Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Additional support was provided by Monsanto Co. and by BRSG S07 RR07054-20 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health. NMR spectra were obtained with the expert assistance of Dr. André d'Avignon, director of the Washington University High Resolution NMR Service Facility. This facility was funded in part by NIH Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co. We thank Mr. Dennis Moore (Washington University Chemistry Department) for assistance in obtaining the mass spectrum of 1.

Registry No. 1, 102747-17-1; 2, 102747-18-2; 3, 102747-19-3; 4, 102747-20-6; $(Et_2PCH_2CH_2)_2PPh$, 102747-21-7; $Et_2PCH{=}CH_2$, 13652-21-6; $PhPH_2$, 638-21-1; $MnBr_2$, 13446-03-2; $K^+C_5H_7^-$, 51391-25-4; $K^+C_7H_{11}^-$, 74205-98-4.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, observed and calculated structure factor amplitudes, and significant least-squares planes including subtended dihedral angles (36 pages). Ordering information is given on any current masthead page.

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(16) During the 1970s, Tolman and Ittel[16a,b] demonstrated that electron-rich HM(Np)(dmpe)$_2$ complexes (Np = 2-naphthyl, M = Fe, Ru, Os) react with a variety of bonds that are normally difficult to activate. The features of this compound class which are apparently crucial to its unique reactivity are the ready accessibility of coordinatively unsaturated intermediates (M(dmpe)$_2$) and high electron density at the metal center. (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *Ibid.* **1979**, *101*, 1742. More recently, Bergman[16c] and Green[16d] have used electron-rich (η^5-cyclopentadienyl)M(PR$_3$)$_3$ complexes of the manganese group metals to activate C–H bonds in alkanes and C–O bonds in carbon dioxide, respectively. (c) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (d) Green, M. L. H.; Joyner, D. S.; Wallis, J.; Bell, J. P. Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

([2.2]Paracyclophane)gallium(I) Tetrabromogallate(III): Its Synthesis and Novel Structural Features

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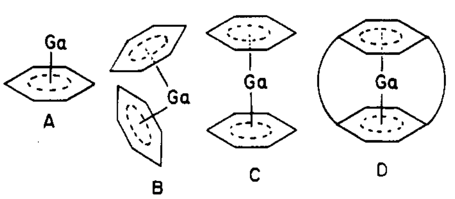
[2.2]Paracyclophane forms 1:1 complexes (1, 2) with Ga_2Cl_4 and Ga_2Br_4, respectively, in benzene at ambient temperature. The products are insoluble in common organic solvents. The crystal and molecular structure determination shows compound 2 to form an intricate highly symmetrical three-dimensional network (orthorhombic, space group *Pnma* with $a = 12.836$ (4) Å, $b = 10.004$ (3) Å, $c = 14.943$ (4) Å, $V = 1918.9$ Å^3, $d_{calcd} = 2.310$ g/cm^3 for $Z = 4$, $R_w = 0.038$ for 106 refined parameters and 1352 unique reflections with $F_o \geq 4.0\sigma(F_o)$). Each Ga(I) center is complexed by two [2.2]paracyclophane molecules, whose parallel pairs of aromatic rings are tilted relative to each other by 56.7°. The 1:1 stoichiometry implies that each paracyclophane in turn is bonded to two Ga(I) atoms which are situated nearly centrically above each of the arene rings at a distance of 2.72 Å. The polydecker chains of alternating gallium(I) ions and paracyclophane molecules thus formed are cross-linked by tetrahedral $GaBr_4^-$ anions, each of which provides one bromine atom to bridge two Ga(I) centers. Thereby the latter adopt a strongly distorted pseudotetrahedral coordination geometry.

Introduction

Compounds of subvalent gallium, indium, and thallium have recently been found to form a variety of arene complexes in which these elements are η^6-bonded to either one or two aromatic hydrocarbons (A and B).[1-7] In type B, the two arenes can be equidistant from the metal[3,6,7] or can show significant differences in their metal–ring distances.[2] In all cases investigated to date, the metal is accommodated perpendicular above the ring centers, however, and if two rings are present, their planes form an angle between 37 and 60°.[1] Compounds of unknown structure are formed in arene oxidation using gallium(III).[8] Though theoretical calculations[1] have shown that the bent form B is energetically favored over a situation with parallel arene rings (C), the special geometrical requirements of, e.g., chelating ligands can be expected to make the parallel sandwich structure D for a corresponding complex also feasible.



