Complexes of π-Prismands with Gallium(I)

Andreas Kunze, Rolf Gleiter,* Sabine Bethke, and Frank Rominger

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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A stable complex between the π-prismand 4,10,15-(1,4)tribenzena-1,7-diazabicyclo[5.5.5]heptadecaphane (**2**) and Ga(I) was synthesized. X-ray investigations on single crystals of $[\mathrm{Ga{\cdot}\mathbf{2}}]^+[\mathrm{GaCl_4}]^-$ revealed that the Ga atom is situated in the center of the cage and is totally separated from the anion. The reaction of **2** with $\mathrm{Tl(CH_3CO_2)}$ yielded $[\mathrm{Tl{\cdot}\mathbf{2}}]^+[\mathrm{CH_3CO_2}]^-$. Spectroscopic evidence is provided for the existence of $[\mathrm{Tl{\cdot}\mathbf{2}}]^+$ by a strong coupling between the ^{13}C nuclei of the arene part of the ligand and the metal. DFT calculations on $[\mathrm{Ga{\cdot}\mathbf{2}}]^+$, $[\mathrm{In{\cdot}\mathbf{2}}]^+$, and $[\mathrm{Tl{\cdot}\mathbf{2}}]^+$ suggest bonding between the metal and the arene rings as well as the nitrogen atoms.

Introduction

The doubly bridged π-systems of cyclophanes **A** can act as ligands toward metal fragments. Examples in which the outside of the π system (e.g. **B**) is attached to the metals are legion, whereas so-called endohedral cyclophanes (**C**)[1] are rare (Scheme 1). One of the first examples of the **C** type was the complex between Ag(I) triflate and [2.2.2]paracyclophane (**1**),[2] which was followed by a series of Ag(I) triflate complexes with [2.2.2]- and [2.2.1]cyclophanes of variable connectivities.[1,3] In most cases the silver is bound to one double bond or to one carbon atom, respectively, of each of the three phenyl rings. The coordination sphere is supplemented by one oxygen atom of the triflate anion.[1−3]

Arenes are also able to form complexes with gallium(I)[4,5] and thallium(I)[6,7] salts. The most appealing example is the gallium complex with [2.2.2]paracyclophane (**1**) (Figure 1).[5] A closer look at the structure of this complex in the solid state reveals that the gallium atom is not situated exactly in the center of the ligand but stands out by 0.43 Å. This asymmetry could be attributed to an interaction between a Ga(I) ion and a bromine atom of the $[\mathrm{GaBr_4}]$ anion of the complex.[5] This kind of interaction between a Ga(I) atom and one or two anionic centers was encountered in all Ga(I)−benzene complexes studied so far.[4] The additional stabilization can be rationalized by assuming an interaction between a low-lying empty 4p orbital of the Ga(I) atom with a lone-pair orbital of the anion. In Figure 2 we show the two highest occupied (e′) and the lowest unoccupied (a$_2$″) orbitals of a complex of Ga(I) and three benzene rings adopting D_{3h} symmetry. These frontier orbitals result from an interaction of the highest occupied π MOs of the benzene units with the empty 4p MOs of the metal. In the e′ MOs the 4p$_x$ and 4p$_y$ atomic orbitals of Ga(I) interact considerably with the π MOs of the ligands because they directly point toward the π MOs, thus providing good overlap. The LUMO (a$_2$″) mainly

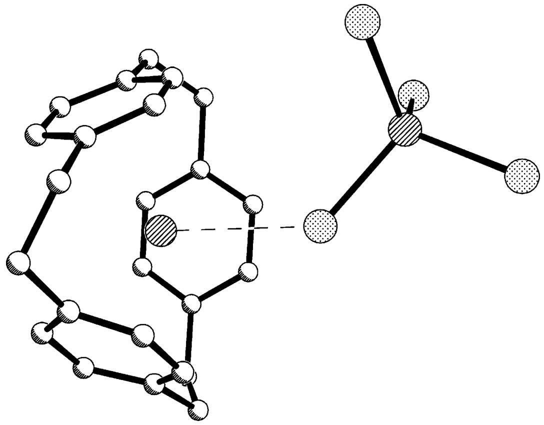
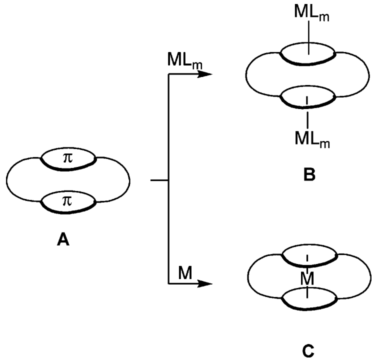


Figure 1. Side view of the complex between [2.2.2]paracyclophane and Ga(I), including the position of the $[\mathrm{GaBr_4}]^-$ anion.

