Organometallics **2008,** *27,* 2361–2395

Reviews

π-Complexation of Post-Transition Metals by Neutral Aromatic Hydrocarbons: The Road from Observations in the 19th Century to New Aspects of Supramolecular Chemistry[†]

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Received October 18, 2007

Compounds of the elements in the three triads of post-transition metals, Ga−In−Tl, Ge−Sn−Pb, and As−Sb−Bi, form in their low-valence states a variety of stable complexes with neutral hydrocarbons. This chemistry is reviewed starting from the early discoveries in the 19th century and including the most recent contributions.

Contents

I. Introduction

Weak forces of chemical binding are currently the subject of many lines of chemical research, because they provide the means to assemble and organize molecular units into larger and even multidimensional aggregates with new bulk properties. For the construction of new organizational patterns, *weak forces* have several advantages in that they exert only a minor influence on the fundamentals of structure and bonding of the individual units, that this minor influence can be tuned, and that the construction process is readily reversible, allowing for greater flexibility in the design of new materials. *Weak forces* can serve this purpose best if, as a lower limit of strength, they can overrule the ubiquitous van der Waals forces in order to induce combinatorial and directional preferences, while, as an upper limit, the interference should not be destructive for the building blocks and not irreversible.

The assembly and reassembly of larger aggregates of molecular units through some kind of discrete chemical bonding fall into the broad definition of supramolecular chemistry.[1] While this general principle includes the whole range of forces of chemical binding, most of the modern research activities in this area have concentrated on the forces of weak or moderate strength. *Hydrogen bonding* is by far the most important and most widespread form of chemical binding in supramolecular chemistry.[2] It is also the prototype of binding in biomimetic supramolecular chemistry, because nature everywhere provides us with a plethora of examples. As a prominent example, hydrogen bonds determine the properties of water (and ice!) and are responsible for its many unusual physical properties and for most of the striking solubility phenomena.[3]

Naturally, the paramount importance of hydrogen bonding is related to the great abundance of hydrogen and its compounds. Specific effects exerted by other elements are often less obvious, owing to the more limited abundance of these elements. Regarding *weak intermolecular forces*, gold and its compounds are examples in case: *aurophilic interactions* are similar in their energy characteristics to hydrogen bonds, their formation is easily reversible, and the directionality is predictable within narrow limits. They can be used to tailor large aggregates with interesting bulk properties.[4] Even though these effects have also been traced into the chemistry of the congeners in the coinage

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[†] In memory of Ernst O. Fischer (deceased July 27, 2007) and Heinz P. Fritz (deceased August 11, 2007).

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10.1021/om701044e CCC: $40.75

metal group (metallophilic interactions), their significance was only appreciated after a substantial growth of gold chemistry in the 1980s.[5]

The present review presents the knowledge on other *weak forces* which determine very considerably the chemistry of three triads of elements, viz. of the nine heavier elements of groups 13−15, governing not only unexpected solubility properties but also the supramolecular chemistry of their compounds in the solid state, thus giving rise to specific characteristics of structure and performance. The first observations were made in the late 19th century for the elements gallium[6] and antimony,[7] but a comprehensive view of the potential was only reached in the late 20th century with the advent of efficient methods for structure determination as routine tools.[8]

π-Complexation of metals taken from the central region of the *transition-metal* series by neutral arenes, as best exemplified by compounds such as (benzene)tricarbonylchromium[9] or bis(benzene)chromium,[10] is associated with high energies of formation and affords robust organometallic compounds. In contrast, both early and late transition metals form rather labile arene π-complexes, as predicted by the simple valence rules which consider mainly the partially filled *n*d acceptor orbitals of these metals (n = 3−5). Similar rules had not been established for the *post-transition metals*, i.e. the *main-group metals* with their filled *n*d states, because for a long time there was no clear experimental evidence that complex formation between neutral arenes and the heavier metals of groups 13−16 would lead to compounds of comparable stability. Although more or less sporadic observations pointed to the fact that in certain cases there was adduct formation which produced isolable products, these results attracted almost no further interest and the phenomena were ascribed in most cases to special forms of solvation or crystal packing. This attitude has changed, since it has been recognized that *weak forces* play an essential role in supramolecular chemistry as mentioned above.

The scope of the present inventory has been deliberately limited to the complexation of the elements Ga−In−Tl, Ge−Sn−Pb, and As−Sb−Bi by *neutral* aromatic hydrocarbons. Regarding the ligands, this excludes *charged* arenes, in particular cyclopentadienyl or phenyl anions, thus ruling out major contributions from simple electrostatic forces to the binding. Regarding the metals, borderline elements of the zinc and copper group, which in their low oxidation states have similar electronic configurations with filled *n*d states, are not included because a separate treatment of the title elements is believed to make the correlations for these elements more lucid.

In the chemistry of the elements gallium and antimony several historical landmarks are highlighted which in their time or later provided the incentive for future work that often was resumed only after long time intervals. It is probably fair to say that the chemistry of the other four elements just followed suit.

II. Arene Complexes of the Low-Valent Group 13 Element Halides and Related Compounds

1. History. The element gallium was discovered in 1875 by Paul Emile Lecoq de Boisbaudran, son of a wine merchant in the French town of Cognac (Figure 1). Applying the correlations of spectral lines newly established by Bunsen and Kirchhoff, he identified the spectral lines of an unknown constituent of zinc blende, and following the lead of these lines he finally isolated 75 g of the metal from 4 tons of ore by electrolysis of the enriched oxide in a potassium hydroxide melt.[11,12] In the following years the anhydrous trichloride $GaCl_3$ was obtained by chlorination (and hydrochlorination) of the metal, and when electrolysis of $GaCl_3$ melts was carried out, the intriguing observation was made[6] that initially deposited gallium metal was redissolved in the electrolyte to give a low-valent chloride formulated as $GaCl_2$. This was a puzzling detail in the chemistry of this element, because the newly discovered gallium was celebrated as the Eka-aluminum missing in Mendeleev's newly formulated periodic table, but aluminum formed no $AlCl_2$. Surprisingly, it was also found that this product $GaCl_2$ could be readily dissolved in benzene and other aromatic hydrocarbons.[6,8,11,12]

Figure 1. Paul Emile Lecoq de Boisbaudran (1838−1912), son of a wine merchant in Cognac, France: worked in his private laboratory on arc spectra of the elements; discovered "Eka-aluminum", predicted by Mendeleev, in zinc blende and named it gallium (1871); prepared gallium metal and low-valent gallium halides; discovered samarium (1879) and dysprosium (1886). Honored, inter alia, by the Croix de la Legion d'Honeur in France and by the Davy Medal in England. Photo courtesy of University of Pennsylvania Library, Edgar Fahs Smith Collection.

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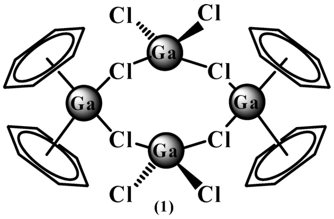
In the 1930s magnetic and spectroscopic studies by Klemm and Tilk demonstrated[13] that Lecoq de Boisbaudran's $GaCl_2$ was actually the mixed-valent salt $Ga[GaCl_4]$, and this type of structure was confirmed (for the dichloride and also for the two polymorphs of the dibromide) by extensive investigations using the complete arsenal of modern physical techniques.[8] However, this ionic formula was even more intriguing regarding the solubility of the compounds in aromatic hydrocarbons, since analogous alkali-metal salts $M[GaCl_4]$ with cations M having similar cation radii are completely insoluble in benzene, whereas $Ga[AlCl_4]$ is again soluble in benzene. Moreover, the solutions of $Ga[GaCl_4]$ in benzene were found to be electrically nonconducting.[14] These observations led to the idea of "benzene-positive ion complexes", presented in a short note by Rundle and Corbett in 1957. It was assumed that the p orbitals of Ga^+ could function as the acceptor orbitals for the π electrons of the arene,[15] referring to the recent model of charge-transfer complexes by Mulliken.[16] For the solutions, "rather unusual solvation forces" in general and "a rather strong solvation of the unipositive cation" in particular were postulated. It was also noted that "recrystallization" of $Ga[GaCl_4]$ from benzene[17] was not straightforward but gave a benzene complex.[17,18] Evidence for the formation of benzene adducts was also derived from the phase diagrams of the $Ga[GaX_4]$/benzene systems for X = Cl, Br.[19,20] The solutions of $Ga[GaCl_4]$ in benzene were shown to exhibit two separate ^{71}Ga NMR signals, of which the high-field resonance was assigned to the benzene-solvated Ga^+ cation.[21] For the complexation of the cation in solution an η^6 hapticity of the benzene molecule was tentatively proposed on the basis of vibrational spectra.[22,23] No detailed investigations on the related indium and thallium compounds were published in the early literature. Potential analogies were only mentioned in passing.[24]

2. Survey of Compositions and Structures of Crystalline Arene Complexes of Binary and Ternary Gallium Halides. Upon cooling of saturated solutions of $Ga[GaCl_4]$ in dry benzene, large, colorless transparent crystals of the phase $[Ga_2 \cdot 2GaCl_4 \cdot 4C_6H_6] \cdot 3C_6H_6$ can be grown.[25] This phase had not been reported previously, but the stoichiometry $Ga[GaBr_4] \cdot 3C_6H_6$ was found in the phase diagram of the corresponding bromide.[20] The result of the crystal structure investigation is shown in formula **1**. The lattice contains the centrosymmetric dimers $\{Ga[GaCl_4]\}_2$ with two benzene molecules attached to each Ga^+ cation. The remaining three benzene molecules are interstitial solvate molecules. The compound is thus the first bis(arene)gallium complex with the benzene molecules being not quite equidistant from the Ga atom (2.758 and 2.929 Å) and forming an angle of 55.6°. The small angles of 2.8 and 3.7° between the normals from the Ga atoms to their arene plane and the lines connecting the metal atom and the ring centroids indicate almost perfect η^6 coordination. The compound loses the interstitial benzene molecules rapidly at room temperature under vacuum. Pumping at −6 °C leaves the 1:1 complex $Ga[GaCl_4] \cdot C_6H_6$ of unknown structure, and the remainder of the solvent is liberated at only slightly elevated temperatures.

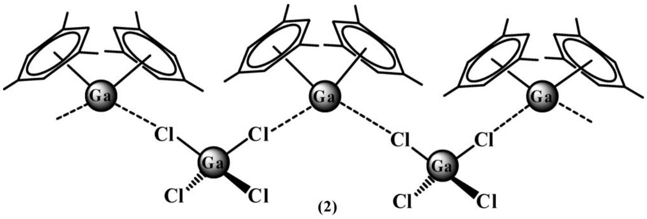


(1)

The structure and properties of the analogous bromide complex are very similar;[26] the crystals of the chloride and bromide are isomorphous. The Ga−arene plane distances are again significantly different (2.784 and 2.996 Å), and the angle between the ring planes is 57.5°, indicating that these values are almost independent of the nature of the GaX_4^- anion.

A variation in the substitution pattern of the arene also results in only minor changes in the structure. Thus, a mixed-ligand complex with one benzene and one durene molecule (1,2,4,5-$C_6H_2Me_4$) per Ga^+ center still has the same crystal type and a similar overall molecular geometry with a center of inversion. However, some details show significant differences. The Ga−durene plane distance (2.642 Å) is very significantly shorter than the Ga−benzene plane distance (3.039 Å), but both rings are almost ideally η^6-bonded, and the interplane angle is 58°.[27]

In crystals of bis(mesitylene)gallium tetrachlorogallate the formation of a cyclic dimer is probably excluded by steric interference of the methyl substituents, and the assembly of the components leads to a chain structure instead (**2**). The $[(1,3,5\text{-}C_6H_3Me_3)_2Ga]^+$ units, with their arene rings tilted against each other by a much smaller angle of 39.7° and with Ga−ring center distances of 2.673 Å (η^6), are bridged by η^1:η^1-coordinated $[GaCl_4]^-$ anions.[28]



(2)

As the steric effects exerted by the hydrocarbons are increased further, 2:1 complexes may still be formed, but these appear as monomers. From solutions of hexaethylbenzene and $Ga[GaCl_4]$ in toluene a 1:1:1 complex is isolated which has the structure shown in formula **3**. The crystals contain an extra molecule of C_6Et_6 not coordinated to the metal atom. The η^6-bonded C_6Et_6 ring is very close to the metal (2.535 Å), while the PhMe ring (also η^6) is much further apart (3.145 Å), supporting the view

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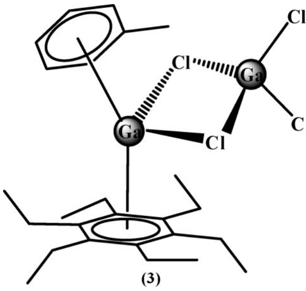
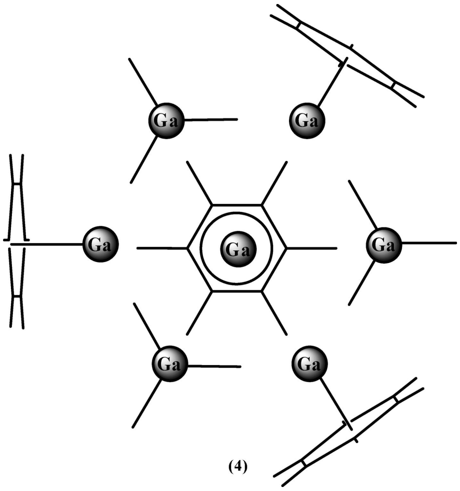
that an increased donor capacity of the ring system leads to tighter bonding. The $[GaCl_4]^-$ anion is chelating the Ga^+ center.[29]



(3)

In contrast, from solutions of hexamethylbenzene and $Ga[GaCl_4]$ or $Ga[GaBr_4]$ in toluene exclusively the 1:1 complexes with C_6Me_6 are obtained, and the toluene is not accepted as a ligand. The chloro complex crystallizes as a compact tetramer with a $\{Ga_4[GaCl_4]_4\}$ core with 3-fold symmetry and each of its four peripheral Ga^+ centers capped by a C_6Me_6 molecule (**4**). The rings are extremely close to the Ga^+ cations with distances of only 2.43 (1×) and 2.51 Å (3×). The coordination mode is strictly η^6 by symmetry.[30]



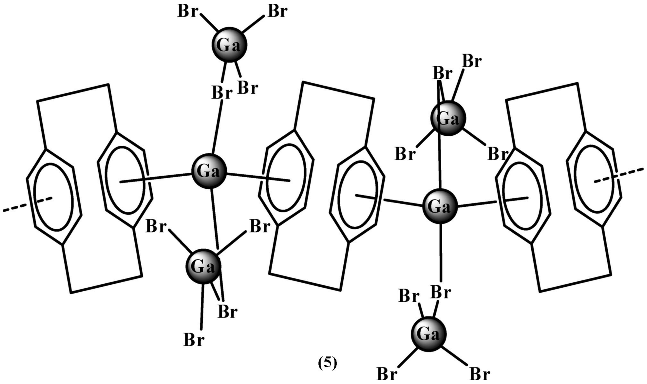
(4)

The assembly of the components $[Ga(C_6Me_6)]^+$ and $[GaBr_4]^-$ of the bromo complex leads to a three-dimensional array in which the anions act as η^2:η^1-chelating/bridging units. The C_6Me_6 ring is again only 2.522 Å above the Ga^+ cation, which is in a square-pyramidal environment of five bromine atoms belonging to three tetrabromogallate(III) tetrahedra.[31] Both complexes of C_6Me_6 are very stable, with melting points of 168 and 146 °C, respectively. Together with the short Ga−ring distances these properties confirm again the strong positive influence of donor substituents at the benzene ring on the π bonding to the metal cation.

Conversely, acceptor substituents appear to weaken the complex stability very considerably. This is illustrated by the observation that both $Ga[GaCl_4]$ and $Ga[GaBr_4]$ can be dissolved in and recrystallized from chlorobenzene and 1,2-dichlorobenzene and from bromobenzene and 1,2-dibromobenzene, respectively, but no arene complexes can be crystallized even at low temperatures.[32]

In attempts to support the formation of bis(arene) complexes of gallium(I) by entropy contributions, diarenes with chelating potential were employed. On the basis of geometrical considerations, *cis*-1,2-diphenylcyclopropane was selected, and indeed ^{71}Ga NMR data of solutions of this diarene with $Ga[GaX_4]$ (X = Cl, Br) in benzene or toluene suggested complex formation, but no crystalline products could be obtained, and the stoichiometry and structure have remained unknown.[33]

Studies with paracyclophanes were more successful. [2.2]Paracyclophane was found to precipitate crystalline 1:1 complexes from benzene or toluene solutions of $Ga[GaCl_4]$ or $Ga[GaBr_4]$. The crystal structure of the bromide complex has been determined. Owing to the narrow vacancy inside the cyclophane, the gallium atoms become attached to both phenylene groups from the outside, but nevertheless a bis(arene) complexation is realized. A 3D array of the components is formed, since the zigzag stacks with alternating Ga^+ cations and paracyclophane molecules are interconnected via the $[GaBr_4]^-$ anions (**5**). Each Ga^+ cation is η^6-coordinated to two phenylene rings of two different cyclophanes with interplane angles (56.7°) and Ga−arene plane distances (2.733 Å) similar to those in the bis(benzene) complexes. The center of each paracyclophane is a crystallographic center of inversion.[34]



(5)

The reaction of a [2.2]paracyclophane in which one of the two phenylene groups is converted into a 1,4-naphthylidene group with $Ga[GaBr_4]$ also affords a 1:1 complex. Core units of the structure of this compound are $\{Ga[GaBr_4]\}_2$ dimers with the two Ga^+ cations η^2:η^1-bridged by two $[GaBr_4]^-$ anions and η^6-bonded to one phenylene and one naphthylene group of two different cyclophanes (**6**). The η^6 coordination of the naphthylene group involves its substituted *p*-phenylene, not the annulated *o*-phenylene ring. The Ga−ring plane distances are significantly different: 2.67 Å for the simple phenylene and 2.85 Å for the phenylene part of the naphthylene. The coordinated rings form an angle of 49.3°. The connectivity pattern of the components leads to a layer structure.[35]

[3.3]Paracyclophane also does not accommodate the Ga^+ cation inside its larger cavity but forms a 1:1 complex with $Ga[GaBr_4]$ having the cations attached to the outside of its phenylene rings. The stacking of alternating Ga^+ cations and

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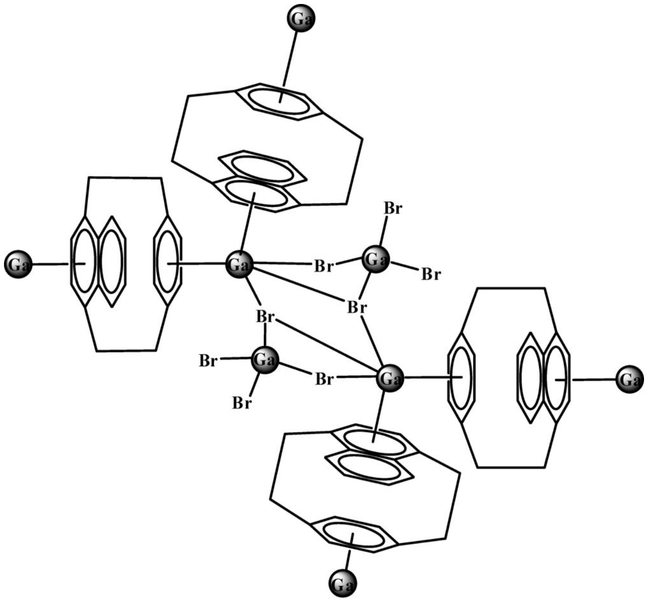
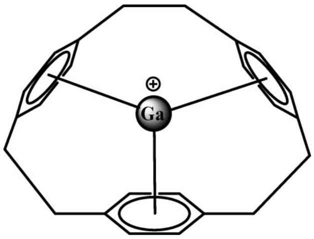


(6)

cyclophane molecules (Ga−ring plane distance 2.75 Å, interplane angle 48.5°) along a chain and the bridging of the former by the $[GaBr_4]^-$ anions leads to the formation of a layer structure.[36]

The cavity of [2.2.2]paracyclophane was finally found to be large enough to accommodate the Ga^+ cation of the 1:1 complex with this cyclophane with $Ga[GaBr_4]$. Colorless crystals precipitated from the benzene solution of the two components. In the cation $\{Ga[(p\text{-}C_6H_4CH_2CH_2)_3]\}^+$ the Ga^+ cation is equidistant from the three ring centers (3 × η^6, 2.65 Å) and is located only 0.43 Å above the plane defined by the three ring centers. There is a long and obviously very weak contact with one Br atom of the $[GaBr_4]^-$ counterion (3.388 Å) (**7**). This cation is the first tris(arene) complex of a main group metal atom.[37]



(7)

3. Solution Studies of Gallium(I) Tetrahalogallates in Aromatic Hydrocarbons. In early investigations of solutions of $Ga[MX_4]$ (with M = Al, Ga and X = Cl, Br) in benzene it has been demonstrated that the solutes are nonelectrolytes,[14] and that the concentration and temperature dependence of the colligative properties are compatible with reversible addition of the solvent molecules to the substrates, leading to a strong decrease of the apparent molecular mass and of the dielectric constant with concentration.[38] The nature of the solutions was also probed by ^{71}Ga NMR spectroscopy. As shown in Table 1, the $Ga[GaX_4]$ compounds show two signals, which are readily assigned to Ga(I) and Ga(III) by their chemical shifts. The second signal is absent in the tetrachloro*aluminates*. The signal of the $[GaX_4]^-$ anion is broad because the quadrupolar nucleus is in a distorted-tetrahedral environment of quadrupolar nuclei, and its chemical shift is almost invariant with the nature of the hydrocarbon solvent. In contrast, the signal of the Ga^+ cation is relatively sharp, owing to shielding by the filled $4s^2$ orbital and an exchange-equilibrated environment, and the chemical shift is solvent-dependent. With increasing substitution in the arenes $C_6H_nMe_{6-n}$, i.e. with increasing donor strength, the signals appear at higher field. For mixed solvents, the ^{71}Ga resonances have chemical shifts which are closer to those of the solutions with the better donor as the solvent. These data are in agreement with a complexation of Ga^+ in coordination geometries similar to those found in the solid state. In no case have separate ^{71}Ga signals been detected for mono- or bis(arene) complexes or for complexes of different arenes in mixed solvents. The binding of the arenes to the cations is probably flexible, with rapid exchange of free and bound molecules in solution. Accordingly, in the ^1H NMR spectra no separate signals were observed for bound arenes and the bulk solvent.[8,39]

Table 1. ^{71}Ga, ^{115}In, and ^{205}Tl NMR Spectra of (Arene)gallium, -indium, and -thallium Complexes[a]

complex	solvent	$\delta(M^I)^{b,c}$	$\delta(M^{III})^d$	ref
$Ga[GaCl_4]$	benzene	−650	+247	8
	toluene	−668	+247	
	p-xylene	−674	+247	
	mesitylene	−675	broad	
	mesitylene/benzene	−675	+247	
$Ga[AlCl_4]$	benzene	−660		8
$Ga[GaBr_4]$	benzene	−609	+62	8
	mesitylene	−624	broad	
$In[GaCl_4]$	benzene	−1350	n.o.	43
$[Tl(toluene)_2]^+X^-$	CD_2Cl_2	−425		55
$[Tl(C_6Me_6)_2]^+X^-$	CD_2Cl_2	−563		

[a] Conditions: $\delta(^{71}Ga)$ in ppm relative to external $[Ga(H_2O)_6]^{3+}$ in dilute aqueous HNO_3; $\delta(^{115}In)$ in ppm relative to external 0.5 M $InCl_3$ solution in concentrated aqueous HCl; $\delta(^{205}Tl)$ in ppm relative to external $[Tl(aq)]^+$ NO_3^- in D_2O; 25 °C. [b] $^{71}Ga^I$ and ^{115}In resonances are narrow, with line widths of ca. 50 Hz at 25 °C. [c] $^{205}Tl^I$ resonances are broad, with line widths of ca. 3500 Hz at 27 °C. [d] $^{71}Ga^{III}$ resonances are broad, with line widths of ca. 2000 Hz at 25 °C.

4. Arene Complexes of Indium(I) Compounds. The knowledge of arene complexes of low-valent indium is very limited. In an early series of preparative experiments aiming at arene complexes of low-valent main-group element metals In(I) complexes were also included, but no details about the composition and structure were presented.[40]

A well-defined product could finally be obtained from the reaction of $In[InBr_4]$ with mesitylene. The indium(I) salt readily dissolves in mesitylene, and on cooling colorless crystals of the 2:1 adduct can be isolated. In the crystals the components $[In(1,3,5\text{-}Me_3C_6H_3)_2]^+$ and $[InBr_4]^-$ form a chain coordination polymer. In the cations the two arenes are η^6-bonded to the In^+ cation with In−ring plane distances of 2.83 and 2.89 Å and an interplane angle of 47.3°. The In^+ cation is further chelated (η^2) by one $[InBr_4]^-$ anion and η^1-coordinated by another anion. All three bromine atoms are located in the plane bisecting the interplane angle of the arenes (**8**). Crystalline compounds were also obtained with $In[InBr_4]$ and hexameth-

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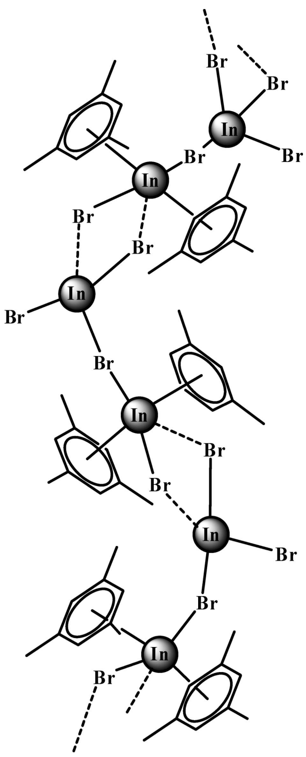
(38) McMullan, R. K.; Corbett, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 4761.