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† X-ray analysis.

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Table I. Crystal Structure Data for 2

formula	$C_{16}H_{16}Br_4Ga_2$
fw	667.36
cryst system	orthorhombic
space group	*Pnma* (no. 62)
a, Å	12.836 (4)
b, Å	10.004 (3)
c, Å	14.943 (4)
V, Å^3	1918.9
Z	4
d, g/cm^3	2.310
$F(000)$, e	1256
μ(Mo Kα), cm^{-1}	110.45
T, °C	−40
radiatn	Mo Kα, λ = 0.71069 Å
scan mode	ω
scan width (in ω)	0.9
scan speed (in ω), deg/min	0.9–29.3
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.595
hkl range	+14,+11,±17
std refl	006, 020, 400
refl measd	3759
refl unique	1760
R_{int}[a]	0.039
refl obsd [$F_o \geq 4.0\sigma(F_o)$]	1352
absorptn correctn	empirical
param ref	106
R[b]	0.034
R_w[c]	0.038
$(\text{shift/error})_{max}$	0.001
$\Delta\rho_{max}$, e/Å^3	+0.78/−0.95

[a] $R_{int} = [\sum(N\sum_n w(\langle F\rangle - F)^2)/\sum((N-1)\sum_n wF^2)]^{1/2}$, where n is the number of reflections averaged. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 1/[\sigma^2(F_o) + 0.0004F^2]$.

[2.2]Paracyclophane is the species with the smallest possible interarene distance in cyclophanes, but previous studies with this molecule showed that metals can still be inserted into the interstice between the aromatic rings.[9] A chromium(0) complex is the prototype for these (cyclophane)metal species, and most studies have focussed on this compound and its derivatives.[9,10]

According to generally accepted tables of atomic and ionic radii,[11] the dimensions of chromium(0) and gallium(I) are quite similar, and this fact suggests experiments oriented toward the introduction of Ga^+ cations in between the rings of cyclophanes. When this program was initiated, with [2.2]paracyclophane, the most readily accessible member of the cyclophane series, as the ligand and with $Ga[GaCl_4]$ and $Ga[GaBr_4]$ as the Ga^+-containing substrates, two compounds with a 1:1 stoichiometry in fact could be isolated without difficulty. In an X-ray structure analysis of one of these materials it was demonstrated, however, that the Ga^+ cations were not accommodated within the cyclophane cages but were attached to the arene rings from their outer sides, giving rise to zig-zag chainlike polydecker columns interconnected by the tetrabromogallate(III) anions. Synthesis and details of this novel structural principle are reported in this paper.

Results

Benzene solutions of $Ga[GaCl_4]$, which are now known to contain the dimeric bis(benzene)gallium(I) tetrachlorogallate(III) complex,[2] afford white precipitates on addition of a benzene solution of [2.2]paracyclophane. Their elemental analysis indicates a 1:1 stoichiometry. The precipitates appear in quantitative yields, and the benzene filtrates are free of Ga^+ if an equimolar quantity of the cyclophane (or an excess) is employed. With $Ga[GaBr_4]$ the results are essentially similar:

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 2[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Ga1	0.5868 (1)	0.2500 (0)	0.5462 (1)	0.020
Br1	0.7081 (1)	0.2500 (0)	0.7188 (1)	0.030
Br2	0.4826 (1)	0.3759 (1)	0.5541 (1)	0.034
Br3	0.6788 (1)	0.2500 (0)	0.3434 (1)	0.026
Ga2	0.9414 (1)	0.2500 (0)	0.3235 (1)	0.032
C1	1.0826 (4)	0.0996 (4)	0.4293 (6)	0.018
C2	1.0184 (5)	0.1300 (4)	0.5317 (6)	0.023
C3	0.9127 (5)	0.1085 (4)	0.5360 (6)	0.022
C4	0.8693 (4)	0.0558 (4)	0.4371 (6)	0.021
C5	0.9265 (4)	0.0427 (4)	0.3209 (6)	0.024
C6	1.0322 (4)	0.0646 (4)	0.3171 (6)	0.024
C7	1.1983 (4)	0.0883 (4)	0.4490 (7)	0.029
C8	0.7748 (4)	−0.0017 (5)	0.4662 (7)	0.030

[a] (U(eq) = $(U(1)U(2)U(3))^{1/3}$, where $U(1)$, $U(2)$, and $U(3)$ are the eigenvalues of the U(ij) matrix. Esd's are in parentheses.

