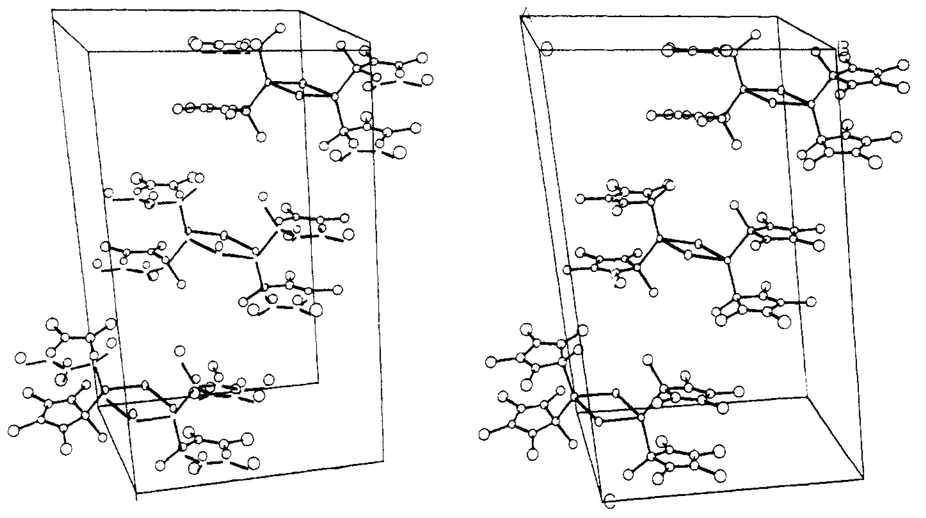

Figure 2. Stereoscopic view of the unit cell of $[Ga(C_5Me_5)_2Cl]_2$.

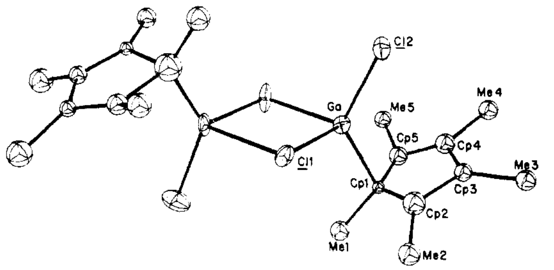

Figure 3. Labeling of atoms in $[Ga(C_5Me_5)Cl_2]_2$. ORTEP-II diagram showing 30% probability contours of the thermal vibration ellipsoids of non-hydrogen atoms.

all non-hydrogen atoms led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.085$. Conversion to anisotropic thermal parameters for Ga and Cl atoms and further refinement gave $R = 0.064$. Hydrogen atoms were located at the calculated positions 1.00 Å from the carbon atoms, and their parameters were not varied. Additional cycles of refinement led to the final values of $R = 0.061$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2} = 0.065$ based on 2007 observed reflections. In the last stage of refinement no parameters shifted by more than 0.01 of its estimated standard deviation. A final difference Fourier showed no feature greater than 0.42 e/Å^3. The final values of the positional parameters of atoms other than hydrogen are given in Table II. Anisotropic thermal parameters for gallium and chlorine atoms and isotropic thermal parameters for carbon atoms are given in Table VIII-S.

Solution and Refinement of the Structure for $Ga(C_5Me_5)Cl_2$. The structure was solved by direct methods (MULTAN 80).[10] Neutral atom scattering factors for Ga, Cl, and C were taken from Cromer and Waber[11] and for H from standard sources.[12] Full-matrix least-squares refinement with isotropic temperature factors led to the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.104$. Refinement with anisotropic temperature factors led to $R = 0.060$ for all non-hydrogen atoms. Hydrogen atoms were located in calculated positions 1.00 Å away from the bonded carbon atoms, and their parameters were not varied. Additonal cycles of refinement gave the final values of $R = 0.052$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.057$. In the last stage of refinement no parameters shifted by more than 0.01 of its estimated standard deviation. A final difference Fourier showed no feature greater than 0.50 e/Å^3. The final values of the positional and anisotropic thermal parameters of all nonhydrogen atoms are given in Tables III and IX-S, respectively. All calculations other than direct methods were carried out with the SHELX 76 system of computer programs.[13]

Results and Discussion

The first examples of fully characterized (pentamethylcyclopentadienyl)gallium compounds are represented by $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$. It is noteworthy that this investigation has also provided the first X-ray structural data for neutral organogallium halogen compounds. The other characterization data for these two new compounds include elemental analyses, molecular weight measurements, ^1H NMR and IR spectroscopic data, and preliminary evaluations of their Lewis acidity.