(39) Schmidbaur, H.; Zafiropoulos, T.; Bublak, W.; Burkert, P.; Köhler, F. H. *Z. Naturforsch.* **1986**, *41a*, 315.

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

ylbenzene (1:1 ratio) and with In[$AlBr_4$] and mesitylene (1:2 ratio), but the structures have not been determined.[41]



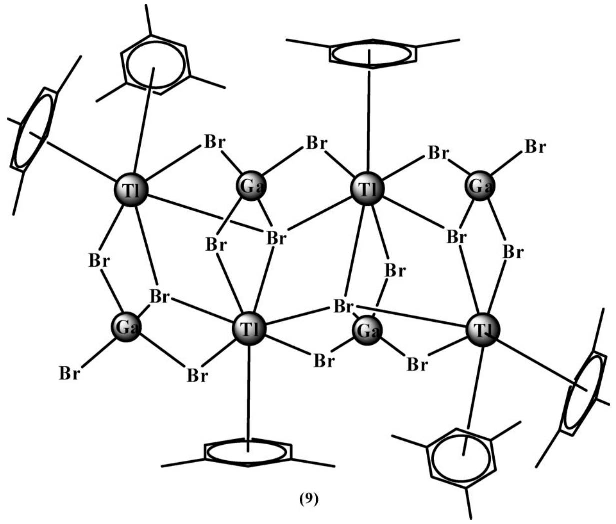
(8)

Addition of equimolar quantities of [2,2]paracyclophane to solutions of In[$InBr_4$] in mesitylene leads to precipitation of a crystalline 1:1 complex of the reactants. The compound is one of the most stable complexes of the series (mp 220 °C) and shows low senitivity to oxygen and moisture. The crystals are isotypic with those of the corresponding compounds of Ga[$GaBr_4$][34] and Tl[$GaCl_4$].[42] The 3D principle of structure of the former has already been described above (**5**). The angle between the two phenylene rings attached to each In^+ cation is 61.2°, and the In−ring center distances (equal by mirror symmetry) are 2.95 Å.[42] It is interesting to note that—as expected—this distance is longer than in the gallium complexes (2.73 Å) but—surprisingly—equal to that in the thallium complex (2.95 Å), indicating not only the relativistic contraction of the Tl^+ radius but also a particularly strong bonding (based on this effect) of Tl as compared to In.

Indium(I) complexes of benzene are produced in reaction mixtures of indium metal with $GaCl_3$ and $GaCl_3$/$BiCl_3$ in benzene as a reaction medium. The cations $[In(C_6H_6)_n]^+$ were detected by ^{115}In NMR spectroscopy and structurally investigated by X-ray absorption fine structure spectroscopy (EXAFS). An η^6 coordination by benzene was assumed. For the solution state the In-ring distance was estimated to be *ca.* 2.9 Å, and the distance to a tetrachlorometallate counterion *ca.* 3.3 Å. According to electrospray mass spectroscopy (ES MS) data, a mono(benzene) complex is the most abundant and stable cationic species ($n = 1$). Benzene complexes of Ga^+ are also present in these reaction mixtures.[43] In these and previous ES MS experiments it has been demonstrated that addition of toluene to the reaction mixtures leads to the formation of 1:1 complexes of toluene with Ga^+ and In^+ in solution, and that toluene is readily replaced by mesitylene, as expected from the increase in donor strengths of these arenes.[44,45]

5. Complexes of Neutral Arenes with Thallium(I) Compounds. Early experiments by Rundle and Corbett in 1957 to prepare benzene complexes of Tl[$AlCl_4$] failed,[46] but a decade later Auel and Amma were able to isolate two adducts of the analytical compositions 1:2 and 2:1: i.e. 2{Tl[$AlCl_4$]}·C_6H_6 and Tl[$AlCl_4$]·2C_6H_6. The structures have not been determined. The benzene-rich compound loses benzene rapidly to the atmosphere and under vacuum.[47]

Later work has confirmed the low stability of benzene complexes of Tl[MX_4] salts with benzene (M = Al, Ga and X = Cl, Br). However, a more stable compound could be obtained with Tl[$GaBr_4$] as the acceptor and mesitylene as the donor components. The crystals precipitated from mesitylene—or from benzene or toluene containing mesitylene—at ambient temperature have an unexpected 2:3 composition and are composed of tetranuclear units {$Tl_4[GaBr_4]_4$} associated with six molecules of mesitylene (**9**).[47] Two of the Tl^+ cations bear two 1,3,5-$C_6H_3Me_3$ ligands, while the other two have attached only one of the hydrocarbon molecules. The complex thus contains examples for both mono- and bis(arene) complexation of Tl^+ cations. All six arenes are η^6-bonded with shorter Tl−arene ring distances of 2.94 Å for the mono coordination and longer distances of 3.00 and 3.02 Å for the bis coordination. The angle between the two ring planes in the latter is 60.3°. Complexes of Tl[MX_4] salts with hexamethylbenzene could not be crystallized.[47]



(9)

The 2:1 complex of Tl[$AlCl_4$] with mesitylene was crystallized from mesitylene solutions by Frank et al. The crystals contain the dinuclear units {$Tl_2[AlCl_4]_2$} in which the Tl^+ cations are bridged symmetrically by six chlorine atoms of the two $[AlCl_4]^-$ anions. Each Tl^+ cation is also η^6-coordinated by two mesitylene molecules at Tl−ring plane distances in the narrow range from 2.93 to 3.02 Å and with angles between the

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(41) Ebenhöch, J.; Müller, G.; Riede, J.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 387.

(42) Schmidbaur, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Chem. Ber.* **1989**, *122*, 265.

(43) Kuznetsov, A. N.; Popovkin, B. A.; Henderson, W.; Taylor, M. J.; Bentsson-Kloo, L. *Dalton Trans.* **2000**, 1777.

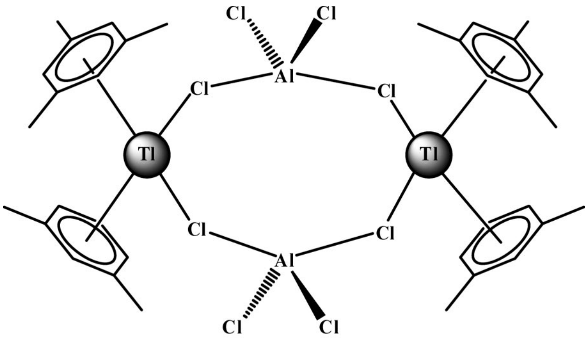
(44) Colton, R.; D'Agostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79.

(45) Canty, A. J.; Colton, R. *Inorg. Chim. Acta* **1994**, *220*, 99.

(46) Rundle, R. E.; Corbett, J. D. *J. Am. Chem. Soc.* **1957**, *79*, 1957.

(47) Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414.

ring planes of 50.8 and 54.4° (**10**). According to DTA studies, the compound loses mesitylene at 61 °C.[48]



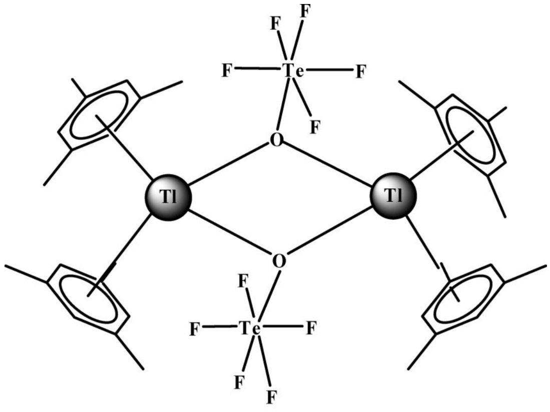
(**10**)

Almost identical structures have been found by the same authors for the 2:1 complexes of Tl[$AlCl_4$] and Tl[$GaCl_4$] with pseudocumene (1,2,4-trimethylbenzene). The core units are isotypic with that of the mesitylene complex. The Tl−arene plane distances (η^6) are in the range from 2.950 to 3.064 Å, and the interplane angles are 61.1 and 62.8°, respectively. The compounds decompose at 58.8 and 50.8 °C.[49]

A 1:1 complex of Tl[$GaCl_4$] can be precipitated from toluene solutions by the addition of [2.2]paracyclophane: Tl[$GaCl_4$]•[(*p*-$C_6H_4CH_2CH_2$)$_2$]. Its crystal structure is isotypic with that of analogous complexes of Ga[$GaBr_4$] and In[$InBr_4$] (**5**). In the 3D network, each Tl^+ has two phenylene groups of two different neighboring paracyclophanes η^6-bonded at distances of 2.95 Å and with an angle of 64.6°.[42]

Arene complexes of Tl^+ with aromatic hydrocarbons have also been obtained with other weakly coordinating anions, including pentafluorotellurate ("teflate") and tetrakis(pentafluorotellurato)borate counterions, by Strauss et al. Both anions have very poor donor capacity and hence leave the Tl^+ cation more strongly exposed to complexation by the aromatic hydrocarbon. Thallium teflate was shown to absorb benzene vapor with a saturation vapor pressure indicating a 1:2 stoichiometry, but no product was isolated. In order to point out the important role of the anion for this absorption it was noted that Tl[ClO_4] does not absorb any benzene vapor. Tl[$OTeF_5$] is also readily dissolved in toluene, most probably owing to Tl^+ complexation, which is reversible upon pumping. A stable compound could be crystallized from mesitylene as a solvent for Tl[$OTeF_5$]. The product was shown to form a dinuclear complex with four mesitylene molecules,{Tl_2[$OTeF_5$]$_2$}•4$C_6H_3Me_3$. In this dimer the two Tl^+ cations are bridged by the two oxygen atoms of the teflate anions and η^6-capped by two mesitylene ligands (**11**). The arene ring planes have distances in the range from 2.97 to 3.07 Å from the Tl atoms and form angles of 59 and 62°. The crystal lattice contains interstitial mesitylene molecules (1:1) which are not coordinated.[50,51]

The compound [Tl($C_6H_3Me_3$)$_2$]$^+$ [B($OTeF_5$)$_4$]$^-$ was obtained from Tl[$OTeF_5$] and B($OTeF_5$)$_3$ in mesitylene as a solvent. The crystals contain [Tl($C_6H_3Me_3$)$_2$]$^+$ cations in which the planes of the two mesitylene molecules form an angle of 55.8°. The Tl atom has only long contacts (in the range 3.17−3.83 Å) with four fluorine atoms of neighboring anions. Owing to this coordinative unsaturation the bonding of the arenes is particularly strong, with Tl−ring plane distances of 2.87 Å.[51]

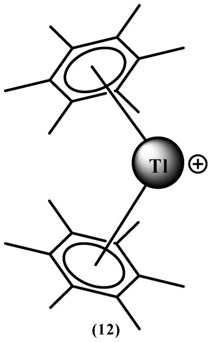


(**11**)

Thallium(I) hexabromo-*closo*-carbadodecaborate was found by Reed and co-workers to crystallize from toluene as the 1:2 complex [Tl(PhMe)$_2$]$^+$[1-CB_{11}-7,8,9,10,11,12-Br_6]$^-$. In the crystals, the cations are also well-separated from the anions, with all Tl- - -Br contacts larger than 3.393 Å. The two arenes are η^6-bonded with Tl−ring centroid distances of 2.99 and 3.09 Å and an interplane angle of 68.2°.[52]

Likewise, a thallium(I) aluminum bis(dicarbanonaborate) was precipitated from toluene/heptane solutions as the 3:2 toluene adduct by Hawthorne and co-workers: [Tl(PhMe)]$_2$Tl[*commo*-3,3′-*Al*-(3,1,2-$AlC_2B_9H_{11}$)$_2$]. Two of the three Tl^+ cations have one of the two toluene molecules η^6-bonded with Tl−arene plane distances of 2.95 Å. The remainder of the coordination sphere of the Tl^+ cations is filled by six nonbonded approaches of carborane hydrogen atoms.[53,54]

As shown in recent work by Bochmann and co-workers, addition of an excess of hexamethylbenzene to a solution of [Tl(Et_2O)$_3$]$^+${H_2N[B(C_6F_5)$_3$]$_2$}$^-$ in toluene and heating the reaction mixture to 75 °C leads to the formation of a 2:1 complex, which crystallizes with 2.5 equiv of interstitial dichloromethane. (It has been noted that the activation energy for the synthesis appears to be rather high, since no reaction takes place at 60 °C.) In the product, the cation is a bent-sandwich complex with the two η^6-bound C_6Me_6 molecules at distances of only 2.789 and 2.855 Å and an interplane angle of 47.6° (**12**). These are the shortest Tl−-arene distances hitherto observed for bis(arene)thallium(I) complexes, indicating again



(**12**)

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(48) Frank, W.; Korrell, G.; Reiss, G. J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 765.

(49) Frank, W.; Korrell, G.; Reiss, G. J. *J. Organomet. Chem.* **1996**, *506*, 293.

(50) Strauss, S. H.; Noirot, M. D.; Andersen, O. P. *Inorg. Chem.* **1986**, *25*, 3851.

(51) Noirot, M. D.; Andersen, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216.

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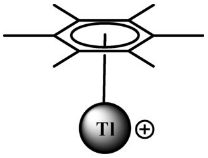
(53) Bandman, M. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 2399.

(54) Schubert, D. M.; Bandman, M. A.; Rees, W. S.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046.

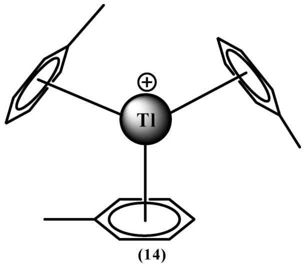
the superb donor properties of this hexaalkylbenzene. This strong bonding is reflected by an extreme ^{205}Tl chemical shift to higher field in the NMR spectra (in CD_2Cl_2; Table 1). The coordination sphere of the Tl^+ cation features no other close contacts. The fluorine atoms of the nearest counterions are more than 3.529 Å away.[55]

A mono(arene) complex of thallium(I) with the shortest Tl−ring plane distance known to date of only 2.723 Å was obtained with the strong donor hexamethylbenzene as the ligand and with the extremely bulky and "super-weakly coordinating" anion $\{H_2N[B(C_6F_5)_3]\}^-$. In the cation of the product, $[Tl(C_6Me_6)]^+$, the C_6Me_6 molecule is η^6-bonded to the metal atom with only a narrow range for variations in the Tl−C distances (**13**). The crystals contain two interstitial molecules of dichloromethane which are not coordinated. The compound was prepared by agitating the 2:1 complex in diethyl ether, extracting with petroleum ether followed by toluene, and removing all volatiles under vacuum.[56]



(13)

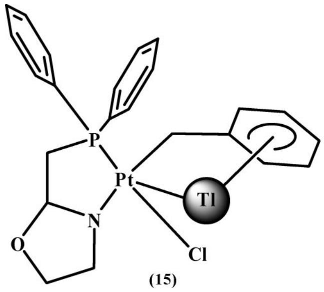
The first tris(arene)thallium(I) complex was obtained with the same counterion. For its preparation, a bis(toluene)thallium(I) compound was first synthesized from TlOEt and $[H(OEt_2)_2]^+\{H_2N(B(C_6F_5)_3]_2\}^-$ in toluene, which was identified by its microanalysis data. Its structure is not known. Recrystallization from toluene surprisingly gave the tris(toluene) complex $[Tl(PhMe)_3]^+\{H_2N[B(C_6F_5)_3]_2\}^-$. The environment of the Tl^+ cation consists exclusively of the three toluene rings, all of which are η^6-coordinated (**14**). The Tl−ring centroid distances are 2.942, 2.947, and 3.010 Å. The sum of the centroid−Tl−centroid angles is 359.7°, clearly indicating trigonal-planar coordination. There is only one precedent for this cation among all other arene complexes of group 13 metals, the Ga^+ complex of [2.2.2]paracyclophane (**7**). The ^{205}Tl chemical shifts in the NMR spectra of the bis- and tris(toluene) complexes are at much lower field than those of the hexamethylbenzene complexes, and there appears to be rapid ligand exchange in CD_2Cl_2 solution (Table 1).[55]



(14)

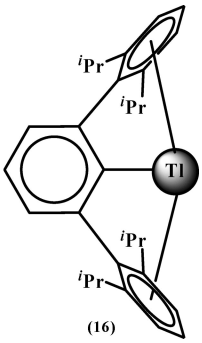
6. π-Interactions in Thallium(I) Complexes with Aryl-Substituted Ligands. π interactions between Tl(I) cations and aryl substituents of their counterions or ligands in the condensed phase are rather common. The phenomenon may or may not occur in one compound or the other, since a number of other effects can easily overrule the small energies associated with the interaction. Apart from geometrical and steric effects, a combination of $\pi-\pi$ stacking, ion−dipole electrostatics, and hydrogen bonding can be the dominant forces that determine the construction of the lattice. Therefore, Tl−arene interactions are not fully dependable, regarding their influence on a given structure. The following examples give a selection of compounds where the effect is obvious and significant for the structural patterns. There are probably many others where contributions of this type remain unnoticed.

A unique case of arene coordination to a terminal Tl atom was discovered by Braunstein and co-workers in the addition compound of the benzylplatinum(II) complex $(PN)Pt(Cl)CH_2Ph$ with $Tl[PF_6]$, shown in formula **15**. The Tl atom is attached to the Pt atom (Pt−Tl = 3.094 Å) and flanked by the benzyl group to produce an η^6 contact (with an average Tl−C distance of 3.3 Å). NMR data suggest that in solution (CD_2Cl_2) there is Pt−Tl dissociation, improving the Tl−arene interaction, which is subject to angle strain in the solid state.[57]



(15)

In another unprecedented (2,6-diarylaryl)thallium(I) compound with an unicoordinated Tl atom, prepared by Power and Niemayer, in the solid state the distance of the Tl atom to the centroids of the aryl substituents are as long as 3.92 Å (**16**). Therefore, no significant contributions to the stability of this unusual structure are to be anticipated, but nevertheless the presence of these groups is indispensable for the stability of the system. It is conceivable that in the solution state one of the phenyl groups is much closer to the metal atom, thus lending it coordinative support.[58]



(16)

The first larger group of examples of Tl−arene interaction includes a series of *thallium(I) amides*. An early case was first recognized by Strähle and Beck in the structures of thallium(I) diphenyltriazenide (Tl[PhNNNPh]) and di-*p*-tolylpentaazenide (Tl[*p*-TolNNNNN-*p*-Tol]). The formula units occur in the form of centrosymmetric dimers which are formed through intermolecular Tl-phenyl or T1-*p*-tolyl interactions (e.g. **17**). The phenyl/

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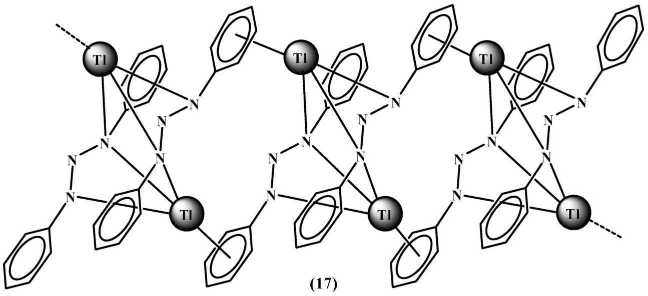
(55) Sarazin, Y.; Hughes, D. L.; Kaltsoyannis, N.; Wright, J. A.; Bochmann, M. *J. Am. Chem. Soc.* **2007**, *129*, 881.

(56) Sarazin, Y.; Kaltsoyannis, N.; Wright, J. A.; Bochmann, M. *Organometallics* **2007**, *26*, 1811.

(57) Oberbeckmann-Winter, N.; Braunstein, P.; Welter, R. *Organometallics* **2004**, *23*, 6311.

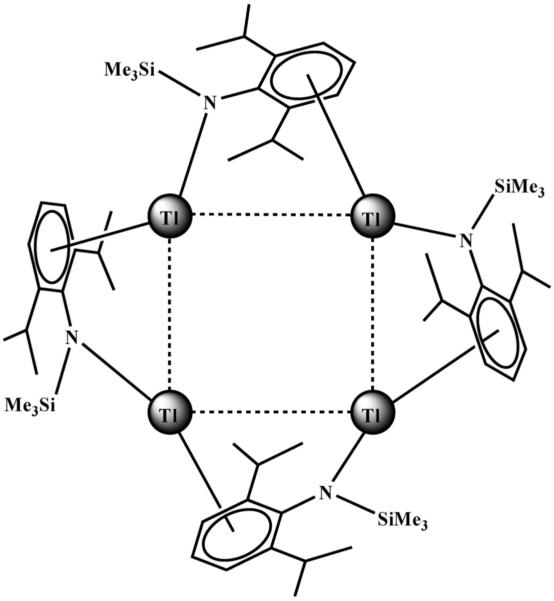
(58) Niemeyer, M.; Power, P. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1277.

p-tolyl groups are η^6-bonded to the Tl atoms at Tl−ring centroid distances of 3.27/3.33 Å.[59]



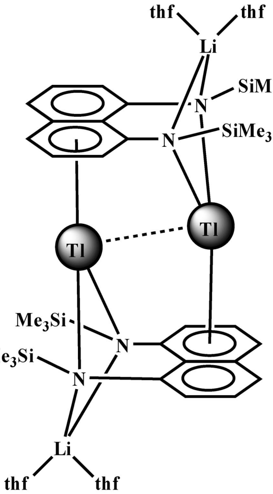
(17)

Similar interactions were subsequently observed by Roesky and co-workers: e.g., in a tetrameric thallium(I) (2,6-diisopropylphenyl)(trimethylsilyl)amide. The association of the monomers is governed by intermolecular Tl--Tl and Tl−phenyl contacts (**18**). Each Tl atom is again η^6-bonded to the arene ring at a distance of 3.11 Å.[60]



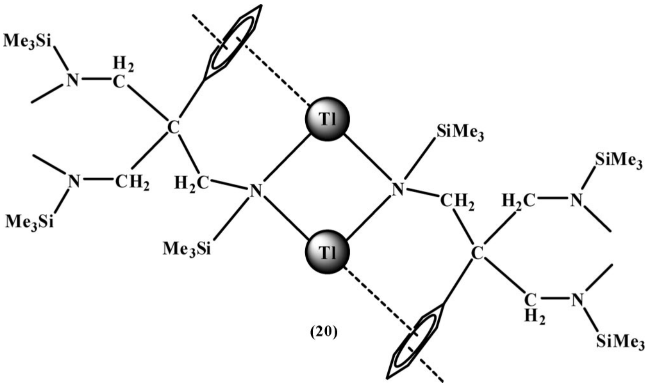
(18)

Much longer Tl−arene contacts were found by Gade and co-workers in a dimeric mixed-metal naphthalenediyl-1,8-bis(trimethylsilylamide), LiTl{$C_{10}H_6[N(SiMe_3)]_2$}, which crystallizes with two Et_2O molecules (attached to the lithium atom). In the dimer, each Tl atom is located above the center of one of the six-membered rings of the neighboring naphthalene unit at a Tl−ring centroid distance of 3.51 Å (**19**).[61]



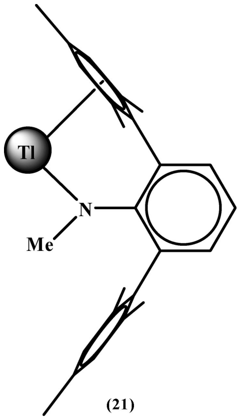
(19)

In the trinuclear thallium salt of the tris(amide) anion {$PhC[CH_2N(SiMe_3)]_3$}^{3} one of the three Tl atoms is engaged in an intramolecular, slightly slipped η^6 coordination with the phenyl ring (Tl−ring centroid distance ca. 3.10 Å), but the same phenyl ring is also attached, on its backside, to a second Tl atom at a distance of ca. 3.25 Å, which is far off center and may thus be described as η^3-bonded (**20**). This is a rare example of an off-center coordination of Tl to an arene and also the only example in which an arene bears a Tl atom above and below the ring. Note that for Sb(III) and in particular for Bi(III) this mode of coordination is quite common (see below).[62]



(20)

The thallium(I) aryl(methyl)amide [TlN(Me)Ar] with Ar = 1-C_6H_3-2,6-(C_6H_3-2,6-Mes_2)$_2$ is a monomer in the solid state, and the Tl atom is bonded to the nitrogen atom and flanked by one of the mesityl substituents (η^6) with a Tl−ring centroid distance of 3.026 Å (**21**). In addition, a second mesityl group (of a neighboring molecule) is located at a distance of 3.569 Å, but its bonding is considered to be much weaker than the intramolecular interaction.[63]



(21)

A rare example of a Tl−*hetero*arene π-interaction was detected in the corresponding 2-pyridyl compound, a dimeric,

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[59] Beck, J.; Strähle, J. *Z. Naturforsch.* **1986**, *41b*, 1381.