Table III. Selected Bond Distances (Å) and Angles (deg) for 2[a]

	Bond Distances		
Ga(1)–Br(1)	2.325 (1)	C(1)–C(2)	1.391 (8)
Ga(1)–Br(2)	2.309 (1)	C(1)–C(6)	1.392 (8)
Ga(1)–Br(3)	2.347 (1)	C(3)–C(4)	1.383 (8)
Ga(2)–Br(3)	3.378 (1)	C(4)–C(5)	1.388 (8)
Ga(2)–Br(3)*	3.474 (1)	C(2)–C(3)	1.394 (8)
Ga(2)–C(1)	3.075 (5)	C(5)–C(6)	1.408 (8)
Ga(2)–C(2)	2.921 (6)	C(1)–C(7)	1.508 (7)
Ga(2)–C(3)	3.021 (6)	C(4)–C(8)	1.514 (8)
Ga(2)–C(4)	3.252 (6)	C(7)–C(8)*	1.586 (7)
Ga(2)–C(5)	3.103 (6)		
Ga(2)–C(6)	3.011 (6)		
Ga(2)···E	2.733 (8)		
	Bond Angles		
Br(1)–Ga(1)–Br(2)	111.2 (1)	Br(3)–Ga(2)···E	97.4 (8)
Br(1)–Ga(1)–Br(3)	107.8 (1)	Br(3)*–Ga(2)···E	93.0 (8)
Br(2)–Ga(1)–Br(2)*	109.1 (1)	Ga(1)–Br(3)–Ga(2)	123.6 (1)
Br(2)–Ga(1)–Br(3)	108.7 (1)	Ga(1)–Br(3)–Ga(2)*	88.5 (1)
Br(3)–Ga(2)–Br(3)*	154.7 (1)	Ga(2)–Br(3)–Ga(2)*	147.9 (1)
E···Ga(2)···E*	131.1 (8)		

[a] See Figure 1 for numbering scheme adopted. E is the centroid of the aromatic rings. Atoms with an asterisk are related to those without an asterisk by the following symmetry operations: Br(2)*, E*, x, $0.5 - y$, z; Br(3)*, $x + 0.5$, y, $0.5 - z$; Ga(2)*, $x - 0.5$, y, $0.5 - z$; C(8)*, $2 - x$, $-y$, $1 - z$.

$$Ga[GaX_4] + (1,4\text{-}C_6H_4CH_2CH_2)_2 \xrightarrow[20\ °C]{C_6H_6} [(1,4\text{-}C_6H_4CH_2CH_2)_2Ga]^+[GaX_4]^-$$

1, X = Cl
2, X = Br

The two products (1 and 2) are less sensitive to air and moisture than the starting materials and other arene complexes of gallium(I).[1] Hydrolysis proceeds much more slowly, and elemental gallium (from disproportionation) is formed only after half an hour at ambient temperature.

The new compounds are insoluble in benzene and other aromatic hydrocarbons but also in diethyl ether, tetrahydrofuran, dioxane, and dichloromethane. Thus no high-resolution NMR spectra can be obtained. The initial precipitates are not amorphous, however, and distinct X-ray powder patterns can be recorded. Single crystals of compound 2 of sufficient size for X-ray diffraction formed out of the original mother liquor of the preparation (see below). The [2.2]paracyclophane precipitation is

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[9] Elschenbroich, C.; Möckel, R.; Zenneck, U. *Angew. Chem.* **1978**, *90*, 560. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531.

[10] Koray, A. R.; Ziegler, M. L., Blank, N. E., Haenel, M. W. *Tetrahedron Lett.* **1979**, 2465.