Scheme 1



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(1) (a) Gleiter, R.; Rausch, B. J.; Schaller, R. J. In *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 159−188. (b) Heo, R. W.; Lee, T. R. *J. Organomet. Chem.* **1999**, *578*, 31−42. (c) Park, J.-S.; Lee, T. R. In *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 131−172. (d) Schulz, J.; Vögtle, F. *Top. Curr. Chem.* **1994**, *172*, 41−86.

(2) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979−1985.

(3) (a) Lahtinen, T.; Wegelius, E.; Airola, E.; Kolehmainen, E.; Rissanen, K. *J. Prakt. Chem.* **1999**, *341*, 237−244. (b) Lahtinen, T.; Wegelius, E.; Rissanen, K. *New J. Chem.* **2001**, *25*, 905−911. (c) Seppälä, T.; Wegelius, E.; Rissanen, K. *New J. Chem.* **1998**, 789−791. (d) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P.; Lehne, V. *J. Org. Chem.* **1993**, *58*, 2781−2784. (e) Schmidbauer, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem.* **1986**, *98*, 1108−1109; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089−1090.

(4) Review: Schmidbaur, H. *Angew. Chem.* **1985**, *97*, 893−904; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 907−918.

(5) Schmidbaur, H.; Hager, R.; Huber, B.; Müller, G. *Angew. Chem.* **1987**, *99*, 354−356; *Angew. Chem., Int. Ed.* Engl. **1987**, *26*, 338−340.

(6) Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5941−5942.

(7) (a) Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem.* **1985**, *97*, 402−403; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414−415. (b) Wiesbrock, F.; Schmidbaur, H. *J. Am. Chem. Soc.* **2003**, *125*, 3622−3630.

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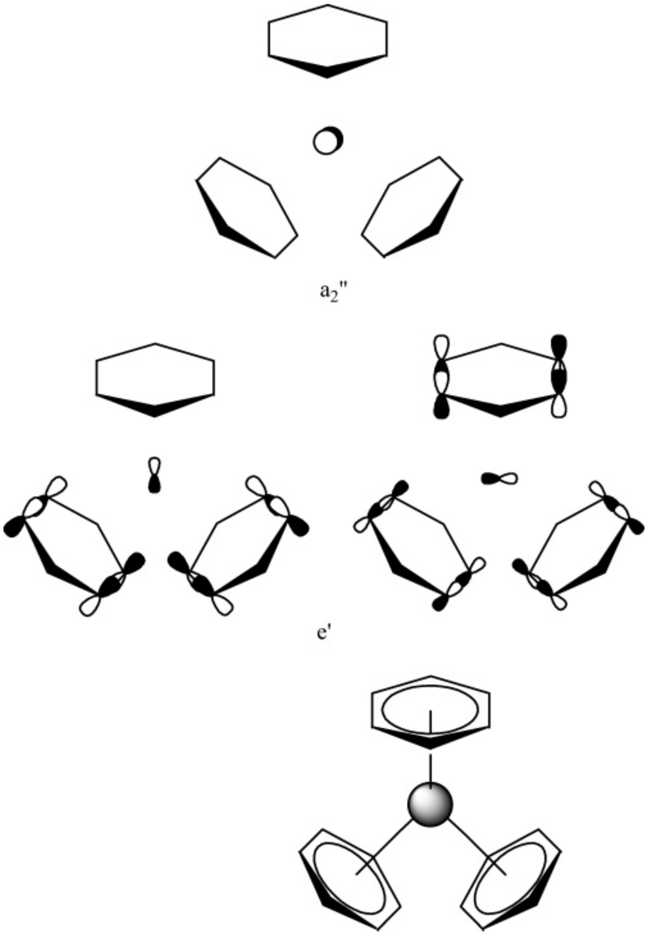


Figure 2. Schematic drawing of the frontier MOs e′ and a$_2$″ of $[Ga(C_6H_6)_3]^+$.

has 4p$_z$ character, and further interaction with an anion or a lone pair combination of the same symmetry leads to an additional stabilization, resulting in an increased HOMO−LUMO gap.