[60] Waezsada, S. D.; Belgardt, T.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed.* **1994**, *33*, 1351.

[61] Hellmann, K. W.; Galka, C.; Gade, L. H.; Steiner, A.; Wright, D. S.; Kottke, T.; Stalke, D. *Chem. Commun.* **1998**, 549.

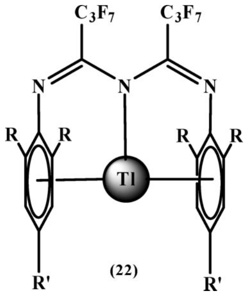
[62] Galka, C. H.; Gade, L. H. *Inorg. Chem.* **1999**, *38*, 1038.

[63] Wright, R. J.; Brynda, M.; Power, P. P. *Inorg. Chem.* **2005**, *44*, 3368.

dinuclear thallium tris(amide) of the formula $\{(2\text{-}C_5H_4N)\text{-}CMe[CH_2N(SiMe_3)Tl]_2\}$.[64]

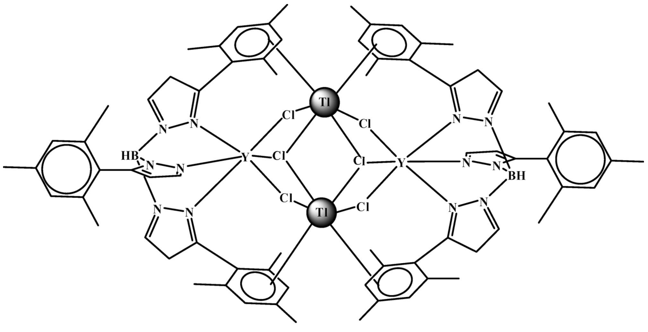
In a dinuclear, mixed-valent Tl(I)/Tl(III) tris(amide) of the formula $HC[SiMe_2N(p\text{-}Tol)]_3(^{n}BuTl)Tl$ upon dimerization the two low-valent Tl atoms become η^6-bonded to a *p*-tolyl group (ring centroid distance 3.093 Å).[65]

In the mononuclear thallium(I) 1,5-diaryl-1,3,5-triazapentadienides $\{TlN[C(C_3F_7)NAr]_2\}$ (Ar = mesityl, 2,6-diisopropylphenyl), with two perfluoropropyl substituents in the 2,4-positions, the Tl atoms are η^6-flanked by the two Ar groups at ring centroid distances of 3.000 and 3.100 Å (**22**).[66]



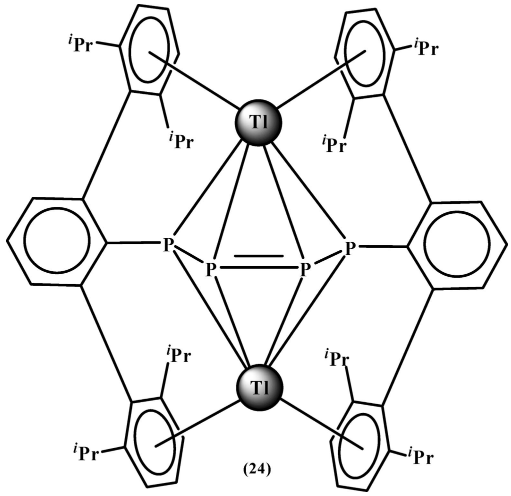
(22)

Thallium−arene contacts are discernible in a thallium(I) salt of an yttrium tris(mesityl−pyrazolyl)hydroborate. In the structure of the centrosymmetrical dimer, each of the two thallium atoms becomes attached to two mesityl rings, but the hapticity is reduced from η^6 to η^3, owing to a significant ring slippage. The Tl−C distances are shorter than 3.55 Å only for three of the six ring carbon atoms (**23**).[67]



(23)

Tl−arene interactions were also detected in a dithallium(I) diaryltetraphosphenediide, $[Tl_2(ArPP{=}PPAr)]$, with Ar = $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)$. Each of the two Tl^+ cations is η^4-bonded to the tetraphosphorus chain and η^6-bonded to two substituents of two different Ar groups (Tl−ring centroid distances 3.204 and 3.290 Å) (**24**).[68]



(24)

A second large group of compounds with distinct Tl−arene contacts includes *thallium(I) arylcarboxylates*.[69,70] In the 3D assembly of the components of thallium anthranilate, $Tl^+[1,2\text{-}C_6H_4(NH_2)COO]^-$, each Tl^+ cation becomes η^6-attached to a phenylene ring at a Tl−ring centroid distance of 3.37 Å. Similar modes of aggregation are found for the corresponding 3- and 4-methylanthranilates, but with significantly shorter distances of 3.23 and 3.17 Å, in agreement with the improved donor capacity of the benzene ring in the methylated anions.[70]

Thallium hydrogensalicylate appears to be dimorphic. In a monoclinic form it is associated via Tl−arene contacts to give a structure in which two benzene rings are attached to each Tl^+ cation with Tl−ring centroid distances of 3.29 Å.[69,70] No such contacts are present in the structure of the 3-methylhydrogensalicylate, but they reappear in the structures of 4-methyl- and 4-aminohydrogensalicylate, of 3,4- and 3,5-dimethoxybenzoate,[69] and in "Thallium Lasalocid A" (an ionophore with salicylate groups), the last species also with a typical Tl−arene distance of 3.24 Å.[70–72] These discrepancies show that many factors have an influence on the motifs of structure in these compounds with their great variety of intermolecular forces.[69,70] In an orthorhombic form of thallium(I) hydrogensalicylate, $Tl[1,2\text{-}C_6H_4(OH)COO]$, the distance of the Tl^+ cation from a benzene ring of a neighboring anion is exceedingly long, with Tl−C distances in the range 3.69−3.90 Å, which suggest very weak, if any, bonding.[72] Closer contacts were found in the structure of a thallium(I) diphenyl-2-carboxylate nitrate, $[Tl_3(Ph\text{-}C_6H_4\text{-}2\text{-}COO]_2NO_3]$, with Tl−ring centroid distances of 3.32 and 3.43 Å for two different η^6 contacts. Tl−arene contacts are absent in thallium(I) hydrogenphthalate.[73]

Thallium(I) diphenylacetate, $Tl[Ph_2CHCOO]$, crystallizes as a tetramer based on a distorted cubic Tl_4O_4 core unit with inversion symmetry (**25**). One of the two phenyl groups of each diphenylacetate anion is located over a Tl- - -Tl diagonal of a face of this cube with short and long Tl−C distances (3.38 and 3.56 vs 3.82, 3.88, 3.98, and 3.99 Å) suggesting η^1/η^3 bonding of each Tl atom. The structure is a unique case for π-bonding of a benzene ring to two neighboring Tl atoms (at the same face of the ring).[74]

Thallium(I) 1,3-diphenylpropanedionate (dibenzoylmethanide) crystallizes as a dimer, $[Tl(PhCO)_2CH]_2$, in which one of the two Tl^+ atoms is η^6-bonded to one of the phenyl rings, while the second one has only distant η^2 contacts.[75]

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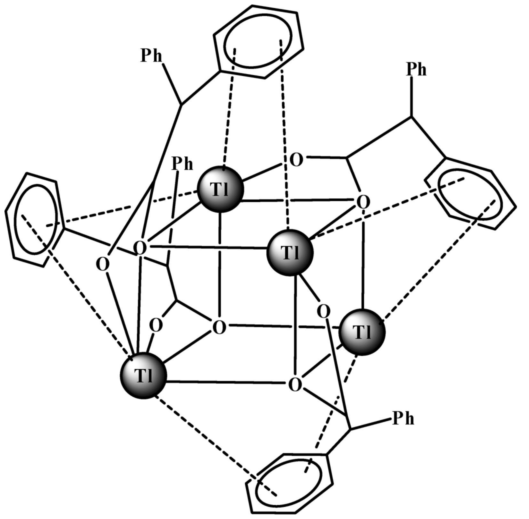
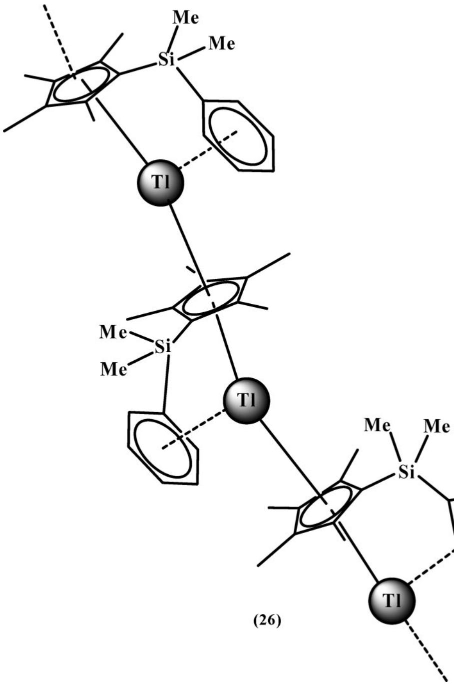


(25)

In thallium(I) cyclopentadienyl compounds generally the Tl^+ cations are η^5-bonded to the cyclopentadienyl (cp) rings. However, if the cp rings bear flexible benzyl or phenylsilyl substituents, the phenyl groups can also contribute to the coordination sphere of the metal cation (**26**). In compounds prepared by Schumann et al., distant Tl−Ph contacts are discernible in $Tl[C_5H_4\text{-}Bz_5]$, $Tl[C_5H_4\text{-}Me_4(SiMe_2Ph)]$, and $Tl[C_5H_4\text{-}Me_4(SiMe_2CH_2Ph)]$, but in the solid state the Tl−C distances are generally well beyond 3.60 Å, indicating that therein the interactions are very weak.[76–78] The thallium(I) derivative of 2-cyclopentadienyl-2-(9-fluorenyl)propane is an exception, in that the η^3 coordination observed therein has short Tl- - -C contacts of ca. 3.45 Å.[79] This work has been summarized in a review by Janiak.[80]

Contributions by phenyl groups to thallium coordination are also of low significance in the fullerene complex $Tl[C_{60}Ph_5]$, owing to the even larger Tl- - -Ph distances.[81]

7. Chemical Bonding in Low-Valent Group 13 Metal Arene Complexes. Early qualitative rationalizations of arene bonding to low-valent gallium, indium, and thallium cations employed the general concepts of charge transfer and electron donor−electron acceptor interactions with the arene as the donor and the metal cation as the acceptor.[15] Subsequently, in qualitative MO diagrams based on the predominantly observed local C_{6v} symmetry the p orbitals of the Ga^+ cation were considered the most relevant acceptor orbitals.[8] The picture was refined in discrete variational (DV) Xα molecular orbital calculations focusing on the $[Ga(C_6H_6)]^+$ and $[Ga(C_6H_6)_2]^+$ cations with C_{6v} and C_{2v}/D_{6h} symmetry, respectively, the latter representing bent and parallel sandwich complexation.[82] From the results it has been deduced that the charge transfer occurs mainly into the vacant Ga 4p orbitals. For the first benzene molecule, the charge transfer is 0.131 e, while for the second the increase in this transfer is only 0.044 e, indicating that the bonding to this second arene molecule is much weaker, in good agreement with experimental observations. The distortion from a parallel to a bent-sandwich structure leads to a slight increase in charge transfer of 0.007 e, making the bent conformation the ground-state structure. Inclusion of a $[GaCl_4]^-$ counterion in a molecule of C_{2v} symmetry as a model for the anion coordination shows that the cation−anion interaction is of the same strength as the cation−arene interaction, the former being based mainly on a Cl 3p−Ga 4p electron transfer. It is interesting to note that similar calculations for $[K(C_6H_6)]^+$, $[K(C_6H_6)_2]^+$, and $[K(C_6H_6)_2]^+[GaCl_4]^-$ have shown that there is no significant electron transfer from benzene to K^+, which can explain at least in part the insolubility of $K[GaCl_4]$ in benzene.[8] As mentioned in the Introduction, this difference in solubility as compared to $Ga[GaCl_4]$—in light of the fact that both cations have about the same ionic radius—was one of the incentives for many experimental studies and theoretical considerations in this area.



(26)

Ab initio molecular orbital calculations were reported for the interaction of gallium atoms (Ga^0) with the benzene molecule, but the results were not considered in context with the interaction of the gallium cation (Ga^+) with benzene.[83]

The interactions of the In^+ cation with a benzene molecule have been considered using ab initio molecular orbital and density functional theory. On various levels of theory, the ion affinity was calculated, and the following results (in kcal mol^{-1}) were obtained: 22.38 (HF), 30.28 (MP2), 26.30 (QCISD), 26.31 (CCD), 24.24 (B3LYP), 28.63 (B3PW91). Since B3PW91 also gives an ionization energy for In in good agreement with the experimental data, the value of 28.63 kcal mol^{-1} for the benzene complex in the above series is considered a reliable approximation. It shows that the species $[In(C_6H_6)]^+$ should be stable and observable by mass spectrometry.[84]

Bond orders of Tl−arene binding in the $[Tl(Mes)_2]MX_4$ complexes have been estimated using the Brown formalism (based on an empirical correlation between bond lengths and bond orders) by Frank et al. For each Tl−mesitylene interaction

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a bond order of ca. 0.25–0.35 was obtained. Since shorter bonds are observed for alkylated benzenes, this value will be smaller for substituent-free benzene and larger for hexamethylbenzene. The bond orders estimated with this approximation for Tl^+ are surprisingly large and in fact are comparable to those for the Tl–X contacts in the same complexes.[49]

DFT calculations carried out by Power and co-workers in order to model the Tl–arene interactions in the thallium(I) methyl(aryl)amide **21** gave a very low interaction energy of only 3 kcal mol^{-1} for the attachment of a benzene molecule to the Tl atom in thallium methyl(phenyl)amide. It was acknowledged, however, that weak interactions of this nature have a strong influence on the stability and structure of compounds with low-coordinate Tl atoms, in particular if significant entropy contributions are to be expected, as in the amide originally under investigation.[63]

In the context of a DFT study of the thallium(I) triazapentadienides with their almost parallel aryl rings (**22**), the simple $[Tl(C_6H_6)_2]^+$ model cation was considered and shown to have an equilibrium Tl–ring distance of 2.92 Å (D_6 symmetry). The gas-phase dissociation of this species into its three components was endothermic by no less than 42 kcal mol^{-1}: i.e., ca. 21 kcal per Tl–arene bond. For the complete experimental species, this interaction energy is 13 kcal mol^{-1}. For the three MOs which display significant interactions, there is a considerable contribution from the Tl 6s orbital.[66]

Density functional theory calculations have very recently been carried out by Bochmann and co-workers for $[Tl(C_6Me_6)]^+$ as contained in the $\{H_2N[B(C_6F_5)_3]_2\}^-$ salt (see above). The calculated Mulliken charge on the Tl^+ cation of 0.88+ is close to the formal oxidation state (1+). The interaction energy for Tl^+ and benzene was found to be 163 kJ mol^{-1}. An orbital analysis has been conducted which showed that virtually all the valence orbitals have predominantly ligand character. The MOs with Tl character involve almost exclusively the Tl 6s orbital.[55,56]

In calculations on $[Tl(C_6Me_6)_2]^+$ it first was established that the change from a parallel to a bent-sandwich geometry has a very flat energy profile. A bending from 180 to 145° is associated with an energy change of only 1 kJ mol^{-1}, but below this limit the energy is greatly increased, indicating steric interference. Note that this limit of 145° is in excellent agreement with the experimental value of 142.4°. It appears that the bending to this angle is induced by the approaching anion, which gives rise to significant electrostatic and additional donor–acceptor interactions. The calculated Mulliken charge on the metal atom is 0.91, suggesting a Tl^+ cation between two almost neutral rings. There are very few valence MOs (mainly a_1 in C_{2v} symmetry) for the $[Tl(C_6Me_6)_2]^+$ cation with significant Tl character, and these are largely nondirectional in terms of metal–ring bonding. The calculated interaction energy of Tl^+ and two C_6Me_6 molecules in this geometry is 243.4 kJ mol^{-1}, which allocates 121.7 kJ to each $Tl-C_6Me_6$ interaction. This value is significantly lower than the energy calculated for the 1:1 complex (163 kJ) and explains the experimental observation that the first arene is more tightly bound to a group 13 metal cation than the second arene. (For a hypothetical intake of a third C_6Me_6 molecule, the energy gain is only 28 kJ mol^{-1}.) A comparison with values calculated for (hypothetical) $[Tl(PhMe)_2]^+$ and $[Tl(C_6H_6)_2]^+$ cations gives clear evidence that the bonding is strongest for the most highly substituted benzene ligand (C_6Me_6).[55,56]

As a model for the tris(toluene)thallium(I) cation, the benzene analogue $[Tl(C_6H_6)_3]^+$ has been investigated by DFT calculations. The optimized geometry with the three benzene molecules η^6-coordinated to the metal atom, and with coplanarity of the ring centroids with the metal atom, was found to have a Tl–centroid distance of 3.06 Å, only slightly, but significantly longer than the experimental values for the toluene complex, which is not unexpected. Starting with the 2:1 complex cation, the addition of the third arene to give the 3:1 complex yields only 4.9 kJ mol^{-1}, indicating the rapid decrease of interaction energy with an increase in the number of arenes. The Mulliken charge of the Tl atom in the cation $[Tl(PhMe)_3]^+$ is 0.90, and the total interaction energy relative to Tl^+ and three free toluene molecules is 221 kJ mol^{-1}, an average of 73.7 kJ per Tl–arene bond. Only three MOs of the cation have low, but significant, Tl 6s contributions. The Tl–arene interactions are thus low in covalent character, with the main contribution from "polarization bonding", and are rather flexible regarding Tl–arene distances, arene–Tl–arene angles, and ring slippage (from η^6 to lower hapticities).[55,56]

8. Remarks. In an attempt to summarize the important aspects of the above inventory of arene bonding to the heavy, low-valent group 13 elements, the following points can be highlighted.

1. In the absence of external restraints, neutral aromatic hydrocarbons become attached to Ga^+, In^+, and Tl^+ cations exclusively in the η^6 coordination mode. The three cations can accommodate up to three arene molecules.

2. The arenes act as electron donor ligands and the metal cations as electron acceptors. The interaction energy is thus increasing with the donor capacity of the arene and with the acceptor power of the metal atom. Employment of extensively alkylated hydrocarbons and metal salts with noncoordinating anions affords the most stable complexes.

3. The cation–arene plane distance is a reliable indicator of the affinity between the components for the same element; the distances increase with an increasing number of arenes coordinated to the same cation. This distance increases from Ga^+ to In^+, but the increase from In^+ to Tl^+ is much less pronounced, and complexes of Tl^+ appear to be particularly stable. This is not only obvious from the far greater number of (arene)thallium(I) complexes, but also from the general properties of the compounds. The phenomenon that the largest cation forms the most stable complexes most probably is to be ascribed to the relativistic contraction of the Tl 6s orbital.[85]

4. Theoretical calculations of Ga/In/Tl–arene bonding at various levels of sophistication have given a whole range of data which reflect the difficulties associated with the approximations used in these studies. The results agree with the general statement that the interactions should be considered "weak" and to a high degree are based on electrostatic polarization interactions. However, in particular for gallium and thallium, there is a significant participation of the 4p and 6s orbitals, respectively, to the bonding MOs.

5. Calculated gas-phase interaction energies were found to be as low as 3 kcal mol^{-1} and as high as 35 kcal mol^{-1} for Tl^+ and benzene or hexamethylbenzene, respectively, in different systems. It is obvious that these results are often difficult to evaluate, since the counterions, auxiliary ligands, and environment in the solid state all affect the stability of the structures. There is no doubt that the interactions in question codetermine very significantly the structures and properties of many molecules and in particular their assembly in supramolecular aggregates, well beyond the influence of standard van der Waals interactions.

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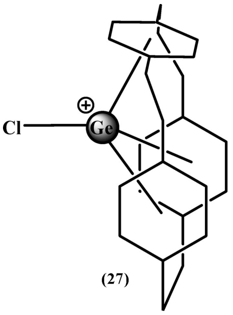
6. Except for work on intercalation of graphite and substituted fullerenes,[81] there appear to be no documented studies on the capacity of carbon allotropes to bind low-valent group 13 metal cations.

III. Arene Complexes of Low-Valent Germanium, Tin, and Lead

In comparison to the long history and the volume of present knowledge of the chemistry of arene complexes of the heavier group 13 and 15 elements (Ga, In, Tl; As, Sb, Bi), the chemistry of the corresponding group 14 elements (Ge, Sn, Pb) is both more recent and accordingly less developed. This is particularly true for Ge and Pb, for which only less than 6 and 24 references, respectively, reflect the rather limited information on areas which probably have the same potential as has already been opened up for the other elements.

1. Germanium. Low-valent germanium halides and related compounds have become available rather late in the history of germanium chemistry. The preparative routes to $GeCl_2$, as the most important example, are experimentally difficult and the products readily undergo decomposition with disproportionation. The solid-state structure has remained elusive, and the compound therefore is used for most purposes in the form of its 1:1 complex with 1,4-dioxane, $GeCl_2 \cdot$(dioxane). $GeCl_2$ appears to be at best very sparingly soluble in benzene or other aromatic hydrocarbons, and the nature of the solute is unknown. $GeBr_2$ and GeI_2 are more stable than $GeCl_2$ but are also insoluble in arenes.[86]

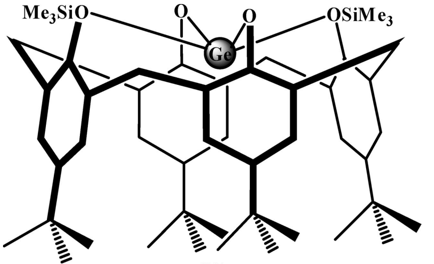
$GeCl_2$ becomes soluble in aromatic hydrocarbons upon the addition of $AlCl_3$. A product has been fully characterized only from the reaction with 3 equiv of $AlCl_3$ in benzene containing 1 equiv of [2.2.2]paracyclophane.[87] Crystallization was strongly delayed, and during the long waiting period traces of water vapor entered the benzene solution, which led to the isolation of the compound $[Ge(C_6H_4CH_2CH_2)_3Cl]_2[Al_4O_2Cl_{10}] \cdot 4C_6H_6$. The tetranuclear anion is known from other salts and will not be discussed here any further,[88] and the four benzene molecules are interstitial solvate molecules. In the two equivalent cations the Ge atoms are coordinated quite symmetrically to all three phenylene rings with Ge–ring centroid distances of 2.715, 2.722, and 2.797 Å. However, in contrast to the situation in a related Sn complex (below),[87] the Ge atom is not coplanar with the three ring centroids but is strongly bound to a chlorine atom with the short distance Ge–Cl = 2.224 Å. In the IR spectrum, an intense band for ν(Ge–Cl) was observed at 429 cm^{-1}. The Ge atom can thus be described as tetrahedrally coordinated by this chlorine atom and three phenylene rings (**27**).[87] This tetrahedral geometry of Ge^{2+} in this complex is at variance not only with the trigonal-planar coordination of Sn^{2+} and Ga^+ in their [2.2.2]paracyclophane complexes (**7**)[87,37] but also with that of Tl^+ in a tris(toluene) complex (**14**).[56] It should be observed, however, that it is only the germanium atom that carries a chloride ligand, whereas the charge of the latter three (Ga^+, Sn^{2+}, Tl^+) is compensated by noncoordinating or poorly coordinating anions. The substrate $Ge(MX_4)_2$ would be required for an anion-free coordination environment of the germanium atom. The structure of the [2.2.2]paracyclophane complex of the $[GeCl]^+$ unit is further remarkable in that it appears to be a case of a "stereochemically inactive" lone pair of electrons at the Ge^{2+} center. It could be assumed that the Ga 4s orbital (or its sp_z hybrid, the coordinate of the p_z orbital coinciding with the Ge–Cl bond, under C_{3v} symmetry) is mainly involved in the interactions with the linear combination of the a_1-symmetric π orbitals of the three arenes, but no calculations have been carried out yet to test this hypothesis.