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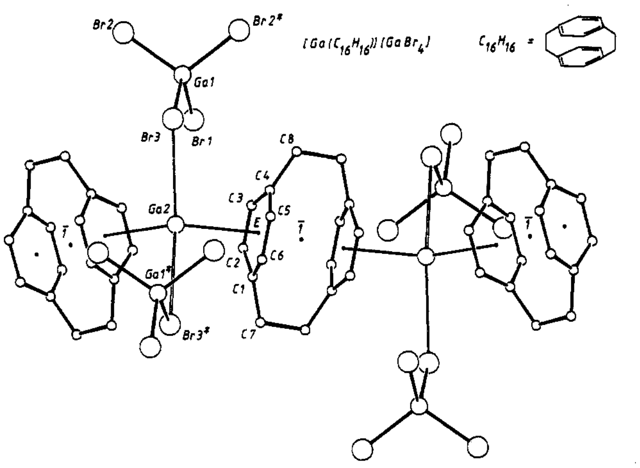

Figure 1. Details of the bent gallium(I)–paracyclophane–gallium(I) chains running parallel to the crystallographic *b* axis together with the $GaBr_4^-$ tetrahedra coordinated to the gallium(I) centers (ORTEP, atoms with arbitrary radii). Atoms Ga(1), Ga(2), Br(1), and Br(3) are situated on crystallographic mirror planes which relate Br(2) and Br(2)* as well as the centrosymmetric [2.2]paracyclophane molecules. The $GaBr_4^-$ tetrahedra are crystallographically related by a twofold screw axis along *a*.

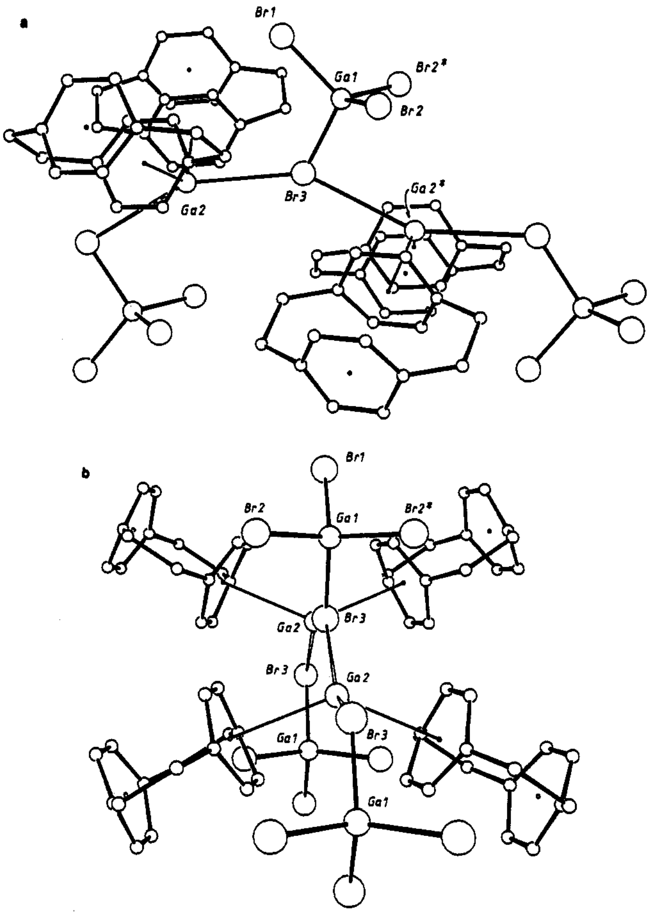

Figure 2. (a) A plot of the extended Ga(I)–Br–Ga(I) chain cross-linking the polydecker columns depicted in Figure 1 (ORTEP). The atoms forming the chain are situated on the mirror plane parallel to *a*. (b) A "end on" view of the Ga(I)–Br–Ga(I) chain (ORTEP).

specific for gallium(I). Indium(I) or thallium(I) salts gave little (In) or no precipitate (Tl) with the cyclophane. It was therefore of prime interest to determine the crystal structure of the products 1 and 2, which obviously represent the ideal metal(I)/cyclophane combination, either due to accommodation of the Ga^+ between the arene planes of the ligand or due to perfect aggregation of outer-coordinated metal/cyclophane moieties.