The synthesis of $Ga(C_5Me_5)_2Cl$ from reactions designed to yield $Ga(C_5Me_5)_3$ is a very surprising result. Our experiments, which employed $LiC_5Me_5/GaCl_3$ reactant mole ratios of greater than 3/1 in a variety of solvents and at different reaction temperatures, produced only $Ga(C_5Me_5)_2Cl$. These reactions suggest that LiC_5Me_5 does not react with $Ga(C_5Me_5)_2Cl$ in either diethyl ether or tetrahydrofuran at either 0 °C, room temperature, or the reflux temperature of the reaction mixture. These experiments also demonstrate that $Ga(C_5Me_5)_2Cl$ is a surprisingly weak Lewis acid. Diethyl ether and tetrahydrofuran do not form adducts which are stable to dissociation at room temperature. Consequently, $Ga(C_5Me_5)_2Cl$ is the only neutral organogallium compound from which the strong base tetrahydrofuran can be readily removed. Diethyl ether can be readily removed also from $Ga(C_5H_5)_3$[2] and $Ga(CH_2SiMe_3)_3$.[14] The compound $Ga(C_5Me_5)_2Cl$ is such a weak Lewis acid that the donor–acceptor chlorine bridge bonds observed for the crystal are readily broken. Molecular weight measurements in benzene solution suggest the presence of only monomeric species. There is no concentration dependence to the molecular weight data. These observations suggest that the entropy of solution is apparently able to more than compensate for the change in enthalpy associated with bridge bond formation to enable only monomers to be present in solution.

The dichloro derivative $Ga(C_5Me_5)Cl_2$ is readily prepared by a standard ligand redistribution reaction from equal mole quantities of $Ga(C_5Me_5)_2Cl$ and $GaCl_3$ in pentane solution. Unlike $Ga(C_5Me_5)_2Cl$ which is a colorless solid and has a distinct melting point, $Ga(C_5Me_5)Cl_2$ has a very light yellow color and it decomposes to a purple liquid upon heating. The compound is also readily soluble

---

[13] SHELX, a system of computer programs for X-ray structural studies by G. M. Sheldrick, University of Cambridge, Cambridge, England, 1976.

[14] Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 1021.

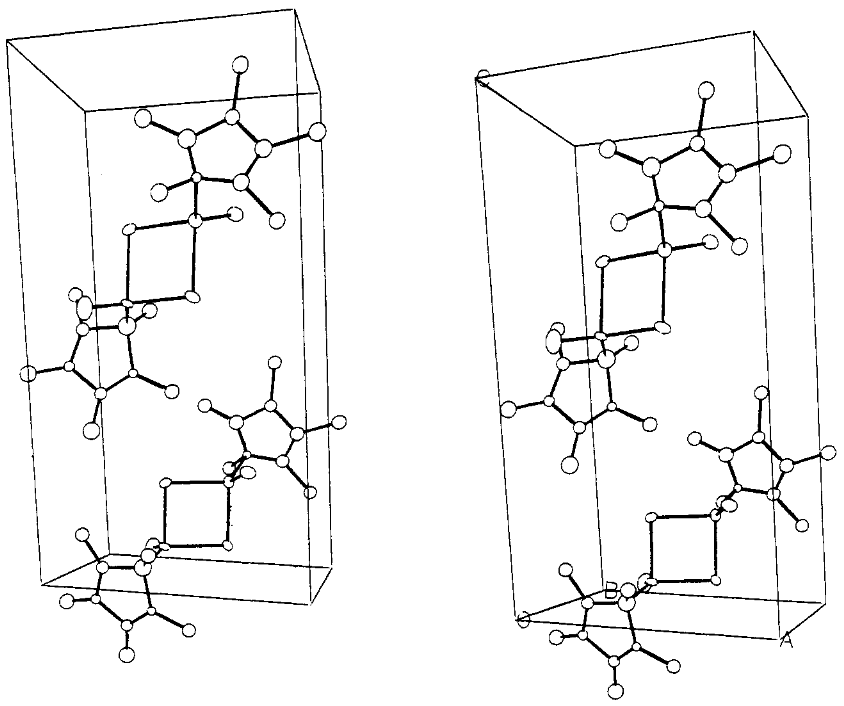

Figure 4. Stereoscopic view of the unit cell of $[Ga(C_5Me_5)Cl_2]_2$.