(27)

In the absence of any other experimental evidence, the formation, stability, and structure of **27** are the only proof that arene complexation by subvalent germanium is a significant reality. It is surprising that no mono- and bis(arene) complexes have been identified for Ge(II). Experimental efforts in this direction should be more than promising, particularly if $GeCl(ECl_4)$ or $Ge(ECl_4)_2$ with E = Al, Ga are employed. The reagents for the preparations with the [2.2.2]paracyclophane were chosen for the above experiment because the analogous experiments with Sn(II) had been successful.[87]

The reaction of bis[bis(trimethylsilyl)amino]germanium with an O,O′-disilylated *p-tert*-butyl[4]calixarene proceeds with formation of an exo and an endo isomer of the Ge–calixarene complex. In the endo isomer, the Ge atom may be engaged in bonding with the phenylene rings of the calixarene funnel, but the interaction can only be weak owing to an unfavorable orientation of the phenyl groups. Nevertheless, the distance of about 3 Å to the inner three carbon atoms of each phenylene ring at least can be taken as evidence for significant η^3 hapticity (**28**).[89,90]



(28)

A series of alkali-metal germanium(II) tris(2,6-diphenylphenoxides), $M[Ge(OC_6H_3Ph_2)_3]$, with M = Li, Na, K, Rb, Cs have been prepared and structurally characterized. M–arene π bonding was observed in all cases, but the role of Ge–arene interactions has not been discussed.[91]

2. Tin. It appears that there are no observations documented in the early literature which suggested that tin(II) halides would

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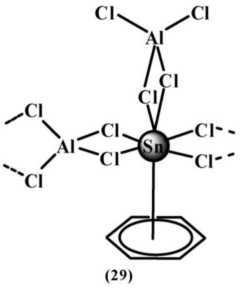
form complexes with aromatic hydrocarbons.[1] While tin(IV) halides SnX_4 are volatile liquids (X = Cl) or low-melting solids (X = Br, I), the anhydrous tin(II) halides are solids with much higher melting points and high sublimation temperatures, suggesting a high lattice energy.[92a,b] Not unexpectedly, therefore, $SnCl_2$, $SnBr_2$, and SnI_2 were found to be virtually insoluble in benzene.[93,94]

A coverage of the first reports on arene complexation by tin(II) compounds is contained in a Gmelin volume from 1995.[92b] This summary confirms that meaningful investigations in this area were initiated as late as the mid-1960s.

a. Tin(II) Complexes of Neutral Arenes. According to a report from 1968, the results of investigations of arene complexes of other metal halides prompted Auel and Amma to study the reaction between $SnCl_2$ and $AlCl_3$ in benzene. It was observed that the solid anhydrous $SnCl_2$ dissolved rapidly and completely in dry benzene upon the addition of anhydrous $AlCl_3$. If the molar ratio $SnCl_2$:$AlCl_3$ exceeded the value of 1:2, excess $AlCl_3$ could be filtered off and the product recovered from the clear solution. The adduct could be crystallized, and according to elemental analysis it was found to have the stoichiometry of a 1:2:2 complex: $Sn(AlCl_4)_2 \cdot 2C_6H_6$. The Sn Mössbauer and IR spectra were recorded and taken as an indication for high local symmetry of the arene coordination.[24] In subsequent structural studies it was shown that the compound had to be reformulated as the 1:2:1 complex $[Sn(AlCl_4)_2 \cdot C_6H_6] \cdot C_6H_6$ because one of the two benzene molecules was not attached to the tin atom but was contained in the lattice as an interstitial solvate molecule. The structure of the compound is shown in formula **29**. The Sn^{2+} cation is chelated by three $AlCl_4^-$ anions and attached to the benzene molecule in an almost perfect η^6 coordination mode with a Sn−ring plane distance of 2.74 Å. It was noted by the authors that the Sn−C distances (average 3.08 Å) are much shorter than the sum of the van der Waals radii of the two elements and thus indicated unusual bonding. In an analysis of the bonding using a qualitative MO diagram, the Sn−ring interaction was suggested to be of a weak donor−acceptor type, predominantly involving Sn 5s and 5p acceptor orbitals (a_1 and e_1 in local C_{6v} symmetry) and symmetry-equivalent benzene π-donor orbitals. The tin atoms bearing the benzene molecules are associated via one of the two $AlCl_4$ units, which function as η^2−η^2 donors to give 1D chains. The second $AlCl_4$ unit is only η^2-chelating and not chain-propagating.[95,96]



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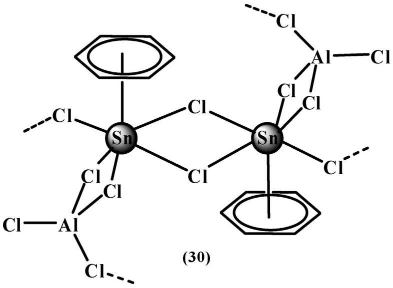
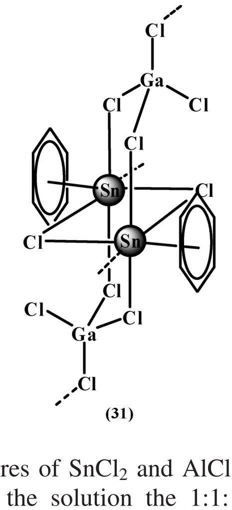
With a reduced amount (<1:2) of $AlCl_3$, anhydrous $SnCl_2$ reacts with benzene to form a precipitate of the composition $SnCl(AlCl_4) \cdot C_6H_6$. This compound contains a rectangular $Sn_2Cl_2^{2+}$ core unit with each Sn atom further coordinated by one chelating and one bridging $AlCl_4^-$ anion and one benzene ring (η^6 mode, Sn−ring plane distance 2.85 Å; **30**). The association of the $Sn_2Cl_2^{2+}$ and $AlCl_4^-$ units via Al−Cl−Sn bridges also leads to inorganic strings with each peripheral Sn atom covered by a benzene ring. It should be noted that the phase diagram of the system $SnCl_2 \cdot AlCl_3$ indicates the existence of a 1:1 compound.[97,98] This phase thus appears to become soluble in benzene through arene coordination.[99,100]



(30)

The reaction of $SnCl_2$ and $GaCl_3$ (mole ratio 1:1) in benzene yields a very labile crystalline product which is difficult to characterize by conventional analytical techniques, because it loses benzene rapidly at room temperature.[101,102] However, a low-temperature single-crystal structure determination has shown that the stoichiometry is as expected (1:1:1), and that the structure is also based on $Sn_2Cl_2^{2+}$ units with the two Sn atoms bridged by two $GaCl_4^-$ anions to generate an eight-membered ring (**31**). Each Sn atom is also attached to a benzene ring in a quasi-η^6 coordination (Sn−ring plane distances of 295.5 and 300.5 Å for two inequivalent Sn atoms, one of the two benzene rings being rotationally disordered). Additional Sn−Cl−Ga linkages between the dinuclear units give rise to an assembly into inorganic layers.[102]



(31)

Equimolar mixtures of $SnCl_2$ and $AlCl_3$ dissolve readily in toluene, and from the solution the 1:1:1 complex α-SnCl($AlCl_4$)·PhMe can be crystallized in high yield. If the solution also contains durene (1,2,4,5-tetramethylbenzene), the expected durene complex is not formed, but a second polymorph (β) of the toluene complex is obtained.[103] The differences between

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(93) Brewer, M. F. *J. Phys. Chem.* **1927**, *31*, 1817.

(94) Dilung, J. J.; Dain, B. Y. *Russ. J. Phys. Chem.* **1959**, *33*, 605.

(95) Lüth, H.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 7515.

(96) Rodesiler, P. F.; Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 7405.

(97) Kendall, J.; Crittenden, E.; Miller, H. K. *J. Am. Chem. Soc.* **1923**, *45*, 963.

(98) Belt, R. F.; Scott, H. *Inorg. Chem.* **1964**, *3*, 1785.

(99) Weininger, M. S.; Rodesiler, P. F.; Gash, A. G.; Amma, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 2135.

(100) Weininger, M. S.; Rodesiler, P. F.; Amma, E. L *Inorg. Chem.* **1979**, *18*, 751.

(101) Schmidbaur, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Chem. Ber.* **1989**, *122*, 265.

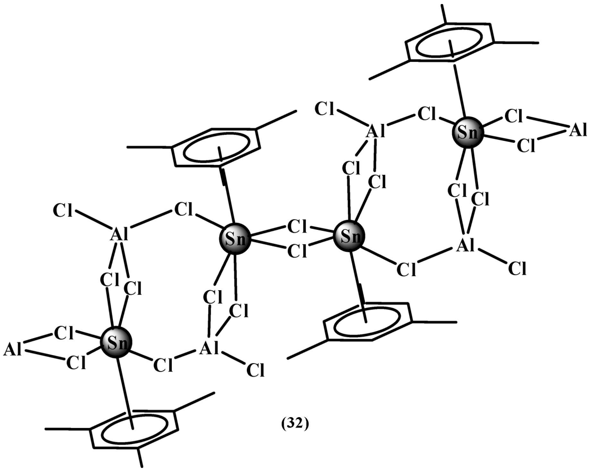
(102) Frank, W. *Chem. Ber.* **1990**, *123*, 1233.

(103) Frank, W. *Z. Anorg. Allg. Chem.* **1990**, *585*, 121.

the structures of the two polymorphs, and between those of the two polymorphs and the corresponding benzene and *p*-xylene complexes, are very small. The crystallographic details have been analyzed by Frank and related to the steric requirements of the three hydrocarbons. The toluene molecules have distorted η^6 hapticity with average Sn−ring plane distances of 2.81 Å.[103]

As just mentioned as a structural reference for the toluene and benzene complexes, $SnCl_2$ and $AlCl_3$ also afford a 1:1:1 complex with *p*-xylene, $SnCl(AlCl_4)\cdot p\text{-}C_6H_4Me_2$, the crystals of which have the same principle of structure as the benzene complex with a Sn−ring plane distance of 2.75 Å for a quasi-η^6-bound *p*-xylene molecule.[100]

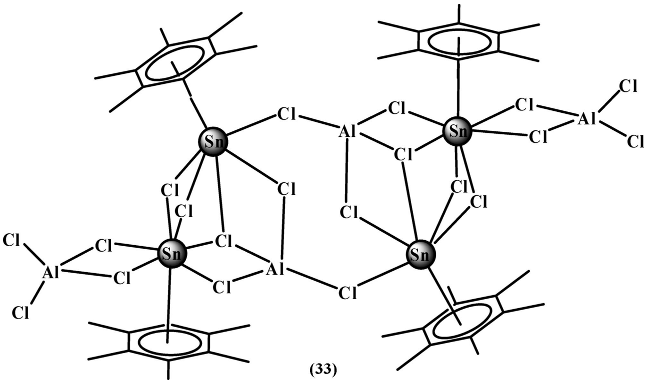
Another structural organization of the units $Sn_2Cl_2^{2+}$ and $AlCl_4^-$ was found with mesitylene as the hydrocarbon ligand, in $SnCl(AlCl_4)\cdot 1,3,5\text{-}Me_3C_6H_3$, in two independent studies published in the same year.[103,104] Through η^2 chelation of each Sn atom by one $AlCl_4^-$ anion and η^1 bridging by another, two different centrosymmetrical ring systems are established which alternate along the chain of the coordination polymer (**32**). The mesitylene molecule is η^6-coordinated to the tin atom with a short Sn−ring plane distance of 2.71 Å, which indicates improved donor properties of mesitylene as compared to benzene.



(32)

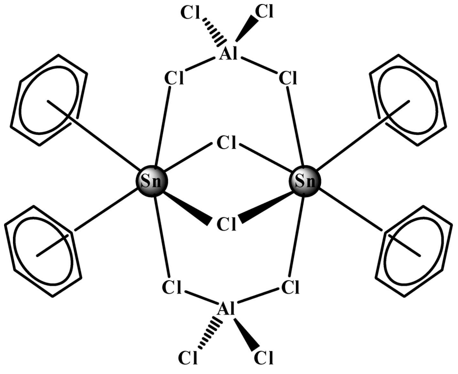
Yet another different assembly has been revealed for the analogous complex with hexamethylbenzene. From chlorobenzene as a solvent, crystals containing the centrosymmetrical tetramer $[SnCl(AlCl_4)\cdot C_6Me_6]_4$ are formed (**33**). In the crystals, this formula unit is accompanied by three interstitial C_6H_5Cl solvate molecules which are not Sn-coordinated. Each Sn atom of the two pairs of inequivalent Sn atoms is attached in an η^6 mode to a hexamethylbenzene molecule with Sn−ring plane distances of 2.60 and 2.73 Å, signaling an even tighter binding than for mesitylene. The angles between the normal from the Sn atom to the ring planes and the line connecting the Sn atom and the ring centroid was found to decrease with increasing methyl substitution of benzene: benzene, 10.7°; toluene (average), 8.75°; xylene, 6.9°; mesitylene, 6.9°; hexamethylbenzene, 5.7°. Thus, as the donor strength of the arene increases, the arene is attached more closely, and the deviation from ideal η^6 mode (ring slippage) becomes smaller.[103,104]

The first bis(arene)tin(II) complex was obtained upon dissolving a sample of $Sn(AlCl_4)_2$, prepared by reacting $SnCl_2$ and Al_2Cl_6 to a clear melt and cooling this melt to room temperature, in boiling benzene. The colorless crystals which precipitated



(33)

upon cooling of the solution (mp 110 °C) contain dinuclear molecular units of the composition $[SnCl(AlCl_4)\cdot 2C_6H_6]_2$ (**34**). It is as yet unclear why the 1:2 stoichiometry ($SnCl_2$:$AlCl_3$, after melting the two together) with an excess of benzene leads to a 1:1:2 complex under the given experimental conditions,[105] while for the stoichiometry <2:1 (with separate reagents) in benzene the 1:1:1 complex is obtained.[99,100] The crystals also contain one interstitial benzene solvate molecule. The tin atoms of the $Sn_2Cl_2^{2+}$ core unit of this 1:1:2 complex are bridged by two $AlCl_4^-$ anions to give an eight-membered ring, also observed in the 1:1:1 complex (above). However, each of the two tin atoms bears two benzene rings, thus covering its coordination sites and preventing the assembly into chains through Al−Cl−Sn bridges, as observed for the 1:1:1 complex. The four Sn−ring plane distances have values between 3.11 and 3.26 Å, and the four angles between the normal from the tin atoms to their arene plane and the line connecting the Sn atoms with the ring centroids are in the range from 5.0 to 10.4°, indicating η^6 coordination with a small ring slippage. The two benzene molecules at the tin atoms are tilted against each other with interplane angles of 66.3 and 65.3°. From the structural details of this first bis(arene)tin(II) complex, it appears that the benzene rings are less tightly bound to the Sn center as compared to the mono(arene)tin(II) complexes.[105]



(34)

A case of deliberately arranged bis(arene)tin(II) coordination was the synthesis of a complex with triptycene. The reaction of anhydrous $SnCl_2$ with anhydrous $AlCl_3$ in benzene containing triptycene in a Soxhlet apparatus afforded colorless crystals of the centrosymmetrical dinuclear complex $[SnCl(AlCl_4)\cdot C_{20}H_{14}]_2$. The crystals also contain two interstitial molecules of benzene. The structure of the product is shown in formula **35**. Each tin atom is inserted into one of the three clefts of the hydrocarbon with its D_{3h} symmetry.

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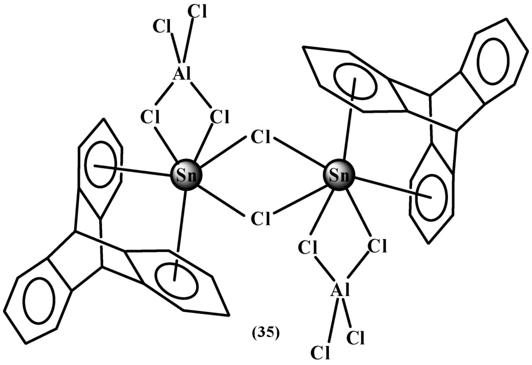
(104) Schmidbaur, H.; Probst, T.; Steigelmann, O.; Müller, G *Heteroat. Chem.* **1990**, *1*, 161.

(105) Schmidbaur, H.; Probst, T.; Huber, B.; Steigelmann, O.; Müller, G. *Organometallics* **1989**, *8*, 1567.

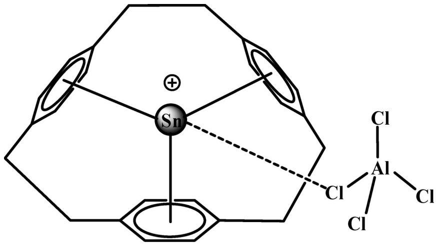
The distances to the two phenylene rings are significantly different at 2.90 and 3.38 Å. It appears that even though the two phenylene rings of the trypticene are drawn together upon complexation, the Sn−phenylene distances are still too large to allow symmetrical bonding. The interplane angle of the coordinated phenylene rings is 108.2° (as compared to 120° in free trypticene), while the other two are widened to 125.8 and 126.0°. One of the two coordination modes is clearly a slightly distorted η^6, while the other is more strongly offset, with angles between the normal from the Sn atom to the ring plane and the line connecting the Sn atom and the ring centroid of 3.42 and 13.20°, respectively.[106]



(35)

Complexation of [2.2]paracyclophane by SnCl(GaCl$_4$), prepared fromSnCl$_2$ and GaCl$_3$ in benzene, affords a product of the formula SnCl(GaCl$_4$)·[(p-C$_6$H$_4$CH$_2$CH$_2$)$_2$], which crystallizes from toluene. The product is a stable material (mp 139−142 °C), but its structure could not be determined. On the basis of analogies with the corresponding Ga(I) and In(I) compounds, a fixation of a Sn atom to each phenylene ring from the outer side of the parayclophane molecule, resulting in a chain structure with alternating [SnCl(GaCl$_4$)]$_2$ and (p-C$_6$H$_4$CH$_2$CH$_2$)$_2$ units, is the most likely line of assembly for this compound. A complexation of the Sn atom within the small cavity of this [2.2]paracyclophane is unlikely. No example of this kind has been recorded with any main-group metal.[107]

[2.2.2]Paracyclophane, in contrast, offers a much larger inner space and therefore is able to accommodate even relatively large metal cations. Its reaction with SnCl$_2$ and AlCl$_3$ in the molar ratio 1:1:2 in benzene affords a crystalline product of the composition [Sn(AlCl$_4$)(p-C$_6$H$_4$CH$_2$CH$_2$)$_3$]$^+$AlCl$_4^-$ in high yield. Crystal structure determination has shown that the Sn atom is η^6-coordinated to all three phenylene rings with short Sn−ring centroid distances of 2.534, 2.623, and 2.666 Å. This compound therefore is the first example of a tris(arene) complex of a tin cation. One of the two AlCl$_4^-$ anions entertains a single, weak Sn−Cl−Al contact, but the coordination geometry at the Sn atom is almost perfectly trigonal planar, as indicated by a sum of 358.1° for the three ring centroid−tin−ring centroid angles. The second AlCl$_4^-$ anion may be described as an isolated counterion (**36**).[108] For the flat tricoordination of Sn(II) the question about the nature of the Sn 5s^2 lone pair of electrons arises. If a 5sp^2 hybridization is assumed for the orbitals associated with binding of the phenylene rings, the "lone pair" must be ascribed an unusual pure 5p$_z$ character.

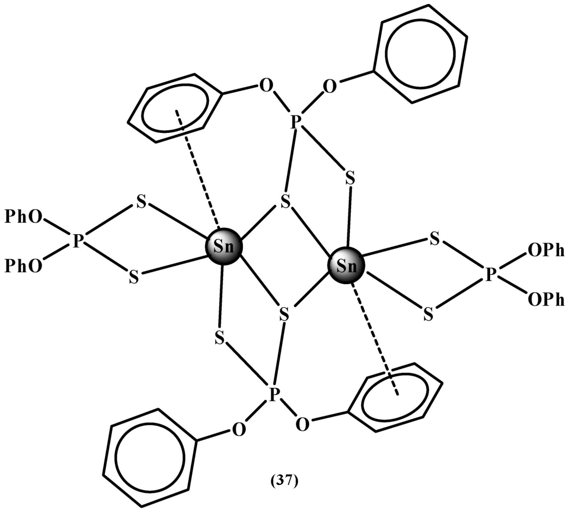


(36)

If the above reaction of the same components is carried out with an excess of AlCl$_3$, a complex of the same cation with the dinuclear anion Al$_2$Cl$_7^-$ can be crystallized.[108]

It should be noted that the overall bonding situation in the cation resembles that of the corresponding Ga(I) complex **7**.[37]

b. Tin(II) Compounds with Internal and External Sn Coordination to Aryl Substituents. There are still very few examples of compounds in which a tin(II) center shows π interactions with an aryl group of a ligand and/or its substituents. A prototype was first observed by Zuckerman and co-workers, who determined the structure of tin(II) bis(O,O'-diphenyldithiophosphate). The compound was shown to form a dimer with a rectangular Sn$_2$S$_2$ core unit (**37**). Each tin atom is chelated by one dithiophosphate anion, while the second anion is in a bridging position. One phenyl group of each bridging dithiophosphate anion is attached to a Sn atom in a quasi-η^6 fashion, but the Sn−ring centroid distance is long at 3.655 Å, suggesting only very weak bonding.[109]



(37)

Tin(II) bis[dibenzoylmethanide] forms dinuclear compounds of the formula {Sn[(PhCO)$_2$CH]$_2$}$_2$, in which the Sn atoms with a "hemi-directed coordination sphere" are exposed at the periphery. In crystallographic work by Harrowfield et al. it was demonstrated that in the solid state these molecules are stacked, adopting a structural motif in which each metal atom becomes capped by a phenyl group of the adjacent molecule with a Sn−ring centroid distance of 3.550 Å. The Sn atom shows a significant deviation from an ideal η^6 coordination, much larger than for the analogous Pb(II) complex, for which a more symmetrical array was observed (**38**).[110,111]

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(106) Schmidbaur, H.; Probst, T.; Steigelmann, O. *Organometallics* **1991**, *10*, 3176.

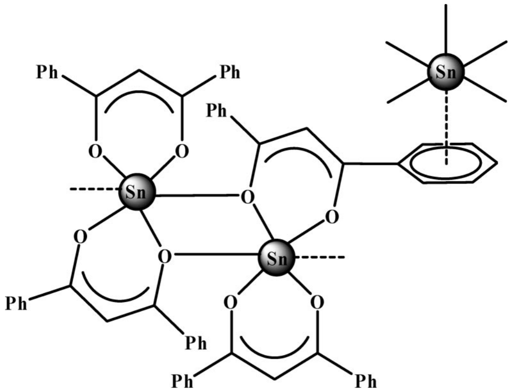
(107) Schmidbaur, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Chem. Ber.* **1989**, *122*, 265.

(108) Probst, T.; Steigelmann, O.; Riede, J.; Schmidbaur, H. *Angew. Chem., Int. Ed.* **1990**, *29*, 1397.

(109) Lefferts, J. L.; Hossain, M. B.; Molloy, K. C.; van der Helm, D.; Zuckerman, J. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 309.

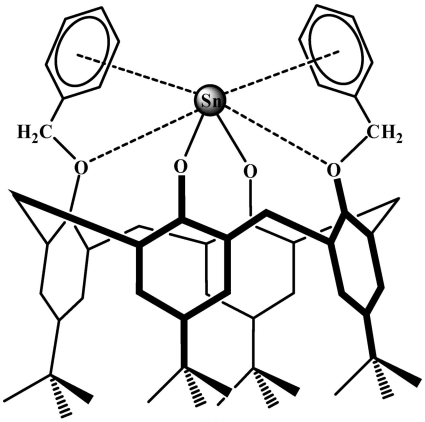
(110) Uchida, T.; Kozawa, K.; Obara, H. *Acta Crystallogr.* **1977**, *B33*, 3227.

(111) Harrowfield, J. M.; Maghaminia, S.; Soudi, A. A. *Inorg. Chem.* **2004**, *43*, 1810.



(38)

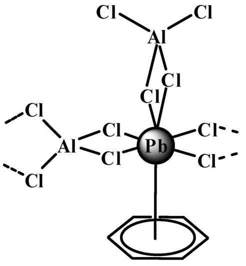
Tin(II)−arene interactions may also play a role in the formation and structure of calixarene tin(II) complexes. Both exo and endo isomers of complexes with the 1,3-diethers of *p-tert*-butylcalix[4]arene, e.g. [*p*-calix$^{t\text{-}Bu}$(O)$_2$(OSi^{i}Pr$_3$)$_2$]Sn, have been prepared by Parkin and co-workers. These are analogues of the related germanium(II) complexes (**27**). However, from the crystal structures of the endo isomer it again appears that such interactions will probably be weak. The Sn atom has distances of ca. 3 Å from the three inner C atoms of each phenylene ring, which may indicate η^3 hapticity for all four rings, but the interpretation of the data regarding Sn−arene complex formation must remain a tentative one.[112,113] Capping of an exo tin(II) atom by *p-tert*-butylphenoxy groups can also be recognized in [calyx-$^{t\text{-}Bu}$(O)$_2$(OCH$_2$C$_6$H$_4{}^t$Bu)$_2$]Sn (**39**).[112,113]



(39)

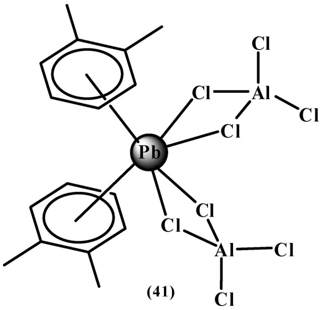
3. Lead. Lead(II) chloride is insoluble in aromatic hydrocarbons. However, in the late 1960s it was observed that upon addition of a strong halide acceptor such as aluminum trichloride, it becomes soluble in benzene. With 2 equiv of AlCl$_3$ for 1 equiv of PbCl$_2$, a complex of the composition Pb(AlCl$_4$)$_2\cdot$2(C$_6$H$_6$) was isolated and its formula established by microanalysis and preliminary X-ray data. The triclinic crystals had a calculated density of 1.96 g cm^{-3}, in agreement with the experimental value of 1.93 g cm^{-3}. The IR spectrum was tentatively interpreted in terms of a sandwich complex with high symmetry.[24]

A few years later the crystal structure of this compound was determined, and the compound was reformulated as the mono(arene) complex [Pb(AlCl$_4$)$_2\cdot$C$_6$H$_6$]$\cdot$C$_6$H$_6$, with one of the two benzene molecules not engaged in π bonding with the metal atom. In the crystals, which were found to be isomorphous with those of the analogous tin(II) compound (**29**),[95] the cation Pb^{2+} and one of the anions AlCl$_4^-$ form chains in which the anions are η^2:η^2 double-chelating units. Each Pb atom is further chelated by a terminal (not propagating) AlCl$_4$ unit and attached to one benzene molecule (η^6) with a Pb−ring centroid distance of 2.77 Å (**40**). The average Pb−C distance (3.11 Å) is only slightly larger than the average Sn−C distance in the Sn analogue (3.06 Å). A qualitative molecular orbital energy level diagram was proposed, identifying the a$_1$ and e$_1$ orbitals of benzene (under C_{6v} symmetry) in combination with the symmetry-equivalent orbitals of the metal atom as the main contributors.[114]



(40)

The first bis(arene) complex of lead(II) with independent arene ligands was reported in 1997 by Frank and Wittmer with the full characterization of Pb(AlCl$_4$)$_2\cdot$*o*-Me$_2$C$_6$H$_4$. The crystals contain discrete molecular complex units with the lead atom bearing two chelating AlCl$_4$ units and two *o*-xylene molecules which are approximately η^6-coordinated with Pb−ring centroid distances of 2.874 Å. The complex may be described as a bent sandwich with C_2 symmetry and an angle between the phenylene planes of 71.7° (**41**). The yellow compound is thermally unstable and loses xylene at 54 °C. Taken together with the longer Pb−ring centroid distances in this bis(xylene) complex as compared to that in the mono(benzene) complex, these observations show that arene bonding is weaker in the former even though the better donor xylene is employed therein.[115]



(41)

From benzene solutions of Pb(GaCl$_4$)$_2$, prepared in situ from PbCl$_2$ and GaCl$_3$ in the molar ratio 1:1, a complex with [2.2]paracyclophane precipitated. According to microanalytical data the composition of the product is Pb(GaCl$_4$)$_2\cdot$[(*p*-C$_6$H$_4$CH$_2$CH$_2$)$_2$], with one molecule of the cyclophane. The structure of the complex could not be determined, but on the basis of the analogy with the related In(I) complex, a chain structure with bis(arene)lead coordination is the most likely structural principle, the paracyclophane acting as a double-η^6 bridge for the lead atoms.[101]

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(112) Hascall, T.; Rheingold, A. L.; Guzei, I.; Parkin, G. *Chem. Commun.* **1998**, 101.