The single-crystal structure determination of compound 2 (Tables I–III) reveals a complicated three-dimensional network. Each gallium(I) center (designated Ga(2)) is situated on a crystallographic mirror plane and coordinated to two arene moieties of two centrosymmetric [2.2]paracyclophane molecules (Figure 1).

Approximate η^6-coordination of the aromatic systems follows from comparable Ga(2)–C bond lengths which range between 2.921 (6) and 3.252 (6) Å (Table III). The longer distances to the bridgehead carbons C(1) and C(4) result mainly from the boat distortion of the aromatic system induced by the double bridging through CH_2CH_2 moieties. The short Ga(2)–C(1) distance indicates that a small ring tilt also determines the Ga(2)–C distances, however. (C(1) and C(4) deviate by 0.152/0.155 Å from the plane through the remaining four ring atoms.) The distance of Ga(2) to the best plane through all six aromatic carbon atoms is 2.72 Å, and the line Ga(2)–E (the center of the benzoid rings) forms an angle of 4.8° with the normal to this plane also indicative of a slight deviation from perfect η^6-coordination. The arene planes of two different cyclophanes are tilted against each other to give an interplanar angle of 56.7° and a E–Ga(2)–E* angle of 131.1°.

As a consequence of the boat distortion of the aromatic rings, the distance between the two arenes within the [2.2]paracyclophane varies between 2.749 (8) Å at the bridgehead carbon atoms (C(1), C(4)) and 3.048 (8) Å at the other four ring atoms (C(2), C(3), C(5), C(6)).

The 1:1 stoichiometry implies that each [2.2]paracyclophane molecule in turn coordinates to two gallium(I) centers, thus leading to a centered coordination of *both* aromatic rings of the [2.2]paracyclophane species in the coordination polymer. The resulting chain-like polydecker column of alternating gallium(I) centers and doubly capped paracyclophanes runs parallel to the crystallographic *b* axis (Figures 1 and 3). A zig-zag arrangement is induced by the bent coordination geometry at Ga(2) whereas the centrosymmetry of the double-bridged arene systems implies a linear gallium(I)–paracyclophane–gallium(I) portion of the chain.

The coordination geometry around the gallium(I) centers (Ga(2)) is completed by two bromine atoms (Br(3), Br(3)*) from two neighboring $GaBr_4^-$ tetrahedra whose gallium(III) atoms (designated Ga(1)) lie on the same crystallographic mirror plane as Ga(2) (Figure 1). The Ga(2)–Br(3) contacts are rather long (3.378 (1) and 3.474 (1) Å), in contrast to the values found in the tetrahedral $GaBr_4^-$ units (Table III), where the Ga–Br bond lengths are shorter by more than 1 Å. Not unexpectedly, the Ga(1)–Br(3) bond length to the bridging Br(3) is slightly longer than the other three Ga(1)–Br distances, however. It should be noted that by virtue of the crystallographic mirror plane containing Ga(2), Br(3), and Br(3)*, the Ga(2)–Br(3)/Br(3)* contacts exactly bisect the angle formed by the two arene systems coordinated to Ga(2). Severe distortion of the pseudotetrahedral coordination geometry at Ga(2) results mostly from an Br(3)–Ga(2)–Br(3)* angle (154.7 (1)°) which approaches *linearity* (Table III and Figure 2a). The other Ga(2)–Br distances, e.g., Ga(2)–Br(1) (4.961 (1) Å) and Ga(2)*–Br(2)/Br(2)* (4.253 (1) Å), are certainly too long to be considered coordinative.