Table VI. Comparison of Distances (Å) and Angles (deg) between $(GaCl_3)_2$, $[Ga(C_5Me_5)Cl_2]_2$, and $[Ga(C_5Me_5)_2Cl]_2$

	$[GaCl_3]_2$[a]	$[Ga(C_5Me_5)Cl_2]_2$	$[Ga(C_5Me_5)_2Cl]_2$
$Ga-Cl_{term}$	2.06 (3)	2.124 (4)	
$Ga-Cl_{bridge}$	2.29 (9)	2.352 (3), 2.373 (3)	2.432 (7), 2.499 (8) 2.431 (7), 2.460 (6) 2.417 (7), 2.446 (7)
$Cl_{bridge}\cdots Cl_{bridge}$	3.35	3.300	3.261 3.217
$Ga\cdots Ga$	3.12	3.382	3.700 3.665
$Ga-C(C_5Me_5)$		1.97 (1)	2.03 (2), 1.96 (2) 1.98 (2), 1.97 (2) 2.04 (2), 1.96 (2)
$X_{term}-Ga-Y_{term}$	123 (1.5)	128.1 (4)	130.7 (9) 130.5 (9) 129.7 (9)
$Cl_{bridge}-Ga-Cl_{bridge}$	94 (2)	88.6 (1)	82.8 (2) 82.3 (2) 82.8 (2)
$Ga-Cl_{bridge}-Ga$	86 (2)	91.4 (1)	97.2 (3) 97.5 (2) 97.5 (2)
d_{calcd}, g cm^{-3}	2.50	1.47	1.28

[a] Reference 15.

in pentane and benzene, in which it exists as a dimer according to cryoscopic molecular weight measurements. The X-ray structural study demonstrates that dimeric molecules with chlorine bridges also exist in the crystals. Lastly, it is noteworthy that $Ga(C_5Me_5)_2Cl$ and $[Ga(C_5Me_5)Cl_2]_2$ cannot be distinguished by their ^1H NMR spectra in benzene solution. The chemical shifts of the single lines observed for each compound are 1.75 and 1.76 ppm for $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$, respectively. These observations that all methyl groups are equivalent according to ^1H NMR data implies fluxionality for these molecules. No attempt has been made to study these processes by temperature-dependent NMR.

The X-ray structural study of $[Ga(C_5Me_5)_2Cl]_2$ demonstrates that the crystal consists of discrete isolated molecules separated by normal van der Waals distances. There are three molecules in the unit cell. Therefore according to the symmetry of the space group of the crystal, one type of molecule (A) possesses a crystallographic center of inversion whereas the other two do not. The molecular structure of type A and the atom numbering scheme are shown in Figure 1, while the stereoview of the unit cell is shown in Figure 2. Selected interatomic distances and angles are presented in Table IV. A complete listing of interatomic distances and angles are given in Table VII-S. Both types of molecules in the unit cell are dimers in which the chlorine atoms serve as bridging ligands between the two gallium atoms. The pentamethylcyclopentadienyl rings are planar and exhibit η^1-coordination to gallium as shown by the C–C bond length patterns within each cyclopentadienyl ring. The gallium atoms have distorted tetrahedral environments.