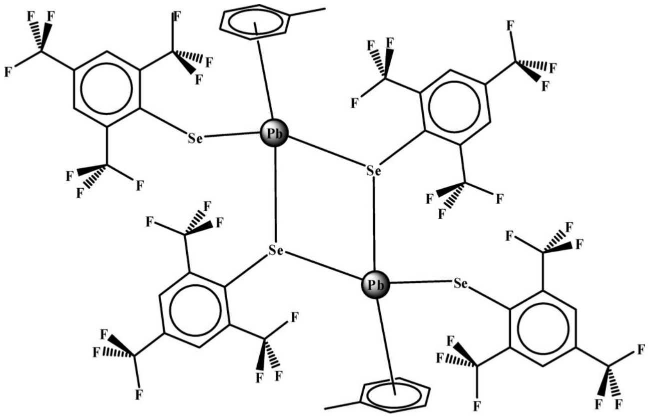
(113) Hascall, T.; Panf, K.; Parkin, G. *Tetrahedron* **2007**, *63*, 10826.

(114) Gash, A. G.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2429.

(115) Frank, W.; Wittmer, F.-G. *Chem. Ber./Recl.* **1997**, *130*, 1731.

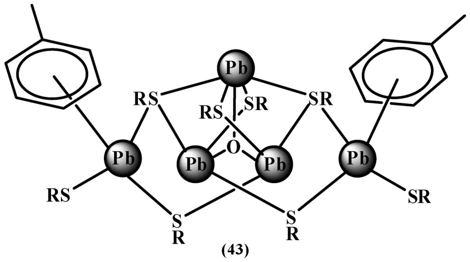
Triptycene reacts with $PbCl_2$ and $AlCl_3$ (molar ratio 1:1:2) in benzene to give colorless crystals of the complex $[Pb(AlCl_4)_2 \cdot C_{20}H_{14}] \cdot 0.5C_6H_6$, which rapidly loses the contained crystal benzene upon exposure to a stream of dry nitrogen or to a vacuum. Its structure could not be determined, but it is most likely that the Pb atom is inserted between two of the three phenylene rings to give a bent-sandwich complex in which the coordination sphere of the lead atom is completed by two chelating $AlCl_4$ units, similar to the structure of the bis(*o*-xylene) and the triptycene complexes of Sn(II) (**35**).[115,106]

Lead(II) bis[2,4,6-tris(trifluoromethyl)selenophenolate], $Pb(SeR)_2$ with R = 2,4,6-$(CF_3)_3C_6H_2$, crystallizes from toluene as a dinuclear complex with two molecules of solvent, each of which is attached to a Pb atom roughly in an η^6 mode (**42**). Regarding the methyl substituents, the toluene molecules are disordered.[116]



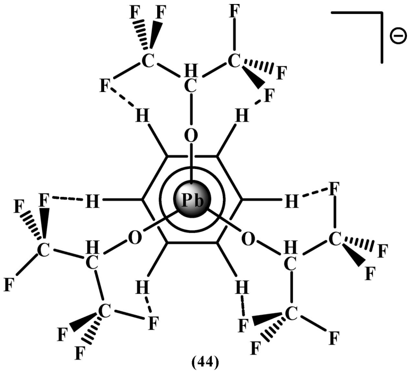
(42)

The pentanuclear cluster of the formula $Pb_5O(SR)_8$ with R = 2,4,6-$(CF_3)_3C_6H_2$ was found by Edelmann et al. to crystallize with two molecules of toluene which are attached in an η^6 fashion to the two peripheral Pb atoms (**43**). The Pb−ring centroid distances are very long (3.548 and 3.705 Å), indicating that the binding is extremely weak. It appears that the oxide−mercaptide substituents of the compound make the Pb atom a very poor acceptor, as compared to the effect of halide substituents.[117]



(43)

Lithium hexafluoroisopropoxide and lead bis(hexafluoroisopropoxide) form a 2:2 tetranuclear mixed-metal complex which crystallizes with one benzene molecule to give a product of the stoichiometry $[Li_2Pb_2(OR)_6] \cdot C_6H_6$, with R = $CH(CF_3)_2$. In studies by Caulton and co-workers, the components were shown to form a chain structure with alternating complex and benzene molecules. Each benzene molecule is η^6-bonded to a lead atom on both sides to form the inverse sandwich-type unit Pb−(C_6H_6)−Pb with approximate D_{6h} symmetry. In formula **44** only the η^6 attachment of the benzene molecule to one of the two anions $[Pb(OCH(CF_3)_2)_3]^-$ is shown in the projection along the Pb−ring centroid−Pb axis. It appears that six F- - -H−C contacts further support the assembly as drawn. The lithium cations are coordinated to the oxygen atoms. This is the first case of a structurally characterized bis(lead) complex of a neutral aromatic hydrocarbon. The Pb−ring centroid distances of 3.31 Å are much larger than those found in the mono- or bis(arene) complexes of lead, indicating that the bonding may be the weakest of all three types. It should be remembered, however, that bis(bismuth) complexation of substituted benzenes of the type Bi−(C_6R_6)−Bi is quite robust and therefore quite common, suggesting that polyalkylated benzenes may also bind lead more strongly. A peculiar structural detail observed in the above Li/Pb alkoxide is the C−H- - -F−C hydrogen bonding pattern of benzene hydrogen atoms with alkoxide fluorine atoms. These interactions may well reduce quite strongly the donor properties of the benzene molecule and thus its donor function toward the lead atoms.[118]



(44)

Lead(II) bis(dibenzoylmethanide), $Pb[(PhCO)_2CH]_2$, crystallizes in dinuclear units with the Pb atoms exposed at the periphery of the dimer.[110] The structure shows close analogy with that of the corresponding tin(II) compound (**38**).[111] In the crystal, these dimers are stacked in such a way that each Pb atom is η^6-capped by a phenyl ring of the adjacent molecule. The Pb−ring centroid distance is 3.408 Å. In the discussion of the nature of bonding involved, the authors have considered both a Pb $6s^2$ lone-pair donation to π orbitals of the phenyl ring (depleted of electron density by the carbonyl−enolate system), and a donation of π electrons from the phenyl ring to vacant orbitals of the metal atom.[110]

In more recent work, Power and co-workers have prepared compounds containing novel monoaryllead cations, RPb^+, associated with weakly coordinating anions X^-. A compound with R = 2,6-(2,4,6-triisopropylphenyl)phenyl and X = $MeB(C_6F_5)_3$ was found to crystallize with one molecule of toluene, which becomes attached to the Pb atom in an η^2 mode (**45**). The distances to the two closest toluene carbon atoms are 2.832 and 2.907 Å, while the other four have distances of up to 3.438 Å. It is conceivable that a greater hapticity, approaching ideal η^6 coordination, is obstructed by steric effects.[119] The authors have carried out DFT calculations for the model species $[PhPb \cdot C_6H_6]^+$ and $[PhPb \cdot PhMe]^+$ in the gas phase. The energy of interaction was found to have a maximum at Pb−ring centroid distances of ca. 3.2 Å, which is significantly longer than the

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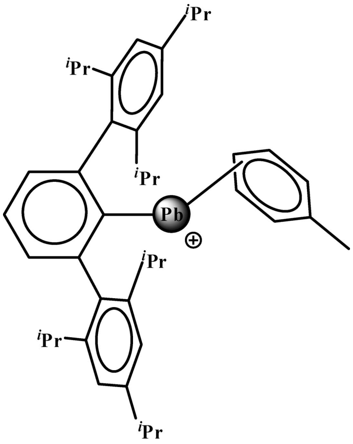
(116) Labahn, D.; Bohnen, F. M.; Hebst-Irmer, R.; Pohl, E.; Stalke, D.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 41.

(117) Edelmann, F. T.; Buijink, J.-K. F.; Brooker, S. A.; Herbst-Irmer, R.; Kilimann, U.; Bohnen, F. M. *Inorg. Chem.* **2000**, *39*, 6134.

(118) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1997**, *36*, 4372.

(119) Hino, S.; Brynda, M.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2655.

experimentally observed distance (2.85 Å). The energy of formation calculated for the equilibrium distance was ca. 8−9 kcal mol^{-1} and for the experimental molecule ca. 5 kcal mol^{-1}. This is the first estimation of the binding energy of arenes to a low-valent group 14 element.[119] It compares well with the results calculated for interactions with low-valent group 15 elements, giving confidence to the assumption that a closely related mechanism is operative for both groups of compounds.



(45)

The complexation of lead atoms and cations by the fullerene C_{60}, corannulene, and related molecules with cyclopentadiene and benzene faces has been probed by quantum chemical calculations. The results suggest that π bonding to the five-membered rings is strongly preferred over that to six-membered rings.[120,121]

4. Remarks. The chemistry of arene complexes of the low-valent group 14 elements Ge, Sn, and Pb shows significant differences from results for the related group 13 elements (above). The following points have become obvious:

1. The chemistry is less developed, in particular for the germanium(II) compounds, but there is clear evidence for a considerable potential. Again several stable mono-, bis-, and tris(arene) complexes have been prepared and structurally characterized. The physical properties of the compounds have not been investigated in detail. There is no information on phase diagrams and other thermochemical data, but from the general properties of the compounds it appears that the lead(II) complexes are the most stable.

2. Polyalkylbenzene molecules $C_6H_nR_{6-n}$ are more tightly bound than benzene, and M^{2+} centers associated with anions of poor donor character are the strongest acceptors. The arenes are less firmly bound as their number increases from 1 to 3. In one case, bis(lead) coordination to a benzene ring (from above and below) has been observed. This inverse sandwich bonding is common for 1:2 complexes of arenes with bismuth(III) compounds.

3. Qualitative molecular orbital diagrams have been proposed for the arene binding in simple units such as $M(C_6H_6)^{2+}$ with M = Sn, Pb, but a more detailed quantum chemical analysis has been carried out only for an $RPb(C_6H_6)^+$ model complex. The arene binding energies estimated for this species are in the same order of magnitude as for related Tl^+ complexes. Relativistic Pb 6s orbital contraction may be the main factor contributing to the enhanced stability.

4. Regarding the molecular structures, some of the tin(II) complexes have a marked tendency for deviations from the η^6 hapticity of arene binding. This phenomenon is rare with group 13 elements, but the underlying ring slippage is very obvious with group 15 elements and, in particular, with antimony (see below). The reasons for this reduction of hapticity have not yet been elucidated.

IV. Arene Complexes of the Low-Valent Group 15 Element Halides and Related Compounds

1. History. In 1879, Watson Smith reported to the Royal Society in London that he investigated the action of antimony trichloride on benzene and naphthalene in a red-hot tube and observed that after the experiment with naphthalene—while carbon was adhering to the interior of the apparatus—"beautiful long white needles with a diamond luster fell from the tube". He subsequently found that red heat was not required to obtain these crystals from the two components. Melting together a simple mixture of naphthalene and antimony trichloride and leaving the mixture to cool gave "clino-rhombic crystals of this body", and similar results were obtained with benzene.[7a] Five years later, Smith and Davis described the crystallization of the product, observing that "the perfectly symmetrical clino-rhombic tables in their rapid growth performed singular gyrations on the liquid surface on which they floated". Attempted elemental analysis gave a 3:2 molar ratio for the crystals obtained with both naphthalene and benzene.[7b] Rosenheim and Stellmann carried out experiments with aromatic hydrocarbons and antimony tri- and pentachloride in 1901 and also obtained a crystalline adduct of $SbCl_3$ and benzene, to which they assigned the stoichiometry 3:1,[122] correcting the value of Smith and Davis. Later work has shown that both molar ratios were in fact incorrect.

Chemistry textbooks of the late 19th and early 20th century contained the information that molten antimony trichloride ("antimony butter") was used as a cleaning agent for musket and gun barrels. This practice was based not only on the hardening effect of antimony as a component of various alloys but also on the efficiency of antimony trichloride as a rust remover and its unique property to readily dissolve oil and grease. This solubility of heavy oil (naphtha) in molten $SbCl_3$ and the solubility of anhydrous $SbCl_3$ in hydrocarbons were probably the first observations indicating a mutual affinity of these components.

The free miscibility of solid and molten antimony trichloride with xylene, cumene, mesitylene, diphenyl, stilbene, anthracene, and fluorene was first pointed out and investigated in some detail in work by Toloczko in 1899. The author carried out the first molecular weight determinations through melting point depressions and boiling point elevation but found no anomalies.[123] The affinity underlying this almost unlimited miscibility of an inorganic and an organic compound was unexpected, considering not only the general rule of solubility established by Paracelsus ("similia similibus solvuntur") but also the high polarity of SbX_3 dipolar molecules on one hand and the low polarity of nonpolar hydrocarbons on the other. No explanation was offered for this paradox.

Systematic work in this area was resumed about a decade later in the laboratory of Boris N. Menshutkin (Figure 2) at the Polytechnic Institute at St. Petersburg, who produced the first

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(120) Stankevich, I. V.; Chistyakov, A. L. *Mol. Mater.* **2000**, *13*, 315.

(121) Chistyakov, A. L.; Stankevich, I. V. *Russ. Chem. Bull.* **1999**, *48*, 1628.

(122) Rosenheim, A.; Stellmann, W. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 3383.

(123) Tolloczko, S. *Z. Phys. Chem.* **1899**, *30*, 706.

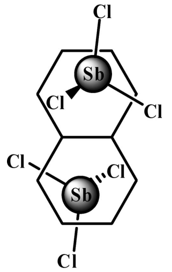
Figure 2. Boris Nikolayevic Menshutkin (1874−1938), son of the famous Russian professor of chemistry at the University of St. Petersburg, *Nikolaj Alexandrovic Menshutkin* (1842−1907), a contemporary of Mendeleev. Studied chemistry at St. Petersburg, Moscow and Dorpat; subsequently professor of chemistry at the Polytechnic Institute in St. Petersburg; characterized in great detail, inter alia, the "Menshutkin complexes" between antimony halides and aromatic hydrocarbons (1905−1915). *B. N. Menshutkin* was also a great science historian (Davis, Z. L. *J. Chem. Educ.* **1938**, *15*(5), 203). Used with permission from the *Journal of Chemical Education*; copyright 1938, Division of Chemical Education, Inc.

reliable phase diagrams for a large selection of mixtures of antimony trihalides with various aromatic hydrocarbons. In a series of publications in the years 1910−1914,[124–126] he was able to prove, for example, that the stoichiometries given for the benzene and naphthalene complexes of $SbCl_3$ by Smith and Davis[7b] and by Rosenheim and Stellmann[122] were incorrect, and that the molecular ratios 1:1 and 2:1 prevailed in most of the systems he investigated.[7c] He noted in particular that the melting point of 85 °C of the crystalline phase with naphthalene of the composition $(SbCl_3)_2 \cdot C_{10}H_8$ was significantly higher than that of both pure $SbCl_3$ and pure naphthalene (73 and 80 °C, respectively), indicating the unexpected formation of an addition compound of the two components.

The comprehensive compilation of early literature in the Gmelin Handbook of Inorganic Chemistry[127] shows the impressive list of compounds carefully investigated by Boris Menshutkin. For benzene, toluene, the three xylene isomers, mesitylene, durene and isodurene, biphenyl, naphthalene, and many other binary aromatic hydrocarbons the 1:1 and/or 2:1 compositions of their adducts with $SbCl_3$ and $SbBr_3$ have been firmly established and exact melting points were given, most of which were fully confirmed almost a century later. For example, Shinomiya, in 1940, reproduced Menshutkin's data and pointed out that in his view the strange "melting point elevations", which for $SbBr_3$ are even greater than for $SbCl_3$, in his eyes suggest stronger bonding between naphthalene and the latter.[128]

It should be mentioned that the knowledge of the unusual solubility of hydrocarbons in melts of $SbCl_3$ (and vice versa) several decades later led to attempted applications in the technology of separation and analysis of aromatic hydrocarbons, as shown by reports on the separation of the isomeric xylenes[129] or methylnaphthalenes[130] via their $SbCl_3$ adducts. However, these methods were practiced only for a limited time.[131]

It was not until 1968 that the crystal structure of the compound $(SbCl_3)_2 \cdot$(naphthalene) was finally determined, which was a truly international effort: the data were collected in the laboratory of H. C. Freeman at the University of Sydney and the structure was solved by R. Hulme and J. T. Szymanski at King's College, London, and at the University of Toronto, respectively.[132] (A preliminary report had appeared in 1966.)[133] The components were shown to form a layer structure in which one $SbCl_3$ molecule is coordinated to each of the six-membered rings of the hydrocarbon, but from different sides, to give a centrosymmetrical arrangement. The Sb atoms are located at a distance of 3.2 Å from the plane of the rings and are markedly shifted from the normal to the ring centroids (**46**). The molecular geometry of the $SbCl_3$ units in the compound does not differ greatly from that in crystalline $SbCl_3$. Bond lengths and bond angles are largely retained upon complexation, except for a slight but significant elongation of the Sb−Cl bond pointing away from the ring plane, indicating a certain "trans influence". Extensive later work has demonstrated that these structural features are representative of most of the details encountered quite generally in arene complexes of antimony trihalides.



(46)

In the same paper,[132] a theoretical model of the chemical bonding was proposed which implies in modern terminology an η^3 bonding of the Sb atoms to the atoms C1−C3/C5−C7 of the hydrocarbon, with molecular orbitals of the latter donating electrons into vacant hybrid orbitals of the Sb atoms. A similar type of bonding had already been proposed on the basis of Raman studies of the same compound and its constituents by Raskin in 1958.[134] Theoretical approaches of this type soon replaced the simple charge transfer model generally proposed for donor−acceptor complexes by Mulliken, Briegleb, Perkampus, and others.[135–138]

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(124) Menshutkin, B. N. *J. Russ. Phys. Chem. Soc.* **1911**, *43*, 1294.

(125) Menshutkin, B. N. *J. Russ. Phys. Chem. Soc.* **1911**, *43*, 1805.

(126) Menshutkin, B. N. *J. Russ. Phys. Chem. Soc.* **1912**, *44*, 1079.

(127) *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Gmelin-Verlag: Clausthal-Zellerfeld, Germany, 1949; Sb, Part B, p 436ff.

(128) Shinomiya, C. *Bull. Chem. Soc. Jpn.* **1940**, *15*, 259.

(129) Scott, C. *U.S. Patent 2,888,496*, 1959; *Chem. Abstr.* 1959, 17499.

(130) Kawalec, B. *Acad. Polon. Sci., Ser. Sci. Chim.* **1966**, *14*, 471.

(131) Clar, E. *Aromatische Kohlenwasserstoffe*, 2nd ed.; Springer: Berlin, 1952; p 128ff.

(132) Hulme, R.; Szymanski, J. T. *Acta Crystallogr.* **1969**, *B25*, 753.

(133) Hulme, R. *Acta Crystallogr.* **1966**, *A21*, 143.

(134) Raskin, Sh. Sh. *Dokl. Akad. Nauk SSSR* **1958**, *123*, 645.

(135) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801.

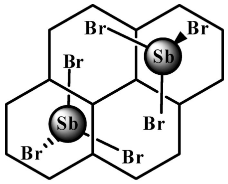
(136) Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*; Springer: Berlin, 1961.

(137) Dewar, M. J. S. *J. Chem. Soc.* **1946**, 406.

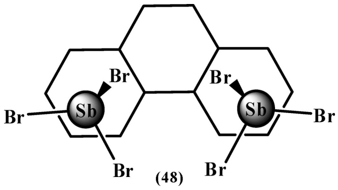
(138) Perkampus, H. H. *Wechselwirkung von π-Elektronensystemen mit Metallhalogeniden*; Springer: Berlin, 1973.

Spectrophotometric studies were initiated by Peyronel et al. at the University of Modena in 1970, selecting systems with pyrene and related hydrocarbons as the donor molecules for $SbCl_3$ and $SbBr_3$ in various solvents.[139] A range of stability constants was determined which, inter alia, suggested that $SbBr_3$ is a better acceptor than $SbCl_3$ for pyrene, at variance with previous findings by the Japanese workers for the solvent-free systems, indicating the significance of solvent effects.[128]

Soon thereafter (1972), crystal structure data on $(SbBr_3)_2\cdot$(pyrene) (**47**)[140] were provided by Bombieri et al., showing that the mode of assembly was very similar to that of $(SbCl_3)_2\cdot$(naphthalene).[132] The Sb atoms are symmetrically located above and below the hydrocarbon plane at a distance of 3.301 Å and are offset from the normal to the centroids of the two rings toward the longer end of the molecule. In contrast, the structure of the 2:1 complex of $SbCl_3$ with phenanthrene, $(SbCl_3)_2\cdot$(phenanthrene), has both $SbCl_3$ molecules on the same side of the hydrocarbon plane with two different Sb−plane distances of 2.94 and 3.27 Å (**48**).[141] In the same decade, the structures of the first 1:1 and 2:1 complexes of $SbCl_3$ with a monocyclic arene were reported by Hulme and Mullen: in $(SbCl_3)\cdot$(*p*-xylene) and $(SbCl_3)_2\cdot$(*p*-xylene), the Sb atom(s) are located strongly off-centered above (and below) the xylene ring at a distance of ca. 3.1 Å in what may be called an η^1 bonding to the carbon atom(s) bearing the methyl group(s).[142] In the 1980s a large number of other compounds of this type were crystallized and their structures determined as summarized below.



(47)



(48)

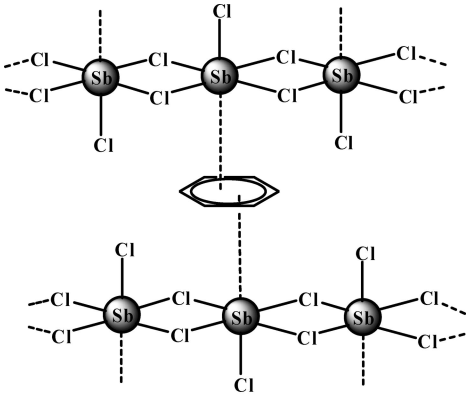
Studies of the colligative properties and structures of triarylstibines Ar_3Sb have not provided any evidence for a significant contribution of any sub van der Waals intermolecular Sb−aryl interactions.[143] It was recognized, however, that Sb−arene interactions may be a factor which codetermines the structures of arylantimony halides Ar_nSbX_{3-n} and related compounds.

A paper by Becker and co-workers, published in 1992, has summarized important benchmark data for the series $PhSbX_2$ (X = Cl, Br, I) and has discussed these data in the context of other Sb−arene complexes.[144] Even to date the information on the structures of diphenylantimony halides Ph_2SbX is still more limited, with data only available for the fluoride and chloride (X = F, Cl).[144,145] The former has a chain structure with the molecules connected only via Sb−F−Sb bridges. The distances and relative orientation of the phenyl groups to the Sb atoms rule out any significant π donor−acceptor interaction.

The reader may have noticed that in this summary of the history the *antimony* compounds played a central role. As shown in two chapters below, for several decades in fact much less had been known for analogous *arsenic* and *bismuth* compounds, and virtually no experimental evidence has been found to date for the analogous phosphorus compounds. For reasons of coherence, these chapters are preceded by a survey of the more recent contributions to the antimony chemistry, thus complementing first the historical introduction for this element.