The double bridging nature of Br(3) between two Ga(2) atoms provides a cross-link connecting the Ga(2)–paracyclophane columns parallel to the crystallographic *a* axis (Figures 2 and 3). As Figure 2a shows, the trigonal geometry at the bridging Br(3) atoms is highly irregular despite the almost equal Ga(2)–Br(3) contacts. An unusually large Ga(2)–Br(3)–Ga(2)* angle of 147.9 (1)° is contrasted by Ga(1)–Br(3)–Ga(2)/Ga(2)* angles of 123.6

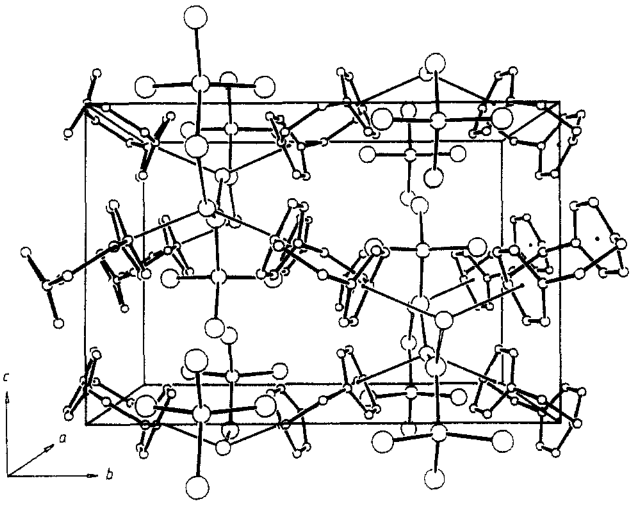

Figure 3. A perspective view of the unit cell contents of 2 as seen along the crystallographic *a* axis (ORTEP). The Ga(I)–paracyclophane–Ga(I) columns are seen parallel *b*. The Ga(I)–Br(3)–Ga(I) chains are perpendicular to the plane of the paper and on the mirror planes at *b* = $^1/_4$ and $^3/_4$. The "pockets" containing the $GaBr_4^-$ tetrahedra are clearly seen.

(1)° and 88.5 (1)°, respectively. The entire arrangement Br(3)Ga(1)Ga(2)Ga(2)* is strictly planar, however, as all atoms reside on a crystallographic mirror plane.

A three-dimensional network instead of a mere sheet structure arises from the fact that the bridging $GaBr_4^-$ tetrahedra each link two gallium(I) centers belonging to different sheets of (cyclophane)gallium stacks, as is clearly seen in Figure 3. This figure also illustrates that the resulting highly symmetrical network contains rather large pockets between the gallium(I)–paracyclophane chains, which are filled by the connecting $GaBr_4^-$ tetrahedra.

Discussion

The structure of compound 2 comprises several novel structural features. Most noteworthy is the bent polydecker arrangement of the gallium(I)–[2.2]paracyclophane–gallium(I) chains with the gallium metal centers being coordinated by two paracyclophane molecules, which in turn have both of their aromatic systems complexed from the outside by gallium(I). The individual bonding parameters are in line with previously characterized gallium(I) arene complexes.[1-5] In particular the metal–arene distance (2.72 Å) as well as the interplanar angle of the coordinated aromatic rings (56.7°) fit nicely into the pattern of parameters obtained from previous work.[1] Comparative values range between 2.52 Å (in $C_6(CH_3)_6Ga{\cdot}GaBr_4$[5]) and 2.76/2.93 Å (in $[(C_6H_6)_2Ga{\cdot}GaCl_4]_2{\cdot}3C_6H_6$[2]) for the Ga arene distance and 39.7° (in $[C_6H_3(CH_3)_3]_2Ga{\cdot}GaCl_4$[3]) and 55.6° (in the bis(benzene)gallium complex[2]) for the bis(arene) interplanar angle. Clearly, there is a preference for the outer coordination of the double-bridged bis(arene) system. The reason for this has to be certainly sought in the long gallium(I) distances perpendicular to the arene of more than 2.5 Å observed in all structures determined as yet.[1] The separation of 2.78–3.09 Å of the opposite ring atoms in uncomplexed [2.2]paracyclophane[12] is far too small to accommodate the 5 Å separation of the aromatic rings expected for a bis(arene)gallium(I) system with parallel arenes on the basis of the hitherto observed distances in the bent systems.[1] On the other hand, an average separation of 2.94 Å might still be feasible for a bis(arene)Cr^0 system, as the arene separation in $(C_6H_6)_2Cr$ amounts only to 3.23 Å.[13,14] The reason for the drastically longer gallium(I)–arene distances is most probably associated with the much weaker bonding.[1]

The molecular dimensions of the bis-complexed [2.2]paracyclophane are astonishingly similar to those of the "free" molecule.[12] Probably most important is a slight reduction in the interarene distances from 2.78/3.09 Å[15] in [2.2]paracyclophane[12] to the 2.749 (8)/3.048 (8) Å in the complex which might reflect a reduction in the inner π-electron density and, consequently, less repulsion of the aromatic systems. This finding is substantiated by a comparison with the mono(tricarbonylchromium) complex of [2.2]paracyclophane[16] where an even smaller interarene distance was found, in line with the more electron-withdrawing nature of the $Cr(CO)_3$ group.