We thought it of interest to offer to the Ga(I) and Tl(I) ions not only three benzene rings but also two additional lone pairs from nitrogen atoms. These nitrogen centers should have an effect similar to that of the lone pairs of the anions in the metal complexes prepared so far.[4] A ligand of that kind which provides three benzene rings and two bridgehead nitrogen atoms is 4,10,15-(1,4)tribenzena-1,7-diazabicyclo[5.5.5]heptadecaphane (**2**).[8]

Syntheses and Spectroscopic Properties

Treatment of a toluene solution of **2** with Ga_2Cl_4 affords in quantitative yield a colorless powder whose analytical data reveal a 1:1 complex (Scheme 2). An X-ray investigation (see below) confirms these results. The C_2H_4 units of the ligand resemble an ABXY system in the NMR spectrum which is resolved very well at lower temperatures in the case of the free ligand.[8a,b] In the $[Ga{\cdot}\mathbf{2}]^+$ complex, one signal is a broad singlet, whereas the second is a triplet at room temperature. Further temperature-dependent NMR analyses were prevented, due to poor solubility of the complex in organic solvents.

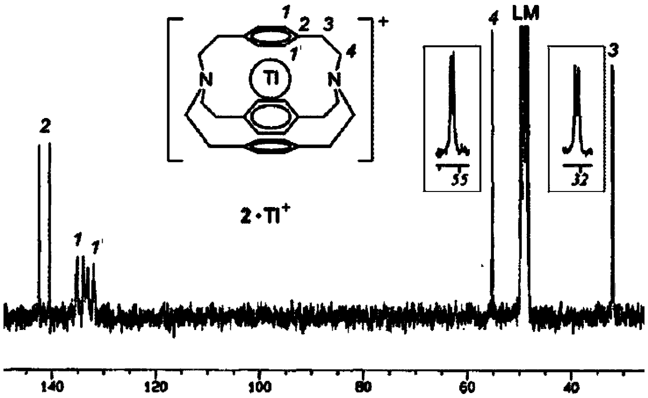
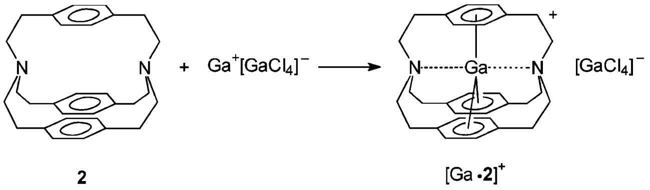


Figure 3. ^{13}C NMR spectrum (75 MHz, CD_3OD) of $[Tl{\cdot}\mathbf{2}]^+$.

Scheme 2



Treatment of a methylene chloride solution of **2** with thallium(I) acetate yields a colorless powder whose analytical data suggest the 1:1 complex $[Tl{\cdot}\mathbf{2}]^+$. Since the thallium complex dissolves reasonably well in CD_3OD, we are able to discuss its NHR spectroscopic properties in more detail. The ABXY system of the bridging C_2H_4 protons is slightly better resolved than in the $[Ga{\cdot}\mathbf{2}]^+$ complex. The signals are, however, more complex, due to ^{205}Tl−^{1}H coupling in the range of 10 Hz. This has also been reported for a Tl(I) cryptate.[9] The further observation that the ABXY signals of the bridge coalesce at ca. 40 °C supports the assumption that the complex should have a dynamic behavior similar to that of the free ligand.[8a,b] From this coalescence temperature we estimate for the conformational change an activation energy of ca. 15 kcal/mol.[10] All ^{13}C signals appear as doublets (Figure 3) with ^{205}Tl−^{13}C coupling constants ranging from 155 to 10 Hz. To find out if the splitting of the signals is not due to chemical shift anisotropy, we also recorded the ^{13}C NMR spectrum at 125 Hz. The strong coupling between the aromatic carbon atoms is indicative of a strong interaction between the metal center and the aromatic rings. The signal at 141.6 ppm is assigned to the quaternary C2, whereas the other two doublets (133 and 134.1 ppm) can be assigned to the tertiary carbons C1 and C1′. The nonequivalence of the C1 signals is further evidence for an equilibrium between C_{3h} and D_3 isomers (cf. Figure 5). For the C_{3h} conformation we expect two nonequivalent tertiary C atoms, whereas for the D_3 conformation only one signal for the tertiary C atoms is expected. At higher temperature (50 °C in CD_3OD) the signals of one of the doublets become broader while the other one is already a singlet. This is further evidence of a dynamic equilibrium between the two (C_{3h} and D_3) conformations in solution.