2. Survey of Compositions and Structures of Arene and Heteroarene Complexes of Antimony Trihalides and Related Compounds.

a. Complexes of Arenes. In the phase diagram of the binary system $SbCl_3$/*benzene*, there is only one congruently melting compound which has the composition 2:1,[146] the structure of which was determined by Mootz and Händler in 1986.[147] At room temperature the triclinic crystals form a layer structure with the benzene molecules sandwiched by layers of $SbCl_3$ molecules aggregated via Sb−Cl−Sb bridges. Each benzene molecule has contacts with an Sb atom above and below the ring with distances of 3.23 and 3.30 Å in slightly offset positions (**49**).



(49)

This structure confirms the results of earlier IR spectroscopic studies by Perkampus and Baumgarten of this phase which predicted a lower local symmetry for the Sb−benzene interaction in the solid.[148] For solutions, extensive dissociation was observed.[149–153] This work was also extended to substituted benzenes.[154] From Raman data it has been concluded that there is significant rotational mobility of the benzene ring in the lattice,[155] and in fact the carbon atom ellipsoids of the structure

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(139) Peyronel, G.; Vezzosi, I. M.; Buffagni, S. *Inorg. Chim. Acta* **1970**, *4*, 605.

(140) Bombieri, G.; Peyronel, G.; Vezzosi, I. M. *Inorg. Chim. Acta* **1972**, *6*, 349.

(141) Demalde, A.; Mangia, A.; Nardelli, N.; Pelizzi, G.; Vidoni Tani, M. E. *Acta Crystallogr.* **1972**, *B28*, 147.

(142) Hulme, R.; Mullen, D. J. E. *J. Chem. Soc., Dalton Trans.* **1976**, 802.

(143) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1981; Sb, Organoantimony Compounds.

(144) Mundt, O.; Becker, G.; Stadelmann, H.; Thurn, H. *Z. Anorg. Allg. Chem.* **1992**, *617*, 59.

(145) Bone, S. P.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1430.

(146) Perkampus, H. H.; Sondern, C. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 1231.

(147) Mootz, D.; Händler, V. *Z. Anorg. Allg. Chem.* **1986**, *533*, 23.

(148) Perkampus, H. H.; Baumgarten, E. *Z. Phys. Chem.* **1963**, *39*, 1.

(149) Ashkanazi, M. S.; Kurnosova, P. U.; Finkelstein, V. S. *J. Phys. Chem. USSR* **1936**, *8*, 438.

(150) Daasch, L. W. *J. Chem. Phys.* **1958**, *28*, 1005.

(151) Daasch, W. *Spectrochim. Acta* **1959**, *15*, 726.

(152) Gerbier, J. *C. R. Seances Acad. Sci.* **1966**, *262*, 1611.

(153) Gerbier, J. *C. R. Seances Acad. Sci.* **1967**, *264*, 444.

(154) Kecki, Z.; Skup, A *Rozniki Chemii* **1964**, *38*, 1235.

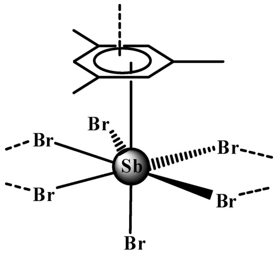
(155) Gross, E. F.; Ginzburg, I. M. *Opt. Spektrosk.* **1956**, *1*, 710; *Chem. Abstr.* **1957**, *51*, 11068h.

solution are indicative of such a movement.[147] NQR data of Sb and Cl nuclei accumulated by Biedenkapp and Weiss and by Grechishkin and Kyuntsel had also shown that in the crystals the two $SbCl_3$ molecules are inequivalent, and that the chlorine atoms of each of these molecules occupy terminal and bridging positions, as borne out by the structure.[156–158] It should be remembered that all elements present in the two antimony halides $SbCl_3$ and $SbBr_3$ have isotopes with quadrupolar nuclei, which prompted NQR specialists, particularly in the former Soviet Union, in the 1960s to 1980s to initiate work on the "Menshutkin" complexes in order to contribute to a solution of the problems associated with the structure and bonding of these compounds. Once single-crystal X-ray diffraction had become an established routine method, the interest in NQR studies greatly diminished.

The structure of the analogous 2:1 complex of $SbBr_3$ and *benzene* has not yet been determined. From NQR spectroscopic studies it appears that crystals of this compound contain equivalent $SbBr_3$ molecules and therefore have a more symmetrical motif of structure.[158–162] It was also possible to distinguish the ^{35}Cl and ^{81}Br resonances for halogen atoms in different modes of bonding in the complexes of $SbCl_3$ and $SbBr_3$ with arenes other than benzene (*p*-xylene, ethylbenzene, diphenylmethane, biphenyl, naphthalene, pyrene, and anthracene).[158] Raman data have shown that the structure of the $SbBr_3$ unit is distorted in its benzene complex.[163] The isolation and structure determination of the 2:1 complexes of $SbCl_3$ with *p-xylene*[142] have already been mentioned above as an important advance in the history of the field regarding the extreme off-center positioning of the Sb atoms.

The exclusive appearance of an adduct with 2:1 stoichiometry in the $SbCl_3 \cdot$(benzene) system has later been confirmed by vapor pressure measurements. In the same study, for *toluene* both a 2:1 and a 1:1 adduct was observed.[164]

Mesitylene (1,3,5-trimethylbenzene) has been shown to form 1:1 complexes with $SbCl_3$ and $SbBr_3$. For the preparation, the two halides were dissolved in excess mesitylene.[165] The structure of the latter has been determined and was found to be isomorphous with that of the $BiCl_3$ complex. The $SbBr_3$ molecules are associated via Sb−Br−Sb briding into a layer-type network. The mesitylene molecules are attached to these layers via Sb−arene contacts. Four inequivalent Sb atoms have distances to the arene planes in the range 3.18−3.32 Å, significantly longer than the distances in the $BiCl_3$ analogue (2.96−3.10 Å). While the Bi atoms are almost perfectly centered, the Sb atoms are markedly off-center, as indicated by angles of 5−9° between the normals to the planes and the lines connecting the Sb atom with the corresponding ring center (only 2−7° for the Bi compound). Formula **50** shows one representative structural unit, which should be seen in context with formulas **51** and **52** (with different substitution patterns).[165] It appears that experiments aiming at the isolation of 2:1 complexes of antimony halides and mesitylene have not been carried out.



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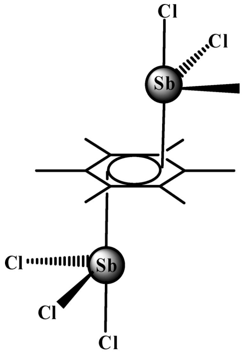
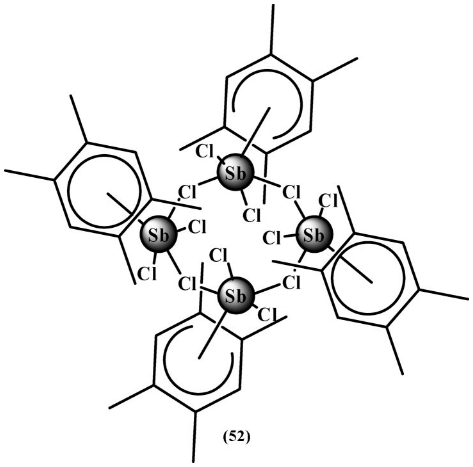


(51)



(52)

Hexamethylbenzene was found to form 2:1 complexes with $SbCl_3$ and $SbBr_3$.[166] The crystals are isomorphous and have the same space group as the analogous compounds of $BiCl_3$ and $BiBr_3$. However, while the Bi compounds are perfectly ordered and have the Bi atoms centered in inverse sandwich arrangements, the molecules of the Sb compounds are disordered owing to a centrosymmetrical, but off-centered positioning of the Sb atoms. The units shown as formula **51** are part of a larger assembly which is presented below in a diagram for the related durene complex (**52**). The Sb atoms in unit **51** have distances of 3.13 and 3.21 Å from the arene planes for X = Cl, Br, respectively. It should again be noted that these distances are significantly longer than those for the $BiCl_3$ complex (3.06 Å), suggesting stronger bonding in the latter, in particular when considering the difference in the covalent radii of Sb and Bi.

It is noteworthy that in an early study by Shaw et al. hexamethylbenzene was found to form a 1:1 addition compound

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(156) Biedenkapp, D.; Weiss, A. *Z. Naturforsch.* **1964**, *19a*, 1518.

(157) Grechishkin, V. S.; Kyuntsel, I. A. *Opt. Spektrosk.* **1964**, *16*, 161.

(158) Wulfsberg, G.; Weiss, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 474.

(159) Okuda, T.; Nakao, A.; Shiroyama, M.; Negita, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 61.

(160) Grechishkin, V. S.; Kyuntsel, I. A. *Opt. Spektrosk.* **1963**, *15*, 832.

(161) Grechishkin, V. S.; Kyuntsel, I. A. *Opt. Spectrosk.* **1963**, *15*, 453.

(162) Okuda, T.; Terao, H.; Ege, O.; Negita, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2398.

(163) Kozulin, A. *Opt. Spectrosk.* **1965**, *17*, 189.

(164) Perkampus, H. H. *Wechselwirkung von π-Elektronensystemen mit Metallhalogeniden*; Springer: Berlin, 1973; p 78 ff (citing work (with illustrations) by H. C. Brown and J. J. Melchiore).

(165) Schmidbaur, H.; Wallis, J. M.; Nowak, R.; Huber, B.; Müller, G. *Chem. Ber.* **1987**, *120*, 1837.

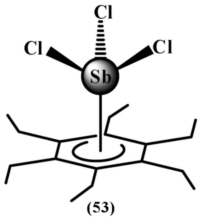
(166) Schmidbaur, H.; Nowak, R.; Schier, A.; Wallis, J. M.; Huber, B.; Müller, G. *Chem. Ber.* **1987**, *120*, 1829.

with *triphenylantimony*, which melts congruently at 137 °C. No further data are available.[167]

Compounds with *pentamethylbenzene*, $(SbX_3)_2 \cdot C_6HMe_5$ with X = Cl, Br, have also been prepared. The crystals were again found to be isomorphous with those of the hexamethylbenzene complexes, indicating rotational disorder of the arenes.[166]

1,2,4,5-Tetramethylbenzene (durene) adds 2 equiv of $SbCl_3$ with formation of a well-ordered structure very similar to that of the corresponding compound with hexamethylbenzene. The Sb−ring distances are virtually the same, and the differences in the off-center shifts of the rings are insignificant (**52**).[168]

Hexaethylbenzene forms only 1:1 complexes with both $SbCl_3$ and $SbBr_3$, regardless of the stoichiometry of the reagents applied (in toluene as a solvent). The yields after crystallization are almost quantitative with respect to C_6Et_6. The crystal structure of $SbCl_3 \cdot C_6Et_6$ has been determined (**53**).[169] The molecules are not associated, and the molecular unit has mirror symmetry. The Sb atom is located 2.96 Å above the benzene ring and is almost perfectly centered. This Sb−arene distance is the shortest ever observed for an SbX_3 adduct of an aromatic hydrocarbon. It must be pointed out that no adducts of C_6Et_6 with PCl_3, PBr_3, $AsCl_3$, $BiCl_3$, and $BiBr_3$ could be isolated. It further remains an open question as to why all attempts have failed to obtain 2:1 complexes of C_6Et_6 with $SbCl_3$ and $SbBr_3$. The molecular geometry of the hydrocarbon at the open side of the 1:1 complex has not changed significantly upon formation of the 1:1 complex, which rules out any steric hindrance for an incoming second $SbCl_3$ component. This leaves repulsive effects of opposing dipole moments as the most probable electronic effect.

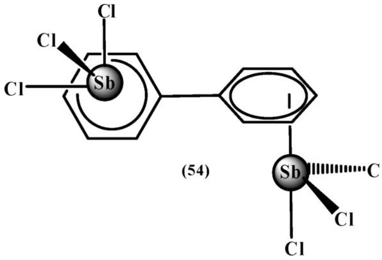


(53)

The 2:1 complexes of $SbCl_3$ with *naphthalene*[132] and *phenanthrene*[141] and of $SbBr_3$ with pyrene[140] have already been introduced as subjects of some of the early structure determinations. These studies were complemented by work on the 2:1 complexes of $SbBr_3$ with phenanthrene[170] and of $SbCl_3$ with pyrene.[170] The phase diagrams of the two quasi-binary systems clearly show that only the 2:1 composition gives congruently melting intermediate solid phases. The melting point of $(SbBr_3)_2 \cdot$(phenanthrene) (114 °C) is distinctly higher than the melting points of pure phenanthrene (100 °C) and pure $SbBr_3$ (98 °C), indicating strong interactions of the components. The ^{81}Br NQR spectra of $(SbBr_3)_2 \cdot$(phenanthrene) have been measured, and the existence of several inequivalent sites of the Br atoms in the crystal has been observed.[171]

Biphenyl was shown already by Menshutkin to form the crystalline 2:1 complex $(SbCl_3)_2 \cdot Ph_2$ with mp 71 °C.[125] This adduct and the $SbBr_3$ analogue were later investigated by NQR and Raman spectroscopy, and it was concluded that in the former the $SbCl_3$ molecules have a nonequivalent environment while in the latter they are symmetry-related.[172–174]

This result was confirmed in the crystallographic work by Mootz and Lipka.[175,176] In crystals of $(SbCl_3)_2 \cdot Ph_2$ the two phenyl rings show a torsion angle of 40.5° and each ring bears an $SbCl_3$ molecule attached from the same side of the hydrocarbon with Sb−ring plane distances of 3.08 and 3.26 Å and very different shifts from the normal to the ring centroids (**54**). These differences may be induced by the geometrical requirements of the association of the $SbCl_3$ units via Sb−Cl−Sb bridges into a two-dimensional network. As in other cases, the $SbCl_3$ units have Sb−Cl−Sb contacts with neighboring molecules.[175]



(54)

In contrast, in $(SbBr_3)_2 \cdot Ph_2$ the $SbBr_3$ units are attached to the biphenyl molecule from different sides of the two almost coplanar phenyl groups, with Sb−ring plane distances of 3.23 Å and a very large offset of the Sb atoms from the normals to the ring centroids, indicating η^2/η^3 coordination. The molecular units have a center of inversion and are further associated into chains.[176]

The 2:1 adduct of $SbBr_3$ and *dihydroanthracene* has one of the most regular structures of the whole series: the molecule has inversion symmetry, and the Sb atoms are placed from above and below to the centers of the two phenylene rings at a distance of 3.26 Å (**55**).[177] The almost perfect η^6 bonding is rather the exception than the rule in this class of compounds, as becomes evident from the list of examples in this chapter. The $SbBr_3$ molecules of neighboring complexes form three weak intermolecular Sb−Br−Sb bridges of different lengths to give double strings $(Sb_2Br_6)_n$ and finally corrugated layers built around herringbone stacks of hydrocarbon molecules. The tricyclic hydrocarbon is completely planar by symmetry. This is a particularly interesting result, since the free hydrocarbon in the gas phase has been calculated to be planar, whereas all crystal structure determinations showed the molecule to be folded by 144.5° (average).[178] It thus appears that the interaction with two $SbBr_3$ molecules and insertion in a crystal lattice have finally allowed the molecule to adopt its most symmetrical structure. 2:1 adducts of $SbCl_3$ and $BiCl_3$ with dihydroanthracene could not be crystallized.[177]

[2.2.2]Paracyclophane adds only two molecules of $SbCl_3$, even if an excess of the antimony trichloride is offered in benzene solution. In the resulting complex one of the three

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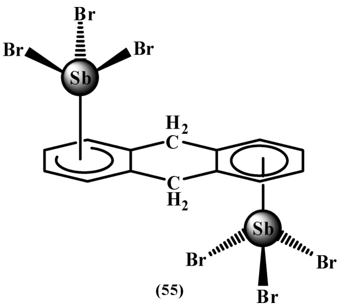
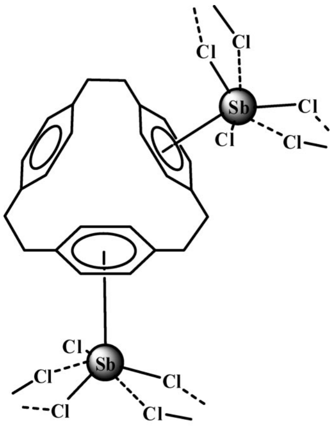
[178] References in ref 177.



(55)

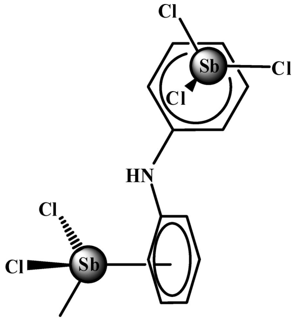
p-phenylene rings thus remains unoccupied (**56**).[179] The two Sb atoms are located 3.047 and 3.050 Å above the rings, with angles of 7.4 and 9.0° between the normals to the ring planes and the lines connecting the Sb atoms with the ring centers. The deviation from true η^6 coordination is thus not large for both independent $SbCl_3$ units. The formula unit of the compound crystallizes from benzene solution with half of a solvent molecule, which is not coordinated, however.



(56)

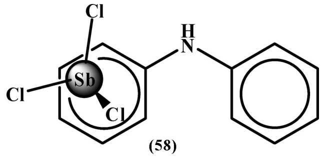
b. π-Complexes of Antimony Trihalides with Arenes and Heteroarenes Containing N- or S-Donor Functions. Ammonia and primary, secondary, and tertiary *alkyl*amines are known to form complexes with SbX_3 molecules in which the nitrogen atoms function as σ-donor centers for the antimony atom.[180] The same is true, for example, for the complex structure of the 2:3 combination of $SbCl_3$ and *4-phenylpyridine*[181] and the yellow 1:1 adduct of $SbCl_3$ with *2,2′-bipyridyl*, first prepared by Roper and Wilkins,[182] which was shown by Lipka and Wunderlich to have the Sb atom chelated by the two N atoms.[183] *Aniline* also was found to form this classical type of N→Sb donor−acceptor interaction in 1:1 and 1:2 adducts, the structures of which have been determined.[184,185]

Very surprisingly, the mode of coordination is entirely different for *diphenylamine* adducts. As demonstrated by Lipka, the phase diagram of the system $SbCl_3/Ph_2NH$ indicates the existence of two congruently melting compounds with melting points of 86−88 and 81−85 °C for the 2:1 and 1:1 stoichiometries, respectively.[186] When the 2:1 complex was first synthesized, a molecular structure with a conventional N→Sb interaction was proposed on the basis of spectroscopic data.[187] The determination of the crystal structure by Lipka has shown, however, that the N atom of Ph_2NH is left uncoordinated and that both $SbCl_3$ units are instead attached to the phenyl rings. The Sb−arene plane distances are 3.08 and 3.09 Å, and with reference to the position relative to the center of the ring the interactions may be described as η^1/η^3 and η^2, respectively (**57**). The $SbCl_3$ units are linked into chains via Sb−Cl- - -Sb bridges.[188]



(57)

In crystals of the 1:1 adduct $(SbCl_3)\cdot Ph_2NH$, there are infinite, meandering chains of $SbCl_3$ molecules of which each Sb atom is coordinated to one of the phenyl rings of a Ph_2NH molecule (Sb−arene plane distance 3.13 Å, clearly off-centroid; **58**). Through stacking of their second phenyl group, the Ph_2NH molecules are also assembled in chains running parallel to the $(SbCl_3)_n$ chains.[189]



(58)

Both structures show that Sb−arene π complexation can compete successfully with standard σ-donor−σ-acceptor interactions. The N-donor capacity in Ph_2NH is known to be strongly reduced compared to that in NH_3 and $PhNH_2$, such that the Sb−N binding energy appears to be shifted toward the range of energies associated with weak interactions characteristic of “Menshutkin complexes”. N-coordination being also hindered by some steric congestion, the π complexation at an aryl group can supersede N-complexation. It is therefore consistent that in a brief note it was mentioned that NPh_3 also forms an arene π complex with $SbCl_3$, but no details are available.[190]

Saturated open-chain and cyclic organic sulfides such as dithiane, $S(CH_2CH_2)_2S$, form addition compounds with $SbCl_3$ with conventional discrete S→Sb σ-donor/σ-acceptor interactions.[190−193] In contrast, the 2:1 adduct of 2,2′-dithienyl, $(SbCl_3)_2\cdot Thi_2$, crystallized from CCl_4 solutions, was found to be a centrosymmetrical bis π complex. The parent ligand is in a planar trans conformation with one $SbCl_3$ unit attached to each thiophene ring from opposite sides and Sb−ring plane distances of 3.16 Å. The Sb atoms are offset from the ring centroids

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(179) Probst, T.; Steigelmann, O.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1991**, *124*, 1089.
(180) Reference 127, pp 436 ($SbCl_3$) and 480 ($SbBr_3$).
(181) Lipka, A. *Z. Naturforsch.* **1983**, *38b*, 341.
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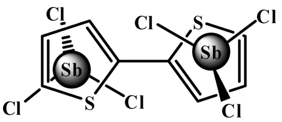
toward an η^2 coordination (**59**).[194] The structure closely resembles that of $(SbBr_3)\cdot(Ph_2)$, and the crystals are in fact isotypic.[176]

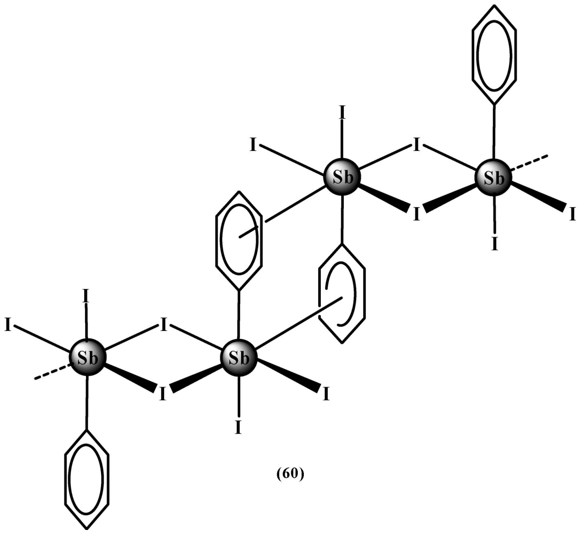


(59)

A bis π complex of $SbCl_3$ with benzo[*b*]thiophene, $(SbCl_3)_2\cdot C_6H_4C_2H_2S$, was crystallized from CS_2 solution and identified as the only congruently melting compound. This complex was shown to have a structure resembling that of $(SbCl_3)_2\cdot$(naphthalene), with which it is in fact also isotypic. Owing to a 2-fold orientational disorder of the parent ligand, the complex has a pseudo symmetry of inversion, which places the two $SbCl_3$ units on different sides of the ligand plane, with the Sb atoms at an average distance of 3.25 Å. This and the remainder of the structural details are of low accuracy owing to the extensive disorder, but there can be no question regarding the mode of the assembly of the components: a π complexation of $SbCl_3$ by both the benzene and the thiophene ring, the former resembling that found in numerous other benzene or phenyl complexes and the latter closely analogous to that found for 2,2′-dithienyl.[194] There is no structural information yet on adducts of related nitrogen and oxygen heterocycles, such as pyrrole and furan, respectively.

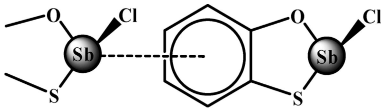
c. Aggregation of Arylantimony Compounds via Sb−Arene π Interactions. Association of triarylstibines Ar_3Sb via Sb−arene π interactions has been mentioned in the literature, but detailed data have not been documented.[143] Introduction of halogen substituents at the Sb atom obviously leads to improved donor−acceptor interactions between compounds Ar_nSbX_{3-n} with Ar = aryl and X = F−I. While in fluorides such as Ph_2SbF the formation of strong Sb−F−Sb bridges is the dominant motif of assembly which appears to prevent Sb−aryl π interactions,[141] Ph_2SbCl was found to be associated also via contacts of the Sb atom with a π system of a neighboring molecule.[144]

For the series $PhSbX_2$ with X = Cl, Br, I such contacts are the rule, as shown by the first extensive and profound study by Becker et al. cited above as major progress in the long history of "Menshutkin complexes".[144] All three phenylantimony dihalides form layer structures through Sb−X−Sb bridges, and the phenyl groups on the surface of each layer are attached to Sb atoms of the two neighboring layers. Each phenyl group thus is capped by an Sb atom with a distance to the phenyl plane of 3.23, 3.27, and 3.28 Å for X = Cl, Br, I, respectively. The angles between the normal from the Sb atom to the plane and the line connecting the Sb atom with the ring centroid are small (9, 8, and 8°), indicating an only slight deviation from η^6 hapticity. These data show very clearly that the interactions between phenylantimony halides are of the same types as those between antimony halides and independent arenes, and that Sb−arene π complexation is a general and common phenomenon in this chemistry (**60**).