Another noteworthy feature are the almost perfectly regular $GaBr_4^-$ tetrahedra linking the gallium(I) atoms. The fact that only one of their bromine atoms acts as a (doubly bridging) link is unprecedented in the structural chemistry of the arene complexes of lower valent gallium. Inspection of Figures 2a and 3 shows that this is most probably caused by the geometrical requirements of the interstices between the bent polydecker chains which might also be responsible for the very long Ga(2)–Br(3)/Br(3)* distances. Similar arguments probably apply for the strongly distorted geometries at Br(3) and Ga(2), in particular for the large Br(3)–Ga(2)–Br(3)* angles. It should be noted, however, that the coordination of Ga(2) by two bromine atoms occurs exactly in the plane bisecting the angle between the coordinated arene rings. As molecular orbital approaches have shown,[1] this appears to be dictated by better orbital overlap. In the arene complexes of the larger indium[6] and thallium[7] ions electrostatic criteria seem to dominate the multiple halogen coordination. For $[C_6H_3(CH_3)_3]_2Ga{\cdot}GaCl_4$,[3] where a pseudotetrahedral coordination geometry of gallium(I) most similar to that of the paracyclophane complex 2 was found, the Cl–gallium(I)–Cl angle is only 69.0°, and the $GaCl_4^-$ tetrahedra provide two (singly) bridging halogens.

Current investigations are oriented toward the synthesis of gallium(I) complexes of cyclophanes with larger interarene distances, where an *internal* coordination of the metal is more likely to be the accommodation of choice. The strong *external* fixation of gallium(I) in the [2.2]paracyclophane compounds 1 and 2 is of some interest for a quantitative precipitation of gallium(I) from organic solvents. It appears to be a means for virtually complete separation without a change in the oxidation state of the metal.

Experimental Section

General Data. All compounds were manipulated under an atmosphere of pure and dry nitrogen. Glassware was dried at 120 °C, evacuated, and filled with dry nitrogen. Solvents were dried over sodium and molecular sieves (4 Å). [2.2]Paracyclophane was purchased from Merck-Schuchardt and used as received. Gallium metal was a generous gift of Siemens AG and Preussag AG. Gallium dichloride and dibromide were obtained by reaction of Ga metal with Hg_2Cl_2 or $HgBr_2$,[17] respectively, and recrystallized

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[15] The first value gives the distance between the C atoms connected by the bridging methylene groups, and the second one is the average separation of the remaining four atoms.

[16] Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2840.

[17] Carlston, R. C.; Griswold, E.; Kleinberg, J. *J. Am. Chem. Soc.* **1958**, *80*, 1532.

from benzene. Elemental analyses were performed by the Microanalytical Laboratory of this institute.

([2.2]Paracyclophane)gallium(I) Tetrachlorogallate(III). A solution of 0.92 g (3.3 mmol) of Ga[GaCl$_4$] in 20 mL of benzene was treated at room temperature with 0.50 g (2.4 mmol) of [2.2]paracyclophane in 40 mL of benzene. The precipitate was washed five times with 10 mL of benzene and dried in vacuo at 25 °C for 8 h: yield, quantitative; mp 120–125 °C dec. Anal. Calcd for $C_{16}H_{16}Ga_2Cl_4$: C, 39.26; H, 3.29; Cl, 28.97. Found: C, 38.55; H, 3.23; Cl, 28.96.