In Table 1 we have compared the chemical shifts of the aromatic protons and carbon atoms in **2**, $[Ga{\cdot}\mathbf{2}]^+$, and $[Tl{\cdot}\mathbf{2}]^+$. As a result of the complexation they are shifted to a lower field as compared to the case for **2**.

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(8) (a) Kunze, A.; Bethke, S.; Gleiter, R.; Rominger, F. *Org. Lett.* **2000**, *2*, 609−612. (b) Kunze, A.; Balalaie, S.; Gleiter, R.; Rominger, F. *Eur. J. Org. Chem.* **2006**, 2942−2955. (c) Koschabek, R.; Gleiter, R.; Rominger, F. *Eur. J. Inorg. Chem.* **2006**, 609−620.

(9) Lehn, J. M.; Sauvage, J. P.; Dietrich, B. *J. Am. Chem. Soc.* **1970**, *92*, 2916−2918.

(10) Kessler, H. *Angew. Chem.* **1970**, *82*, 237−253; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219−235.

Table 1. Chemical Shifts (δ) of the Arene Protons and Carbon Atoms in 2, [Ga·2]$^+$, and [Tl·2]$^+$

	2	[Ga·**2**]$^+$	[Tl·**2**]$^+$
^{1}H NMR	6.57^a	7.25^b	7.30^d
^{13}C NMR	128.8^a	131.0−132.5^c	133.6^d
	136.6^a	140.9^c	141.5^d

^{a} Conditions: $CDCl_3$, 25 °C. ^{b} Conditions: CD_3CN, 70 °C. ^{c} Conditions: CD_3CN, 25 °C. ^{d} Conditions: CD_3OD, 60 °C.

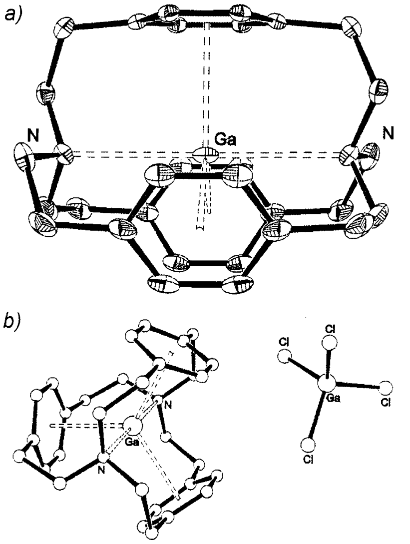

Figure 4. (a) Molecular structure of [Ga·**2**]$^+$. The plot is presented at the 35% probability level. (b) Molecular structure of [Ga·**2**]$^+$$GaCl_4$. The hydrogen atoms are omitted for the sake of clarity. For the cation we chose the D_3 conformation.

Our efforts to prepare [In·**2**]$^+$ from **2** and InCl have failed so far.