The crystal of $[Ga(C_5Me_5)Cl_2]_2$ consists of discrete isolated molecules which possess a crystallographic center of inversion. The molecules are separated by normal van der Waals distances. Selected interatomic distances and angles are presented in Table V. Figure 3 shows the scheme used in labeling the atoms, while Figure 4 provides a stereoview of the unit cell. This dimeric molecule, like that of $[Ga(C_5Me_5)_2Cl]_2$, has bridging chlorine atoms. The pentamethylcyclopentadienyl rings are planar and exhibit η^1-coordination to gallium, which has distorted tetrahedral symmetry. It is also noteworthy that the atoms Cl(2), Ga, Cp(1), and Me(1) are coplanar. This plane is almost perpendicular to the plane of Ga, Cl(1), Ga,[1] and Cl(1)′ and to the plane of the cyclopentadienyl ring. The angles are 87.45° and 92.64°, respectively.

The comparison of structural data for the series of compounds $[GaCl_3]_2$,[15] $[Ga(C_5Me_5)Cl_2]_2$, and $[Ga(C_5Me_5)_2Cl]_2$ provide an evaluation of the effects of re-

---

(15) Wallwork, S. C.; Worrall, I. J. *J. Chem. Soc.* **1965**, 1816.

placing chlorine atoms bound to gallium with bulky pentamethylcyclopentadienyl ligands. For this series of dimeric chlorine bridged molecules, regular changes in bond distances and bond angles as well as in distances between similar but nonbonded atoms in the four-membered rings occur (Table VI). As the molecule changes from $[GaCl_3]_2$ to $[Ga(C_5Me_5)Cl_2]_2$ to $[Ga(C_5Me_5)_2Cl]_2$, the Ga–Cl bridge bonding distances increase significantly. The Cl–Ga–Cl ring angles decrease whereas the Ga–Cl–Ga ring angles increase in the series. These changes in ring angles are also reflected with an increase in the nonbonding Ga···Ga distance and with a decrease in the nonbonding Cl···Cl distance within the four-membered rings of the series. As the Ga_2Cl_2 ring dimensions and angles change, the terminal Ga–Cl distances and the angles between the terminal groups change. The observed changes in the dimensions of the molecules in this series also affect the calculated densities of the compounds. The observation that $[Ga(C_5Me_5)_2Cl]_2$ has the longest Ga–Cl (bridge) distances is also reflected in the ease of dissociation of the dimer. Only monomers are observed in benzene solution according to cryoscopic molecular weight data. The Ga–C distances in the two (pentamethylcyclopentadienyl)gallium compounds are comparable (Table VI) and similar to the average Ga–C distances in $Ga(C_5H_5)_3$[1] (2.05 [3] Å), $Ga(C_6H_5)_3$[16] (1.947 [1] Å), $MeGa(O_2CMe)_2$[17] (1.946 Å), $Me_2GaN_2C_5H_7$[18] (1.995 and 1.969 Å), and $KGa(CH_2SiMe_3)_3H$[19] (2.04 (1) and 2.02 (1) Å). Thus, in both new (pentamethylcyclopentadienyl)gallium compounds, the cyclopentadienyl ligand has no unusual structural features or bonding characteristics. The pentamethylcyclopentadienyl ring is acting as a simple monodentate ligand.

Acknowledgment. This work was supported by the National Science Foundation through Grants CHE-81-3316 (O.T.B.) and CHE-81-11137 (J.L.A.).

Registry No. $[Ga(C_5Me_5)_2Cl]_2$, 97210-83-8; $[Ga(C_5Me_5)Cl_2]_2$, 97210-84-9; $GaCl_3$, 13450-90-3; LiC_5Me_5, 51905-34-1.

Supplementary Material Available: Tables VII-S, VIII-S, and X-S, showing a complete listing of interatomic distances and angles, anisotropic thermal parameters for gallium and chlorine atoms and isotropic thermal parameters for carbon atoms, and calculated structure factor amplitudes for $[Ga(C_5Me_5)_2Cl]_2$, respectively, and Tables IX-S and XI-S, showing anisotropic thermal parameters for all non-hydrogen atoms and the calculated structure factor amplitudes for $[Ga(C_5Me_5)Cl_2]_2$, respectively (22 pages). Ordering information is given on any current masthead page.

---

[16] Malone, J. F.; Mcdonald, W. S. *J. Chem. Soc. A* **1970**, 3362.

[17] Hausen, H. D.; Sille, K.; Weidlein, J.; Schwarz, W. *J. Organomet. Chem.* **1978**, *160*, 411.