([2.2]Paracyclophane)gallium(I) tetrabromogallate(III) was synthesized as described for the chloro analogue. Starting materials: 1.80 g of Ga[GaBr$_4$] (3.9 mmol) in 15 mL of benzene; 0.62 g of [2.2]paracyclophane (3.0 mmol) in 40 mL of benzene. **2**: yield, quantitative; mp 200–205 °C dec. Anal. Calcd for $C_{16}H_{16}Ga_2Br_4$: C, 28.80; H, 2.42; Br, 47.89. Found: C, 28.26; H, 2.45; Br, 47.15.

Structure Determination of ([2.2]Paracyclophane)gallium(I) Tetrabromogallate(III) (2). A suitable colorless single crystal of **2** was obtained by slow addition of a benzene solution of [2.2]paracyclophane to Ga[GaBr$_4$] in benzene and was sealed under argon at dry ice temperature into a glass capillary. Diffractometer measurements indicated an orthorhombic cell, which was confirmed by axial photographs (Syntex P2$_1$). Reduced cell calculations[18] did not indicate any higher symmetry. Systematic absences suggested *Pnma* (no. 62) and *Pna*2$_1$ (no. 33) as possible space groups, of which the first was confirmed by successful refinement. Exact cell dimensions were derived from least-squares refinement of the parameters of the orientation matrix to the setting angles of 15 strong reflections ($8.6 \leq \theta \leq 16.0°$) from various parts of reciprocal space accurately centered on the diffractometer. Pertinent crystal data as well as a summary of intensity data collection and refinement procedures are given in Table I.

The integrated intensities of two forms of data ($+h,+k,\pm l$) were measured on a computer-controlled four-circle diffractometer (Syntex P2$_1$) using graphite monochromated Mo Kα radiation. A multispeed moving crystal–stationary counter technique was used where the peak height at the calculated peak position served to determine the final scan speed. The time spent measuring the background intensities at each end of the scan interval was half that taken to measure the peak. Three monitor reflections, examined after every 50 reflections, indicated only a random intensity fluctuation. The intensity of a reflection and its standard deviation were calculated as $I = k[C - 2(\mathrm{BGR} + \mathrm{BGL})]$ and $\sigma(I) = k[C + 4(\mathrm{BGR} + \mathrm{BGL})]^{1/2}$, where C is the peak intensity, BGL and BGR are the left and right background intensities, and k is a constant that depends on the scanning speed. Intensities were corrected for Lorentz and polarization effects ($F_o = (I/Lp)^{1/2}$; $\sigma(F_o) = \sigma(I)/2LpF_o$), as well as for absorption effects. For the latter an empirical correction based on scans at 10° intervals around the diffraction vectors of eight selected reflections near $\chi = 90°$ was used. After the two independent data sets were merged, structure factors with $F_o < 4.0\sigma(F_o)$ were deemed "unobserved" and not used in all further calculations.

The structure was solved by direct methods (MULTAN 80[19]) and completed by difference Fourier syntheses. After anisotropic refinement of all non-hydrogen atoms four hydrogen atom positions could be taken from a difference map. The four remaining H atoms were calculated at idealized geometrical positions. In the final refinement cycles hydrogen atoms were kept fixed ($U_{\mathrm{iso}} = 0.06$ Å^2), while all other atoms were allowed anisotropic displacement (full matrix, one block). The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/(\sigma^2(F_o) + kF^2)$. k was set to 0.0004 to give a "flat" analysis of variance. Refinement in the alternative space group *Pna*2$_1$ was not attempted as the observed structural parameters were chemically reasonable. Neutral, isolated atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber.[20] Scattering factors of the H atoms, based on a bonded spherical atom model, were those of Stewart, Davidson, and Simpson.[21] Corrections for anomalous scattering were applied to all atoms.[22] Besides several locally written routines, local VAX 780 versions of the following programs were used: SHELX 76[23] for Fourier calculations and least squares, XANADU[24] for geometrical calculations, and ORTEP[25] for the molecular plots. Table II contains the final coordinates and equivalent isotropic temperature factors of the non H atoms, and Table III summarizes important distances and angles.

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Registry No. **1**, 101858-39-3; **2**, 101834-96-2; Ga[GaCl$_4$], 24597-12-4; Ga[GaBr$_4$], 18897-61-5.

Supplementary Material Available: Additional crystal structure data and tables with anisotropic thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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