X-ray Investigation of [Ga·2]$^+$[GaCl$_4$]−

The complex [Ga·**2**]$^+$[$GaCl_4$]$^-$ crystallizes in the space group $P\bar{4}2_1m$ (No. 113) with two molecules per unit cell. The metal atom is located at a special position with symmetry *mm*. This means that there are two orthogonal symmetry planes through the metal and a resulting C_2 axis at the intersection line (C_{2v} symmetry). One of the mirror planes contains both N atoms and the Ga$^+$ center and bisects the upper benzene ring (see Figure 4). The other plane is oriented perpendicular to the N···N axis. Thus, the resulting C_2 axis goes through the center of the top ring and the metal ion. The corresponding symmetry operation (C_2) transforms one of the remaining rings into the other. It is obvious that the resulting C_{2v} symmetry of the X-ray structural model cannot be the real symmetry of the molecules but has to result from the superposition of disordered molecule in the crystal. It cannot be definitively decided whether the observed data result from a superposition of two D_3 enantiomers, differently oriented C_{3h} structures, or even both (see Figure 5). The C_{3h}-symmetrical conformation seems to be the one most likely for smaller ions such as Ag$^+$ and Cu$^+$, but a D_3 symmetry has also been observed.[8] In most cases of C_{3h} symmetry (paddle wheel) the phenyl rings are slightly twisted out of the face-on orientation into a more edge-on one.[8] This effect is not observed in the structure described here. For this reason we propose that this structure is of disordered D_3 symmetry.

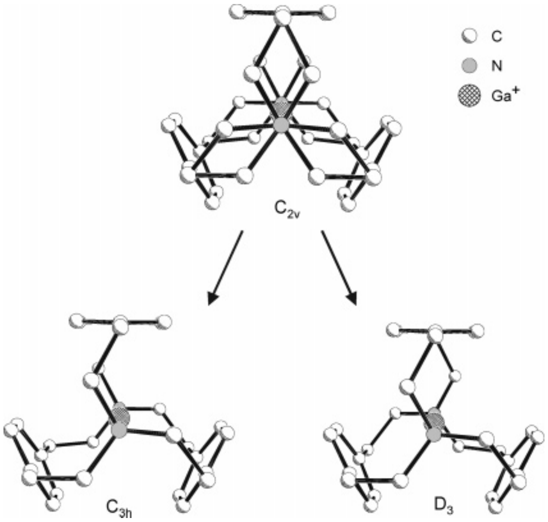

Figure 5. Observed C_{2v}-symmetric structure (special *mm* position, top) resulting from the superposition of either two disordered paddle-wheel molecules (C_{3h}, bottom left) or two disordered screwlike molecules (D_3, bottom right).

Table 2. Most Relevant Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in [Ga·2]$^+$

Ga−N	2.908(3)
Ga−center of arene rings	2.737(3)/2.724(3)
N···Ga···N	179.6(1)

The most relevant bond distances and angles for both conformations are given in Table 2. The distance between the metal atom and the center of the arene rings was determined to be 2.73 Å. It is interesting to note that the transannular distance of the center of the π systems in [Ga·**2**]$^+$ (4.73 Å) is 0.23 Å longer than in **2** (4.50 Å).[8a,b] In the complex [Ga·**1**]$^+$[$GaBr_4$]$^-$ the distance between the metal and the benzene rings was reported to be 2.64 Å.[5] We ascribe the greater distance in [Ga·**2**]$^+$ (mean value 2.73 Å) to the effect of the nitrogen atoms transferring electron density to the metal. The distance between the nitrogen centers and Ga$^+$ amounts to 2.91 Å.

Quantum Chemical Calculations

To check the qualitative MO picture on gallium(I) arene complexes presented in Figure 2, we have carried out quantum chemical calculations on [Ga·**2**]$^+$, [In·**2**]$^+$, and [Tl·**2**]$^+$ using the DFT approach[11,12] and the LANL2DZ basis set,[13] including pseudopotentials.[14] Gaussian 98 was used for calculations,[15] and geometry optimizations were carried out with the gradient technique. Vibrational frequencies were obtained from analytical calculations of the Hessian matrixes. The electronic structures of all three complexes were analyzed by means of the natural bond orbital (NBO) procedure.[16]

The geometrical parameters obtained were close to the experimental ones (see Tables 3 and 4). The energy difference between the structures of C_{3h} and D_3 symmetry was calculated to be very small: 0.04 kcal/mol for [Ga·**2**]$^+$ and [In·**2**]$^+$ and

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(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(12) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.

(13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.

(14) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; Vol. 3.1, pp 1−28.