[18] Rendle, D. F.; Storr, A.; Trotter, J. *Can. J. Chem.* **1975**, *53*, 2944.

[19] Hallock, R. B.; Beachley, O. T., Jr.; Li, Y.-J.; Sanders, W. M.; Churchill, M. R.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1983**, *23*, 3683.

Communications

Pentamethylcyclopentadienyl Acetylacetonate Complexes of Iron(II), Cobalt(II), and Nickel(II). Convenient Synthetic Entries to Mono-η^5-C_5Me_5 Derivatives

Emilio E. Bunel,[†] **Luis Valle,**[†] **and Juan M. Manriquez***[‡]

Comision Chilena de Energia Nuclear
Casilla 188-D, Santiago, Chile
and Universidad Tecnica Federico Santa Maria
Casilla 110-V, Valparaiso, Chile

Received March 26, 1985

Summary: The reactions between $M(acac)_2$ (M = Fe, Co, and Ni; acac = acetylacetonate) and 1 mol of LiC_5Me_5 cleanly yield $(\eta^5\text{-}C_5Me_5)M(acac)$ (**2**, M = Fe; **6**, M = Co; **7**, M = Ni). **2** reacts with CO to give $(\eta^5\text{-}C_5Me_5)Fe(CO)(acac)$ (**3**) with methylmagnesium iodide under CO to give $(\eta\text{-}C_5Me_5)Fe(CO)_2CH_3$ (**4**) and with benzene–$AlCl_3$ followed by NH_4PF_6 to give $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**5**). **2**, **6**, and **7** react with NaC_5H_5 to give $(\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5H_5)$ (**10**, M = Fe; **11**, M = Co; **12**, M = Ni) in high yield. The reactions of **2** with lithium salts of 3,4-dimethyl(*p*-bromophenyl)cyclopentadiene and 2,3,4,5-tetramethyl(*p*-bromophenyl)cyclopentadiene afford $(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5H_2Me_2\text{-}p\text{-}C_6H_4Br)$ (**15**) and $(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5Me_4\text{-}p\text{-}C_6H_4Br)$ (**16**).

The first-row transition-metal organometallic chemistry generally starts with the binary metal carbonyls. Noncarbonyl organometallic complexes starting with other easily accessible binary compounds would provide entries to a broader spectrum of complexes.

Along this line, we report a general method of synthesis of the precursors $(\eta^5\text{-}C_5Me_5)M(acac)$, essential materials for the synthesis of a variety of mono-η^5-C_5Me_5 derivatives.

We find that a convenient procedure to the known $Fe(acac)_2$[1] consists of adding stoichiometric[2] amounts of acetylacetone and piperidine to an ether slurry of the easily available complex $FeCl_2{\cdot}2THF$[3] (THF = tetrahydrofuran) followed by filtration of the piperidine hydrochloride formed, removal of the ether under vacuum, and washing with pentane (eq 1). Crude **1** obtained in this way (50–60% yield) can be used in further reactions.

$$\mathrm{FeCl_2{\cdot}2THF} \xrightarrow[\text{2. piperidine}]{\text{1. acetylacetone}} \underset{1}{\mathrm{Fe(acac)_2}} + \mathrm{C_5H_{11}NHCl} \qquad (1)$$

Whereas the reaction of $FeCl_2{\cdot}2THF$ with 1 equiv of C_5Me_5Li in THF yields only $(\eta^5\text{-}C_5Me_5)_2Fe$,[4] under all conditions examined, $Fe(acac)_2$ reacts cleanly to afford $(\eta^5\text{-}C_5Me_5)Fe(acac)$ (**2**) (eq 2).

[†] Comision Chilena de Energia Nuclear.

[‡] Universidad Tecnica Federico Santa Maria.

[1] Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* **1967**, *20*, 281.

[2] If excess of piperidine is added, complex $Fe(acac)_2(piperidine)_2$ is isolated.

[3] Herzog, S.; Gustav, K.; Kruger, E.; Oberender, H.; Schuster, R *Z. Chem.* **1963**, 428.

[4] King, R. B.; Bisnett, M. B. *J. Organomet Chem.* **1967**, *8*, 287.

0276-7333/85/2304-1680$01.50/0