(60)

An example taken from a quite different class of compounds can serve as a further illustration. The condensation product of the reaction of $SbCl_3$ with 2-hydroxythiophenol, 2-chloro-1,3,2-benzoxathiastibole, shows head-to-tail aggregation into chains via the contact of the Sb atom of a given molecule to the peripheral C−C bond of the phenylene group of the molecule following in the chain (**61**). With an Sb−phenylene plane distance of 3.31 Å and an angle of as much as 18° between the normal to the plane and the line Sb−ring centroid, as a measure of the offset, this example is an extreme case of η^2 coordination.[195]



(61)

In crystals of tetraphenylphosphonium salts with a dinuclear bromo- or iodoantimonite anion, $[Ph_4P^+]_2[Sb_2Br_8]^{2-}\cdot 2CH_2Cl_2$ and $[Ph_4P^+]_2[Sb_2I_8]^{2-}\cdot 2MeCN$, interionic contacts have been observed in chains of alternating cations and anions between the two Sb atoms of the anion and two Ph groups of one of the two cations. The off-center shifts are also extreme and give contacts of the η^2 and η^1/η^3 type, but the Sb−ring plane distances are short at 3.15 and 3.04 Å, respectively, which suggests quite significant interactions.[196]

In the 1:1 adducts of triphenylphosphine sulfide and selenide with $SbBr_3$ of the formula $(SbBr_3)\cdot Ph_3PX$, one of the three phenyl groups of each Ph_3PX ligand (X = S, Se) interacts with an Sb atom in an η^2 fashion (at distances of ca. 3.4 Å; **62**).[197]

Kinetically controlled hydrolysis of the sterically encumbered arylantimony dichloride (2,6-dimesitylphenyl)$SbCl_2$ affords a dinuclear arylantimony oxide chloride in which one of the two mesityl substituents of each Sb-bound aryl ligand caps the second Sb atom in an η^6 fashion with Sb−ring centroid distances of 3.264 and 3.5414 Å (**63**).[198]

d. Influence of Intramolecular Sb−Arene Interactions on Self-Assembly Reactions. Condensation reactions of $SbCl_3$ with α,α′-dimercapto-*p*-xylene lead to a variety of macrocyclic and cage polycyclic molecules with helical structures. An investigation of the possible combinations has shown that the Sb−phenylene π interactions have a marked influence on the course of the reactions and the stability of the products.[199]

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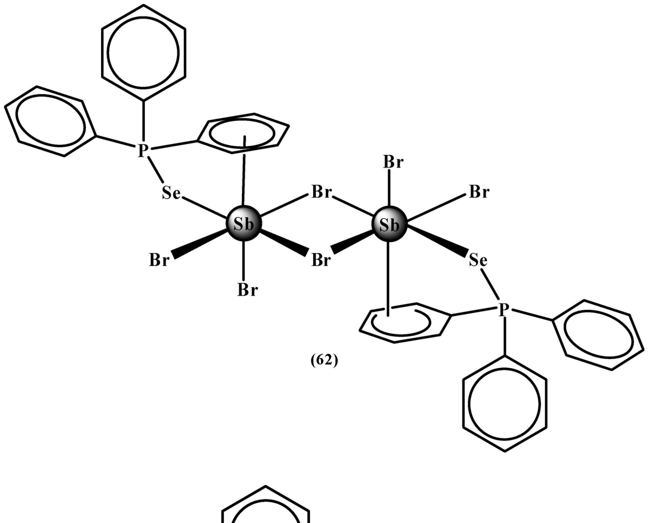

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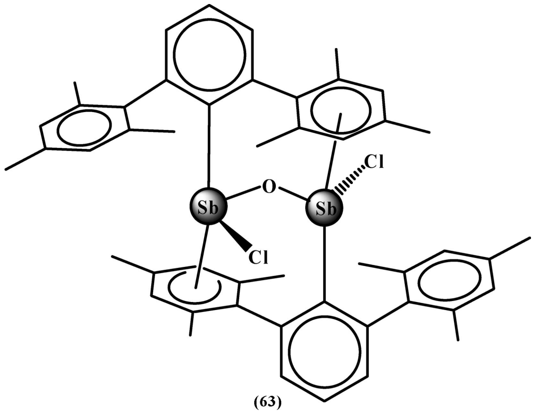

(63)

e. Thermodynamic Data and Chemical Bonding of Antimony(III) Homoarene Complexes. Thermodynamic data of "Menshutkin complexes" are rare, but a few attempts have been made to elucidate the enthalpies of formation of prototypes of the series. Perkampus and Sondern[200] have carried out calorimetric studies to determine the enthalpies and entropies of fusion of no less than 24 complexes of $SbCl_3$ with arenes of 2:1 stoichiometry (Table 2). The ΔH_{fus} values are in the range of 25−65 kJ mol^{-1} and the ΔS_{fus} values are between 77 and 190 J K^{-1} mol^{-1}. Since the former are significantly higher than ΔH_{fus} values of the individual components (e.g. 15.75 kJ mol^{-1} for pure $SbCl_3$), and the latter exceed quite considerably normal entropies of melting of molecular crystals (ΔS_{fus} ca. 50 J K^{-1} mol^{-1}), extensive dissociation of the complexes must be assumed to occur during melting. This must be particularly true for samples with high melting points (Table 2). ΔH_{fus} values of the complexes without dissociation (ΔH_{fus}*) can be estimated by using the above average standard ΔS_{fus} value of ca. 50 J K^{-1} mol^{-1} in combination with the melting temperatures (T_{fus}*). In this way for the complex $(SbCl_3)_2 \cdot C_6H_6$—with $\Delta H_{fus} = 79.0$ kJ mol^{-1}, $\Delta S_{fus} = 128$ J K^{-1} mol^{-1}, and mp 79 °C—the authors arrive at a value for the enthalpy of association of $\Delta H_{ass} = -23$ kJ mol^{-1}, which qualifies this adduct as a "weak complex". However, for the complex $(SbCl_3)_2 \cdot C_6Me_6$—with $\Delta H_{fus} = 192.5$ kJ mol^{-1}, $\Delta S_{fus} = 61.6$ J K^{-1} mol^{-1}, and mp 132 °C—the result is already significantly higher at $\Delta H_{ass} = -31$ kJ mol^{-1}, confirming the experimentally observed increase of stability on going from C_6H_6 to C_6Me_6.[200] Because the extent of dissociation of the complexes at their melting temperature is not known, it is obvious that this estimation is rather crude, but it certainly gives a good lower limit of the energy changes involved.

Table 2. Enthalpies and Entropies of Fusion of Crystalline 2:1 Complexes of $SbCl_3$ with Aromatic Hydrocarbons[a]

arene in $(SbCl_3)_2 \cdot$(arene)	mp (°C)	ΔH_{fus} (kJ mol^{-1})	ΔS_{fus} (J K^{-1} mol^{-1})
benzene	79.0	45.1	128
naphthalene	86.0	43.6	121
1-methylnaphthalene	74.9	46.1	132
2-methylnaphthalene	54.3	41.0	125
2,3-dimethylnaphthalene	59.0	42.0	126
anthracene	109.0	42.9	112
phenanthrene	105.0	58.2	154
chrysene	136.0	58.3	143
terphenylene	99.5	44.5	120
toluene	42.5	32.7	104
o-xylene	33.5	31.4	103
m-xylene	38.0	35.8	115
p-xylene	70.0	37.3	109
1,2,3-trimethylbenzene	52.5	25.3	78
1,2,4-trimethylbenzene	58.0	30.2	91
1,3,5-trimethylbenzene	74.5	35.3	102
1,2,3,4-tetramethylbenzene	93.5	36.9	101
1,2,3,5-tetramethylbenzene	98.5	40.5	109
1,2,4,5-tetramethylbenzene	101.5	40.2	107
pentamethylbenzene	148.5	55.5	132
hexamethylbenzene	192.5	61.6	132
diphenyl	72.0	51.6	150
diphenylmethane	100.0	55.7	149
1,2-diphenylethane	76.0	64.7	185

[a] The melting points are given for the complexes, and the fusion enthalpies were determined by calorimetry.[200]

In an alternative approach the vapor pressures above the liquid and solid mixtures were determined.[146] The dependence of the partial pressure of benzene above the system $SbCl_3$/benzene shows non-Raoult behavior, with activity coefficients indicating significant complex formation. This complex formation is enhanced as the temperature is lowered. From the compositions shown by the phase diagram and the corresponding vapor pressures the formation constant of the complex at the melting temperature could be obtained, which gives direct access to the enthalpy and entropy of formation in the melt equilibrium. For $(SbCl_3)_2 \cdot C_6H_6$, $\Delta H_{form} = -55$ kJ mol^{-1} and $\Delta S_{form} = -135$ J K^{-1} mol^{-1}. The equilibrium constants could also be calculated from the vapor pressures, which yield $\Delta H_{form} = -56.7$ kJ mol^{-1} and $\Delta S_{form} = -141$ J K^{-1} mol^{-1}, in good agreement with the previous data. Finally, calorimetric measurements of the mixing of the components[146] gave direct access to a third set of data and yield the result ΔH_{form}(solid) = −54.7 kJ mol^{-1} and $\Delta S_{form} = -128$ J K^{-1} mol^{-1}. Thus, the results of all three methods are in very good agreement and show that the enthalpies of complex formation between the components is in the order of magnitude of other weak but very significant interactions, including in particular weak hydrogen bonding, and also combinations of poor σ donors and σ acceptors, π stacking of strong π donors and π acceptors, and metallophilic bonding between closed-shell atoms (see the Introduction).

3. Arsenic. At a first glance, compared to the plethora of "Menshutkin complexes" of the antimony trihalides SbX_3 (mainly X = Cl, Br) with aromatic hydrocarbons and the substantial recent growth of the chemistry of related BiX_3 adducts (for X = Cl, Br, I), there appears to be a surprising paucity of information on the corresponding compounds of the arsenic trihalides. While the chemistry of the $SbX_3 \cdot$(arene) complexes dates back to the late 19th century and had enormous publicity through the work of Menshutkin, the observations about the arsenic analogues received little attention. In a monograph on π complexes of metal halides published in 1973, which reflects most of the state of the art regarding SbX_3 complexes of arenes, even the preliminary information already

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(200) Perkampus, H. H.; Sondern, C. *Z. Naturforsch.* **1981**, *36a*, 362.

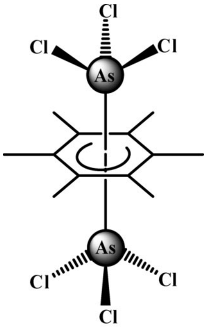
available on the arsenic analogues was still completely ignored.[138] However, a closer look at the literature reveals quite a number of early reports which provided at least preliminary evidence for the existence of arene complexes of the arsenic halides AsX_3 for X = Cl, Br.

It had long been known that liquid $AsCl_3$ (mp −6 °C, bp 130 °C) and crystalline or molten $AsBr_3$ (mp 31.2 °C, bp 221 °C) are freely miscible with or soluble in liquid hydrocarbons.[201] This excellent mutual solubility led to a patent for the extraction of arsenic halides from contaminated effluents (like sulfuric acid) by benzene.[202] The phase diagrams of the quasi-binary system $AsBr_3$/naphthalene were studied by the Menshutkin school in St. Petersburg in 1914, and the existence of the yellow discrete phase $(AsBr_3)_2 \cdot C_{10}H_8$ with a congruent melting point of 19.8 °C was established.[203] Similarly, from the colligative properties of mixtures of $AsCl_3$ and benzene, the formation of the 2:1 adduct $(AsCl_3)_2 \cdot C_6H_6$ was deduced by Sul'gina in 1934.[204] Results of electrochemical measurements in solid preparations from the system $AsCl_3$/perylene also indicated adduct formation, but no firm stoichiometric data could be provided.[205]

It was not until the preparative, thermoanalytical, and NQR studies of the $AsCl_3$/benzene system by Biedenkamp and Weiss[206] that the stoichiometry $(AsCl_3)_2 \cdot C_6H_6$ proposed by Sul'gina could be confirmed.[204] This compound has been identified by a clear maximum in the phase diagram with a melting point of −25.5 °C. It was further characterized by its ^{35}Cl NQR resonances, which showed clear parallels with the findings for the corresponding adduct $(SbCl_3)_2 \cdot C_6H_6$, which was included in the same study.[206] The 1:1 complex $(AsCl_3)_2 \cdot C_{10}H_8$, the $AsCl_3$ counterpart of Menshutkin's $AsBr_3$ complex, melts incongruently at −12 °C. Thermochemical and NQR data have also been compiled for the 2:1 adducts of $AsCl_3$ with *p*-xylene (mp −10 °C) and diphenylmethane (mp 6.5 °C) and for the 1:1 adduct with ethylbenzene (mp −37 °C). The group of Grechishkin et al. at the Siberian University of Perm, in a parallel, independent study, also carried out extensive NQR studies of complexes of $AsCl_3$ and $AsBr_3$ with aromatic hydrocarbons, the results of which were published first in 1966[207] and more extensively in 1976.[208] Complementary results were also obtained in NQR studies of arene complexes using the nucleus ^{75}As, along with ^{35}Cl and ^{81}Br. In addition to those already included by Biedenkamp and Weiss, 2:1 complexes of $AsCl_3$ with toluene and diphenyl and of $AsBr_3$ with mesitylene and naphthalene were investigated. From temperature-dependent measurements the oscillation frequencies[209] have been calculated and correlated with Raman data of the complexes.[210] The NQR shifts observed upon complex formation are a function of the donor properties of the arenes, as derived from the ionization potentials.

To date, no structural information is as yet available for any of the addition compounds of the arsenic trihalides AsX_3 (X = F, Cl, Br, I) with *benzene, toluene, the xylenes, and mesitylene* that may be present in solutions or in the crystalline solids used for establishing the phase diagrams of the products remaining upon removal of the solvents from the solutions. It is only for the *hexaalkylbenzenes* that crystalline compounds with $AsCl_3$ could be isolated and their structures determined.[168,211]

Upon addition of *hexamethylbenzene* to a solution of $AsCl_3$ in toluene, colorless transparent crystals of the 2:1 adduct $(AsCl_3)_2 \cdot C_6Me_6$ can be crystallized (mp 68 °C). The product is deliquescent in air and loses $AsCl_3$ and toluene vapors to a vacuum. The tetragonal crystals, which are isotypic with those of related Sb and Bi compounds, contain "inverse sandwich" units of point group C_{2h} symmetry (**64**) which are associated via As−Cl−As bridges into tetramers and finally into a two-dimensional network. The As atoms are located at a distance of 3.20 Å from the ring center and are shifted slightly away from the normal to this center. The As−ring center distance is larger than the Sb− and Bi−ring center distances found for the $(MCl_3)_2 \cdot C_6Me_6$ adducts (3.15 and 3.07 Å for M = Sb, Bi, respectively) and are thus at variance with the inverse gradation expected on the basis of the accepted covalent radii of the three elements.[168]



(64)

Similar experiments with C_6Me_6 and $AsBr_3$ gave a product with the unusual stoichiometry 5:1, which could not be structurally characterized.[168,211]

Hexaethylbenzene also forms stable crystalline 2:1 complexes with both $AsCl_3$ and $AsBr_3$, which can be crystallized from toluene or petroleum ether (mp 93 and 113 °C, respectively). The crystals are isotypic (space group $R\bar{3}$) and contain isolated molecules of point group S_6 symmetry (**65**). The As atoms are thus equidistant from the arene center with a distance of only 3.14 and 3.16 Å for the chloro and bromo complexes, respectively. The absence of any intermolecular As−Cl- - -As contacts connecting the individual molecules into larger aggregates makes these compounds very distinct in the class of this type of compounds.[211] It is remarkable that hexaethylbenzene, for unknown reasons, forms only a 1:1 complex with antimony trichloride, $(SbCl_3) \cdot C_6Et_6$ (**53**), while hexamethylbenzene again affords the 2:1 complexes $(SbCl_3)_2 \cdot C_6Me_6$ (**52** with C_6Me_6 instead of 1,2-$C_6H_4Me_2$) and $(BiCl_3)_2 \cdot C_6Me_6$ (see below).

The intermolecular interactions between aryl groups and arsenic atoms of arylarsenic halides R_nAsX_{3-n} and related compounds have not received much attention. In a study by Shaw et al. the phase diagrams of the binary systems of hexamethylbenzene with MPh_3 compounds (M = P, As, Sb, Bi) have been studied. Congruently melting 1:1 addition compounds have been found for M = P, As, Sb (mp 145, 144,

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(201) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Verlag Chemie: Weinheim, Germany, 1954; Arsenic, pp 386−389, 401−402.

(202) *Ger. Offen. DP 194 864*, 1906, as quoted in ref 201.

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(204) Sul'gina, M. P. *Zh. Obshch. Khim.* **1934**, *4*, 225.

(205) Traut, M. S.; Eiss, R. *J. Electrochem. Soc.* **1963**, *110*, 769.

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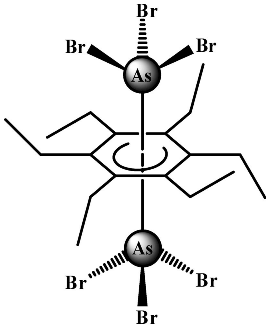
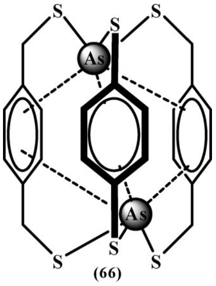
(211) Schmidbaur, H.; Bublak, W.; Huber, B.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 234.



(65)

137 °C, respectively), but no further information is available. No peritektika were discernible for $C_6Me_6/BiPh_3$ and for any of the MPh_3 compounds with naphthalene.[167]

In the condensation products of α,α′-dimercapto-*p*-xylene with $AsCl_3$ of the formulas $(SCH_2C_6H_4CH_2S)_2As_2Cl_2$ and $(SCH_2C_6H_4CH_2S)_3As_2$ the As atoms are interacting with the phenylene rings at As−ring plane distances between 3.18 and 3.33 Å. In some of the reactions there is evidence for an influence of As−arene interactions on the stereoselectivity of the formation of the macrocycles (**66** and **67**).[212–214]



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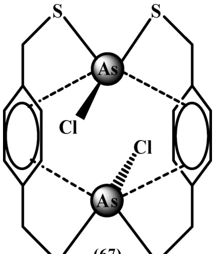
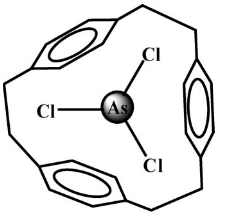


(67)

In this context, Johnson and co-workers have investigated the bonding in the hypothetical 1:1 complex $AsCl_3 \cdot C_6H_6$ by DFT calculations. The authors arrived at a lower limit for the binding energy of 7.4 kcal mol^{-1} at an equilibrium As−ring plane distance of ca. 3.3 Å. It should be kept in mind that this value refers to the isolated molecules in the gas phase. The formation constant and enthalpy of formation may be significantly different in the condensed phase. The energy profile for the movement of the As atom over the ring in the isolated molecule was found to be quite flat, with an energy difference of only 0.5 kcal mol^{-1} for a shift from the centric to an off-center position (at a similar distance) with a 68° tilting angle (normal vs As−centroid line).[212]

[2,2,2]Paracyclophane was found to crystallize with 1 equiv of $AsCl_3$ from benzene solution at room temperature. The colorless product is formed in almost quantitative yield and has a sharp melting point of 53 °C. Very surprisingly, the crystal structure determination revealed that the $AsCl_3$ molecule is not attached to any of the three phenylene rings. Its 3-fold axis coincides with the 3-fold axis of the cyclophane, the apex of the $AsCl_3$ pyramid pointing toward the cavity of the hydrocarbon—like a diamond in its setting (**68**). It appears that particular packing forces in this case overrule the weak forces of arene complexation. It should also be noted that no benzene solvent molecule, which represents another candidate for π-complexation, remains in the crystal.[179] This result is in agreement with the general experience that, although an adduct of $AsCl_3$ with benzene exists as a solid at low temperature (less than ca. −25 °C), it disintegrates at higher temperatures.



(68)

4. Bismuth. In comparison to the history of arene complexes of antimony trihalides and related molecules of the type SbX_3, the history of the analogous bismuth compounds is much shorter. Menshutkin may have also included $BiCl_3$ and $BiBr_3$ in his early "screening" of aromatic hydrocarbons as ligands for $SbCl_3$ and $SbBr_3$, but no details of any results have been documented.[215] However, Ukranian scientists observed in 1937−1938 that $BiBr_3$ becomes soluble in benzene if 1 equiv of $AlBr_3$ is added.[216–218] Cryoscopic and electrochemical studies of these solutions indicated complex formation and electrolytic dissociation of the components, suggesting an equilibrium with $BiBr_2^+AlBr_4^-$. This formula was also suggested by the phase diagram of the system $BiBr_3 \cdot AlBr_3$.[219] In 1958, Corbett reported that anhydrous $BiCl_3$ is appreciably soluble in benzene, allowing him to separate this compound from reaction mixtures containing low-valent bismuth chlorides. The solubility was determined to be 0.287% by weight at 26 °C.[220] The compound $BiCl_2^+AlCl_4^- \cdot C_6H_6$ was first prepared and analytically characterized by Auel and Amma in 1968, but its structure remained elusive.[24]

A review of the general area of organobismuth chemistry, focusing on structural aspects and including for the first time a chapter on arene complexes, was published by Breunig and co-workers in 1999.[221] In a book, edited by Suzuki and Matano in 2001, arene π complexes of Bi(III) compounds have also briefly been considered.[222] The field has grown steadily in recent years, and the following account reflects both the historical background and the latest advances.

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(215) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Verlag Chemie: Weinheim, Germany, 1964; Bismuth, 1st Suppl., pp 682−684.

(216) Plotnikov, V. A. *Zap. Inst. Khim., Akad. Nauk Ukr. RSR* **1937**, *4*, 249. (cited in ref 215)

(217) Jankelevich; Z. A.; Sheka, I. A. *Zap. Inst. Khim., Akad. Nauk Ukr. RSR* **1938**, *5*, 59. (cited in ref 215)

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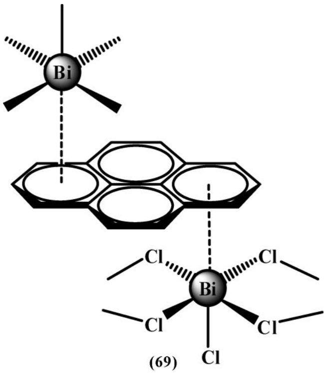
a. Complexes of Neutral Arenes with Bismuth Trihalides. The first series of analytically well-defined complexes was prepared by Peyronel et al. at the University of Modena in 1968. A table contained in this first publication gives no less than 12 aromatic hydrocarbons which were found to give crystalline adducts with $BiCl_3$ and/or $BiBr_3$. The discrete phases were obtained by dissolving the anhydrous bismuth halides in the liquid or molten arenes, only a few cases requiring an auxiliary solvent. Pretty transparent crystals are shown in microphotographs, but no structures have been determined. The prevailing stoichiometry was found to be 1:1 (e.g. $BiCl_3 \cdot C_6H_6$), but other ratios were also encountered for binary systems. With polynuclear arenes, the 2:1 stoichiometry is more common: e.g., for $(BiCl_3)_2 \cdot$(pyrene) (see below). If the auxiliary solvent was also an arene, ternary complexes were obtained (e.g. $BiCl_3$/1,4-diphenylbutadiene/*p*-xylene). All compounds were found to be hygroscopic, and complexes with volatile hydrocarbons lost ligand rapidly when exposed to the atmosphere.[223]

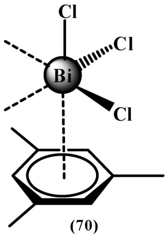
The group of Peyronel continued their studies (in 1970) by investigating their pyrene complexes of $BiCl_3$ and $BiBr_3$ by spectrophotometric methods in the solid state and in organic solvents. In the solid state, the 2:1 complexes $BiX_3 \cdot$(pyrene) (X = Cl, Br) show charge transfer bands at 350−360 and 390 nm for X = Cl, Br, respectively, which was tentatively correlated with the dipole moments of the bismuth halides. In acetonitrile and dichloromethane solutions the effect is less pronounced, indicating extensive dissociation of the complexes into their components. The IR absorptions of the complexes (in Nujol) did not exhibit any major shifts as compared to the spectra of the components.[139]

It was not until 1988 that this work was followed by the first crystal structure analysis of the purple $(BiCl_3)_2$(pyrene) by Vezzosi et al., which not only confirmed the stoichiometry but revealed a centrosymmetrical arrangement of the two $BiCl_3$ molecules, one above and one below the hydrocarbon and each Bi atom roughly η^6-centered above one of the benzene rings at the longer end of the hydrocarbon (**69**). The $BiCl_3$ molecules are aggregated into zigzag chains connected via the pyrene ligands. It should be mentioned that this complex was prepared from its two components in *p*-xylene, but this solvent was not accepted as an additional complexing agent, indicating a preference for pyrene as a ligand.[224] Preliminary crystal data of the analogous $BiBr_3$ complex were reported in a later study, indicating that the two compounds are isostructural.[225]



(69)

This later structure determination was preceded by the elucidation of the structures in 1986 of simple prototypes of 1:1 and 2:1 complexes: viz. $BiCl_3 \cdot 1,3,5\text{-}C_6H_3Me_3$ and $(BiCl_3)_2 \cdot C_6Me_6$. In both compounds the Bi atoms are located above the centers of mesitylene and hexamethylbenzene ligands with Bi−arene plane distances of 3.06 and 3.05 Å (average);[226,227] these data are to be compared with those of the analogous $SbCl_3$ complexes, which are 3.24 and 3.13 Å and are thus much longer (**70** and **71**).[165,166] The findings for $BiCl_3 \cdot (1,3,5\text{-}C_6H_3Me_3)$ confirm the stoichiometry first formulated by Peyronel et al., while $(BiCl_3)_2 \cdot C_6Me_6$ had not previously been described. It represents the first "inverse sandwich" complex formed by arenes and group 15 element halides EX_3. In the crystals, the $BiCl_3$ components are connected via Bi−Cl−Bi bridges to form larger inorganic units. In $(BiCl_3)_2 \cdot C_6Me_6$ cyclic tetramers are present, similar to that shown for the antimony analogue (**52**), while for $BiCl_3 \cdot 1,3,5\text{-}C_6H_3Me_3$ an extended network is formed.[166,226] The analogous $BiBr_3$ complexes have also been prepared, and the crystals were found to be isomorphous.[165,227]



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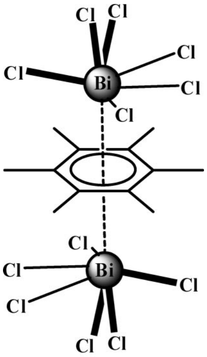

(71)

Similar modes of aggregation were observed in the structural work on the 1:1 complexes of $BiCl_3$ with the three xylene isomers. Extended chains of $(BiCl_3)_n$ polymers with different connectivity patterns have the *p*- and *m*-xylene molecules attached in the η^6 fashion, but ring slippage away from an exactly centered coordination, and away from the methyl groups, is observed for *o*-xylene. An example is given in formula **72**. The compounds are all thermally stable; melting with loss of ligand is initiated on heating to around 160 °C.[227]

The toluene complex $BiCl_3 \cdot PhMe$ has already been mentioned in this earlier work, but no details were disclosed,[227] and it was not until very recently that its crystal structure was reported by Breunig et al.[228] The crystals are built of zigzag chains of a $[BiCl_3]_n$ coordination polymer with each Bi atom η^6 bonded to a toluene ring (**73**). The compound melts and loses toluene vapor at 103−104 °C.