Table 3. Most Relevant Bond Distances (Å) and Angles (deg) Calculated for [Ga·2]$^+$, [In·2]$^+$, and [Tl·2]$^+$ in C_{3h} and D_3 Symmetry

	[Ga·**2**]$^+$		[In·**2**]$^+$		[Tl·**2**]$^+$	
	C_{3h}	D_3	C_{3h}	D_3	C_{3h}	D_3
Me-N	2.94	2.94	2.94	2.95	2.96	2.96
Me−center of rings	2.86	2.85	2.85	2.85	2.87	2.86
N···Me···N	180	180	180	180	180	180
C−N···N−C	0	53.7	0	50.0	0	48.0

Table 4. Energy Partitioning in [Ga·2]$^+$, [In·2]$^+$, and [Tl·2]$^+$ for C_{3h} and D_3 Symmetry[a]

	[Ga·**2**]$^+$		[In·**2**]$^+$		[Tl·**2**]$^+$	
	C_{3h}	D_3	C_{3h}	D_3	C_{3h}	D_3
lone pair (N) → p (metal)	26.0	26.1	18.7	19.1	16.5	16.7
π → p (metal)	39.6	39.8	25.9	25.6	22.0	21.3

[a] All values are given in units of kcal/mol.

0.08 kcal/mol for [Tl·**2**]$^+$. Table 4 shows that the contribution of the interaction between the arene ring and the metal is larger than that between the nitrogen atoms and the metal. The calculations predict that the HOMO transforms according to A′. It can be described as a linear combination between the s orbital of the metal and the symmetrical combination of the nitrogen lone pairs. For the LUMO and LUMO-1 the calculations predict mainly π character with some metal p admixture. The atomic charge on the metal is calculated to be 0.85 for [Ga·**2**]$^+$, 0.72 for [In·**2**]$^+$, and 0.82 for [Tl·**2**]$^+$.

Conclusions

We have shown that the π-prismand **2** forms stable complexes with Ga(I) and Tl(I). The stability of the complexes is due to a strong interaction of the cation with the three arene rings and the two nitrogen atoms at the bridgehead positions. From our NMR studies and the quantum chemical calculations we assume that the [Tl·**2**]$^+$ complex also has a trigonal-bipyramidal structure. The complexes [Ga·**2**]$^+$ and [Tl·**2**]$^+$ are the first complexes in which the metal shows a trigonal-bipyramidal coordination. In all other gallium and thallium arene complexes a distorted-tetrahedral geometry of the ligands was reported.[4−7] The trigonal-bipyramidal surroundings of the metal ion is probably responsible for the stability of the complex toward reactions with oxygen, water, and polar solvents.

Experimental Section

Equipment. All melting points are uncorrected. The NMR spectra were measured with a Bruker AS 300 spectrometer (^{1}H NMR at 300 MHz and ^{13}C NMR at 75.5 MHz) using the solvent for calibration. High-resolution mass spectra (HRMS) were obtained with ZAB-3F (Vacuum Generators) and JEOL JMS 700 high-resolution mass spectrometers. All reactions were carried out in dry solvents under an argon atmosphere in a glovebox.

Table 5. Crystal Data and Stucture Refinement Details for [Ga·2]$^+$[GaCl$_4$]$^-$

empirical formula	$C_{30}H_{36}Cl_4Ga_2N_2$
formula wt	705.8
cryst color	colorless
cryst shape	polyhedron
cryst size (mm^3)	0.39 × 0.20 × 0.08
T (K)	200
wavelength (Å)	0.71073
cryst syst	tetragonal
space group	$P\bar{4}2_1m$
Z	2
a (Å)	13.2202(1)
b (Å)	13.2202(1)
c (Å)	8.7303(1)
V (Å^3)	1525.83(2)
D_{calcd} (g/cm^3)	1.536
abs coeff μ (mm^{-1})	2.139
θ range (deg)	2.18−27.46
index ranges	$-17 \leq h \leq 17$ $-17 \leq k \leq 17$ $-11 \leq l \leq 11$
no of rflns collected	15734
no of unique rflns	1856
max and min transmissions	0.86/0.69
no of obsd data/params	1856/106
GOF on F^2	1.08
$R(F)$	0.027
$R_w(F^2)$	0.066
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.23, 0.57

Synthesis of [Ga·2]$^+$[GaCl$_4$]$^-$. A solution of 14 mg (0.05 mmol) of Ga_2Cl_4 in 5 mL of dry toluene was added dropwise with a syringe to a solution of 18 mg (0.04 mmol) of cryptand **2** in 5 mL of toluene at room temperature. A colorless precipitate was formed immediately. After the mixture was stirred for 2 h at room temperature, the solvent was removed under vacuum. The remaining colorless powder was stable toward water and air and slightly soluble in acetonitrile, and it decomposed above 340 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 2.84 (t, 12H), 2.99 (br s, 12H), 7.25 (s, 12H). ^{13}C NMR (75 MHz, CD_3CN): δ 31.7 (CH_2−Ar), 55.1 (CH_2−N), 131.0−132.5 (s, C_{Ar}), 140.9 (q−C_{Ar}). IR (KBr): 2964, 1447, 1261, 1104 cm^{-1}. UV/vis (CH_3CN): λ_{max} (log ϵ) 258 nm (2.9). HRMS: calcd for $C_{30}H_{36}{}^{71}GaN_2$ *m/z* 495.2134, found 495.2148; calcd for $C_{30}H_{36}{}^{69}GaN_2$ *m/z* 493.2134, found 493.2148. Anal. Calcd for $C_{30}H_{36}Ga_2Cl_4N_2$ (705.9): C, 51.05; H, 5.14; N, 3.97. Found: C, 51.14; H, 5.08; N, 4.10.

Synthesis of [Tl·2]$^+$CH$_3$CO$_2^-$. To a solution of 20 mg (0.05 mmol) of **2** in 3 mL of CH_2Cl_2 was added a solution of 12 mg (0.05 mmol) of thallium(I) acetate in 3 mL of methanol. The solution was stirred overnight at room temperature, and the solvent was removed subsequently. A colorless powder remained which decomposed above 255 °C. The powder could be dissolved in CH_3OH and CH_2Cl_2. ^{1}H NMR (300 MHz, CD_3OD): δ 1.88 (s, 3H, $CH_3CO_2^-$), 2.55 (m, 6H, CH_2−N), 2.87 (m, 12H, CH_2−Ar), 3.19 (s, 6H, CH_2N), 7.21 (s, 6H, H−Ar), 7.42 (s, 6H, H−Ar). ^{13}C NMR (75 MHz, CD_3OD): δ 24.6 ($CH_3CO_2^-$), 32.1 (d, $^2J_{C-Tl}$ = 10.1 Hz, CH_2−Ar), 55.2 (d, $^3J_{C-Tl}$ = 10.3 Hz, CH_2N), 133.0 (d, $^1J_{C-Tl}$ = 151.2 Hz, t C_{Ar}), 134.1 (d, $^1J_{C-Tl}$ = 156.2 Hz, t C_{Ar}), 141.6 (d, $^1J_{C-Tl}$ = 147.2 Hz, q C_{Ar}). IR (KBr): 2961 (m), 2920 (w), 2781 (m), 1627 (m), 1574 (s), 1408 (m), 1221 (w), 1126 (w) cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) 266 nm (3.1). HRMS (FAB$^+$): calcd for $C_{30}H_{36}N_2{}^{205}Tl$ *m/z* 629.2623, found 629.2633; calcd for $C_{30}H_{36}N_2{}^{203}Tl$ *m/z* 627.2602, found 627.2587.

X-ray Crystallography and Structure Solution. Data were collected on a Bruker SMART CCD diffractometer at 200 K.

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(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(16) (a) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066−4073. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746.

Relevant crystal and data collection parameters are given in Table 5. The structure of [Ga$\cdot$**2**]$^+$[GaCl$_4$]$^-$ was solved by using direct methods, least-squares refinement, and Fourier techniques. Structure solutions and refinement were performed with SHELXTL, version 5.10.[17]

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, bond lengths, and bond angles for [Ga$\cdot$**2**]$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. SHELXTL; Bruker Analytical X-ray Systems, Madison, WI, 1997.