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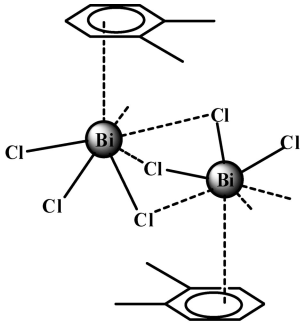
(223) Peyronel, G.; Buffagni, S.; Vezzosi, M. *Gazz. Chim. Ital.* **1968**, *98*, 147.
(224) Vezzosi, I. M.; Zanoli, A. F.; Battaglia, L. P.; Corradi, A. B. *J. Chem. Soc., Dalton Trans.* **1988**, 191.
(225) Battaglia, L. P.; Corradi, A. B.; Vezzosi, I. M.; Zanoli, F. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1675.
(226) Schier, A.; Wallis, J. M.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 757.
(227) Müller-Becker, S.; Frank, W.; Schneider, J. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1073.
(228) Breunig, H. J.; Lork, E.; Rat, C. *Z. Naturforsch.* **2007**, *62b*, 1224.



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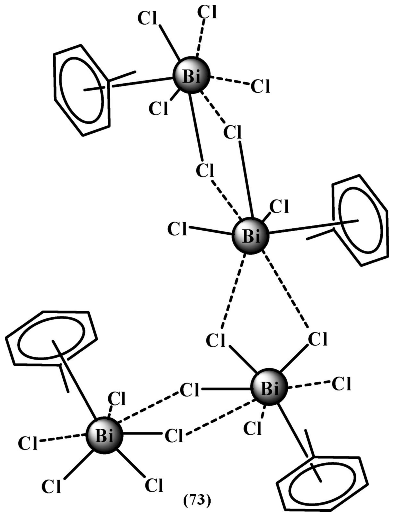
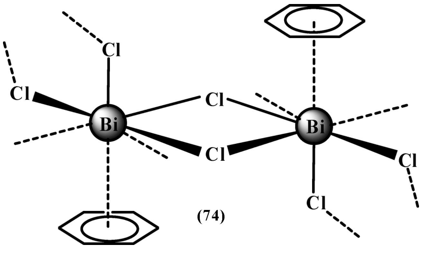


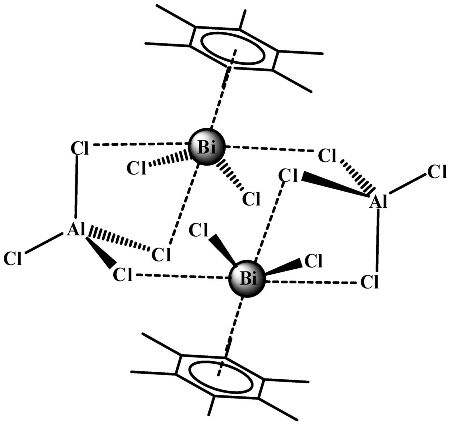
(73)

The 1:1 complex of $BiCl_3$ with unsubstituted benzene is much less stable and loses benzene under vacuum at ambient temperature. The crystals, whose structures were determined by Frank et al., have a layer structure, each layer being composed of unsymmetrical $[BiCl_3 \cdot C_6H_6]_2$ dimers connected via Bi−Cl−Bi bridges (**74**). The distance from the Bi atoms (two independent molecules) to the benzene ring planes (3.08(2) and 3.20(2) Å) are significantly longer than those in most other complexes with substituted benzene rings, indicating particularly weak arene bonding.[229]



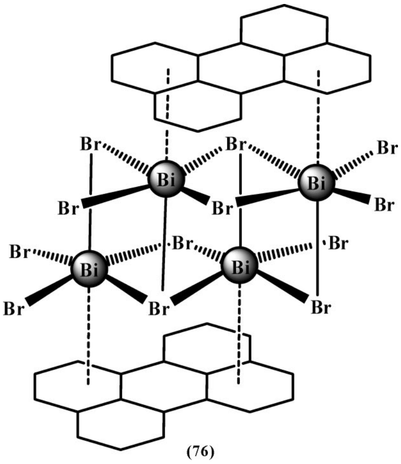
(74)

The type of ionic structure proposed by Auel and Amma[24] for $[(C_6H_6)BiCl_2]^+AlCl_4^-$ was confirmed by Frank et al. in 1987, who employed hexamethylbenzene as the arene ligand: $[(C_6Me_6)BiCl_2]^+AlCl_4^-$. The components are associated into centrosymmetrical dimers with the Bi atoms pentacoordinated by chlorine atoms (**75**). A related complex of toluene was also prepared, but its structure could not be solved.[230]



(75)

Perylene was found by Battaglia et al. to form a black, crystalline adduct with $BiBr_3$ of 4:3 stoichiometry, $(BiBr_3)_4 \cdot 3$(perylene), but a crystal structure analysis showed that one of the perylene molecules is not engaged in bonding to the (Bi_4Br_{12}) core unit. The four $BiBr_3$ molecules form an inorganic cluster which is sandwiched between the other two hydrocarbons, of which two benzene rings have a Bi atom η^6 coordinated (**76**). The compound thus should be formulated as $[(BiBr_3)_4 \cdot 2(\text{perylene})] \cdot (\text{perylene})$.[231]



(76)

Fluoranthene also forms a 2:1 adduct with $BiBr_3$ featuring a $(BiBr_3)_4$ core unit sandwiched by the two tetracyclic arenes. The red-purple compound crystallizes as a *p*-xylene solvate (4:2:1), but the xylene molecules are not coordinated to bismuth atoms. In the same study, several other 2:1 complexes of $BiBr_3$ were prepared using the ligands perylene (dark green), pyrene (dark red), acenaphthene (orange), and phenanthrene (yellow-orange) and their UV/vis spectral data collected. The bands were assigned to charge transfer absorptions and their energies correlated with the ionization potential of the ligands.[225]

The ligand properties of various cyclophanes were investigated in great detail, partly in an effort to induce multiarene coordination through entropy/cooperativity effects. [2.2]Paracyclophane forms a 2:1 adduct with $BiBr_3$ in which each benzene ring is η^6-coordinated to a Bi atom. The $BiBr_3$ molecules are aggregated into one-dimensional strings separated by the *p*-cyclophane ligands (**77**). The complex is surprisingly stable, both to heat and to the atmosphere, and shows a charge-transfer transition at 375 nm in its electronic spectrum.[232] The

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(229) Frank, W.; Schneider, J.; Müller-Becker, S. *J. Chem. Soc., Chem. Commun.* **1993**, 799.

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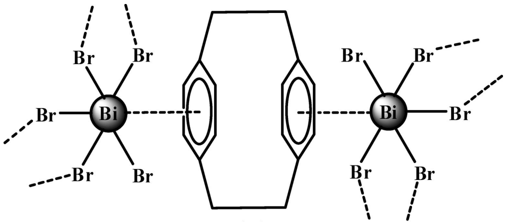
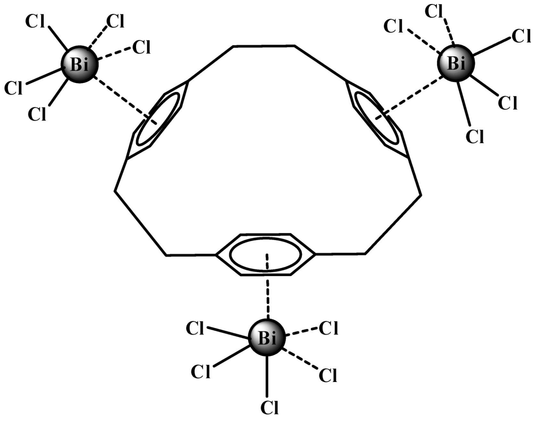
compound cocrystallizes with pyrene to give crystals of the composition $(BiBr_3)_2 \cdot$([2.2]paracyclophane)$\cdot$(pyrene). The structure has strings of associated $(BiBr_3)_2$ dimers with each Bi atom η^6-coordinated to a benzene ring of a paracyclophane in a way as shown in formula **77**. The pyrene molecules are not coordinated to metal atoms and must be considered as spectator solvate molecules. In TGA experiments it was shown that the pyrene molecules are released first on heating. In the UV/vis spectrum the charge transfer band appears at 370−390 nm.[233]



(77)

[2.2.2]Paracyclophane was found to give a 3:1 complex with a $BiCl_3$ molecule attached symmetrically to each of the three benzene rings (**78**). The compound crystallizes as a benzene solvate (1:1), but the solvate molecules are not attached to a bismuth atom, suggesting a preference for cyclophane coordination.[179]

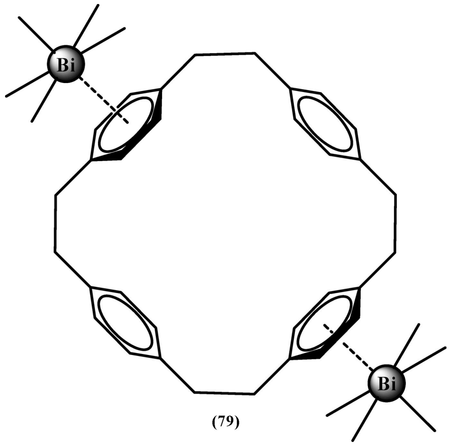


(78)

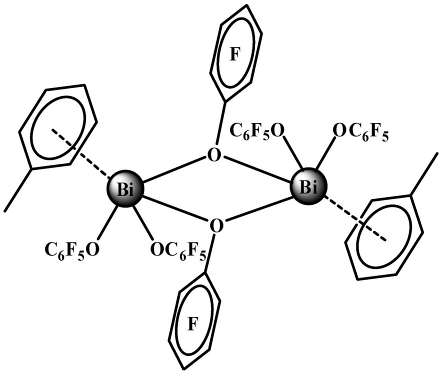
[2.2.2.2]Paracyclophane forms a 2:1 complex with $BiBr_3$ and crystallizes as a toluene solvate. One-dimensional chains of $(BiBr_3)_2$ units are separated by the paracyclophane molecules, with only two of the four benzene rings η^6-coordinated to a Bi atom (**79**).[234]

b. Arene Complexes of BiX_3 Molecules Other Than the Trihalides. The phase diagrams of the binary systems hexamethylbenzene/triphenylbimuth and naphthalene/$BiPh_3$ have been studied. No anomalies were detected.[167]

Dimeric tris(pentafluorophenoxy)bismuth was found by Whitmire and co-workers to crystallize as a 1:1 toluene complex of the type $[Bi(OC_6F_5)_3 \cdot PhMe]_2$. Each of the two toluene molecules is η^6-bonded to a bismuth atom (**80**; these dinuclear units crystallize free of solvate or with two additional toluene solvate molecules which are not shown).[235,236] The distance from the Bi atom to the ring centroid is only 2.96(4) Å and is therefore significantly shorter than that found in the analogous $BiCl_3$ complex of toluene (average 3.065 Å for two independent units),[228] suggesting stronger bonding.



(79)



(80)

A related tri(phenoxy)bismuth compound in which the three phenoxy groups are tethered to a common amine nitrogen atom to give a tripodal, tetradentate ligand was found to form a 2:1 complex with toluene (**81**). In this dinuclear unit both BiX_3 molecules are η^6-bonded to the ring of the same toluene molecule with distances from the Bi atoms to the toluene ring centroid of 3.263(4) Å.[237] Solution NMR studies have shown that the toluene coordination is not retained in solution. Free and bound toluene molecules are fully equilibrated on the NMR time scale. To further characterize the nature of the Bi−(PhMe) bonding, DFT calculations were carried out on a simplified model compound in which the ^{t}Bu groups were replaced by H atoms and benzene was substituted for toluene. The calculated structure closely resembled the experimental data for the parent compound. When C_3 and D_3 symmetry was imposed, the overall stabilization energies due to the $\mu-\eta^6{:}\eta^6$ interaction were calculated to be 3.0 and 5.2 kcal mol^{-1}, respectively. The HOMO−LUMO interactions are consistent with a $\sigma + 2\pi$ model of bonding employing the symmetry-related metal and arene orbitals. It should be noted that the corresponding Sb compound has an entirely different molecular structure and does not form any arene adduct.[237]

A large bismuth oxide *tert*-butylphosphonate cluster of the formula $[(^tBuPO_3)_{10}(^tBuPO_3H)_2Bi_{14}O_{10}]$ prepared by Mehring and Schürmann crystallizes as a tetrahydrate with three molecules of benzene.[238] Six of the bismuth atoms of the cluster

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(233) Battaglia, L. P.; Cramarossa, M. R.; Vezzosi, I. M. *Inorg. Chim. Acta* **1995**, *237*, 169.

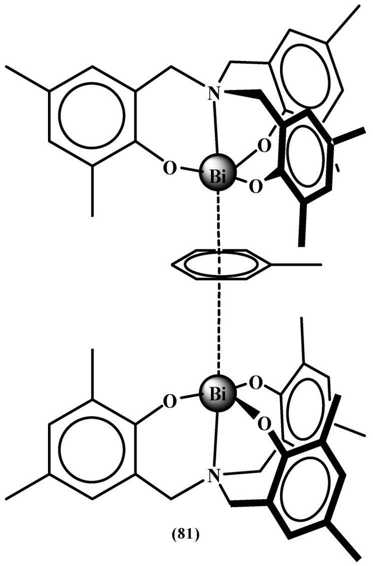
(234) Ferrari, M. B.; Cramarossa, M. R.; Iarossi, D.; Pelosi, G. *Inorg. Chem.* **1998**, *37*, 5681.

(235) Jones, C. M.; Burkart, M. D.; Whitmire, K. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 451.

(236) Jones, C. M.; Burkart, M. D.; Serra, D. L.; Hwu, S.-J.; Whitmire, K. H. *Inorg. Chem.* **1993**, *32*, 5136.

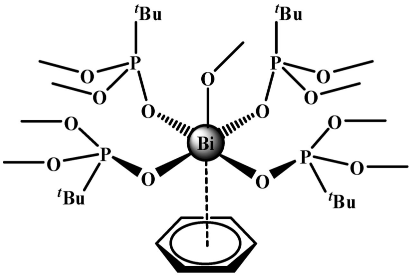
(237) Turner, L. E.; Davidson, M. G.; Jones, M. D.; Schulz, V. S.; Wilson, P. J. *Inorg. Chem.* **2006**, *45*, 6123.

(238) Mehring, M.; Schürmann, M. *Chem. Commun.* **2001**, 2354.



(81)

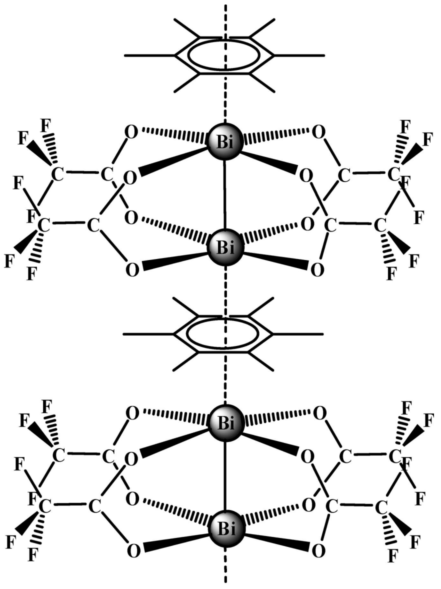
are η^6 bonded to a benzene ring, each of which forms a Bi−(C_6H_6)−Bi bridge to a neighboring cluster, with a Bi−ring centroid distance of 3.194 Å. This may be compared with the distance of 3.07(2) Å found in the "inverse sandwich" prototype $(BiCl_3)_2 \cdot C_6Me_6$ with a highly substituted benzene[165,166,226] or with 3.14 Å (average) for $BiCl_3 \cdot C_6H_6$ with unsubstituted benzene coordinated from only one side.[229] It again appears that C_6H_6 is most weakly coordinated. Formula **82** shows a characteristic unit of the large cluster.[238]



(82)

c. Arene Complex of a Dinuclear Bi(II) Compound. Dark red crystals of the compound $[(Bi_2(O_2CCF_3)_2] \cdot C_6Me_6$ were obtained by Frank et al. in low yield (ca. 20%) by thermolysis of a mixture of bismuth tris(trifluoroacetate) and hexamethylbenzene (3:2) in a sealed glass tube at 100 °C. In the reaction yellow crystals of $[Bi(O_2CCF_3)_3] \cdot C_6Me_6$ were first produced, followed by the red crystals of the Bi(II) compound formed via an unknown route.[239] In the crystal, the dinculear Bi(II) compound forms a linear coordination polymer through alternate stacking with hexamethylbenzene molecules (**83**). Each C_6Me_6 unit is symmetrically η^6-coordinated by two Bi atoms with Bi−ring centroid distances of 3.053(2) Å, very similar again to that in the $(BiCl_3)_2 \cdot C_6Me_6$ reference compound (3.07 Å).[166,226]

d. Arene−Bi Interactions between Arylbismuth Molecules. In crystals of triphenylbismuth, Ph_3Bi, no unusually close contacts between the individual molecules are discernible. The shortest distance between a Bi atom and the centroid of a phenyl ring of a neighboring molecule is 3.69 Å, and at that distance the Bi atom also is not centered. It therefore appears that there



(83)

are only negligible contributions of specific Bi(arene) bonding (other than conventional van der Waals bonding) to the lattice energy.[240,241] It is, of course, of no surprise that triarylbismuth compounds with bulky or very bulky subsituents such as, for example, trimesitylbismuth,[242,243] tris(2,6-dimethoxyphenyl)bismuth,[242] or even tris[2,4,6-tris(trifluoromethyl)phenyl]bismuth are not associated in the crystal.[243]

In contrast, arylbismuth compounds Ar_nBiX_{3-n} ($n = 1, 2$) have been found to undergo intermolecular association in molecular crystals which are based on η^6 coordination of the metal atom to the aryl group. Similar effects can be observed for compounds in which the aryl group is separated from the Bi atom by a spacer. On the other hand, bulky substituents can again be prohibitive, as exemplified by the isolated molecules of bis[2,4,6(trifluoromethyl)phenyl]bismuth chloride.[244]

As an introductory caveat to this subchapter, it has to be pointed out that, even in the absence of steric hindrance, Bi−arene interactions may not be present in crystals of very simple representatives of this type of compounds: phenylbismuth dibromide molecules ($PhBiBr_2$) form chains through Bi−Br−Bi double bridging, keeping the phenyl groups away from the Bi atoms and leaving them rather in an orientation for $\pi-\pi$ stacking. However, since the arenes of indented neighboring strands are somewhat offset against each other, and since the distance between arene planes is as long as 3.928 Å, the phenyl stacking may not really render any significant contribution to the lattice energy. The perfect match of the $BiBr_2$ alignment may be the decisive element in the balance between structure alternatives.[245]

The anionic adducts of $PhBiX_2$ molecules with the corresponding halide anions, $[PhBiX_3]^-$, form the dinuclear units

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(239) Frank, W.; Reiland, V.; Reiss, G. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2984.

(240) Jones, P. G.; Blaschette, A.; Henschel, D.; Weitze, A. *Z. Kristallogr.* **1995**, *210*, 377.

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(242) Ogawa, T.; Ikegami, T.; Hikasa, T.; Ono, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. I* **1994**, 3479.

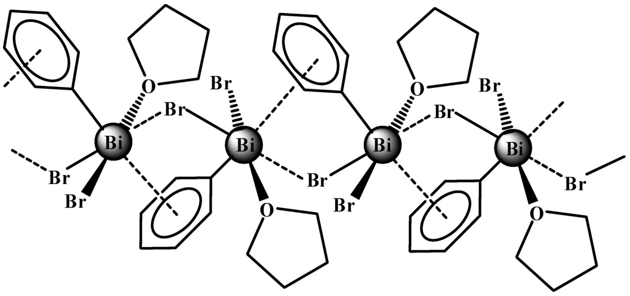
(243) Sobolev, A. N.; Romm, I. P.; Bel'skii, V. K.; Gur'yanova, E. N. *Koord. Khim.* **1980**, *6*, 945; *Chem. Abstr.* **1980**, *93*, 168349.

(244) Whitmire, K. H.; Labahn, D.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *402*, 55.

(245) Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Fisher, G. A.; Norman, N. C. *J. Mater. Chem.* **1994**, *4*, 891.

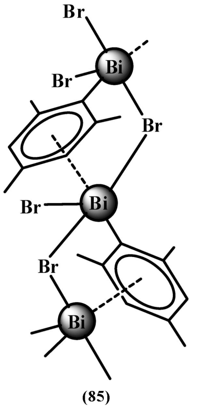
$[Ph_2Bi_2X_6]^{2-}$, which have no interanionic Bi−arene contacts in the tetraethylammonium salt.[246]

In contrast, in crystals of the *1:1 adducts* of the same phenylbismuth dibromide and of the corresponding diiodide *with tetrahydrofuran*, $PhBiX_2 \cdot thf$ (X = Br, I) single Bi−X−Bi bridges connect the molecules into chains, which have the phenyl group of each molecule tilted toward the Bi atoms of the following unit. The Bi atoms are "offset" from the center of the phenyl rings and kept at a Bi−centroid distance between 3.45 and 3.53 Å (**84**).[247] The 1:1 tetrahydrofuran adduct of diphenylbismuth bromide, $Ph_2BiBr \cdot thf$, is a monomer in the crystal, and the anions $[Ph_2BiBr_2]^-$ in the tetraphenylphosphonium salt are also isolated units.[247]



(84)

Mesitylbismuth dibromide molecules, $MesBiBr_2$, are associated into strings via Bi−Br- - -Bi bridges, and conformations are induced which allow for approximate η^6 contacts of each Bi atom with a mesityl ring (**85**). The two Bi−ring centroid distances are 3.20 and 3.31 Å, of which the former in particular is well in the range observed for the $BiX_3 \cdot$(arene) complexes (X = Cl, Br, OC_6F_5, etc.; see above).[248] It thus appears that the acceptor quality of the Bi atom is reduced by introduction of the thf donor molecule and that unsubstituted phenyl groups are poorer donors than alkylated ones.

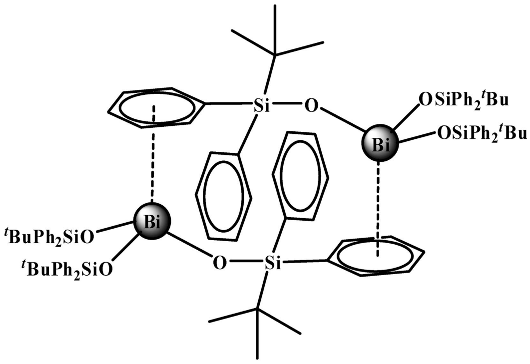


(85)

However, in mesitylbismuth dichloride, $MesBiCl_2$, the Bi−centroid distances are much larger at 3.51 and 3.69 Å and there is a very significant ring slippage of the Bi atom away from the line perpendicular to the ring center, probably due to the change in the halide radii on going from I to Br to Cl.[245,248]

Dimesitylbismuth bromide (Mes_2BiBr) molecules are associated in the crystal into chains through intermolecular Bi- - -Br contacts. The resulting molecular packing places one aryl ring of a given molecule in front of the Bi atom of a neighboring molecule, which at a biased first glance suggests an influence on the stability of the overall structure, but this detail very justly has not been addressed by Breunig and co-workers any further, probably because the Bi−ring centroid distance is in fact very long (3.76 Å).[249] The situation was analyzed by Becker et al. in great detail, however, for the molecular crystals of mesitylbismuth dibromide ($MesBiBr_2$), where much shorter distances are observed, and in this context the literature on related compounds has been summarized and evaluated quite comprehensively.[248]

In tris(2,6-dimethylphenoxy)bismuth each Bi atom to a good approximation is η^6-coordinated to one phenoxy group of a neighboring molecule with a very short Bi−centroid distance of only 2.98 Å, one of the shortest observed in the family of arene complexes of bismuth.[250] In a similar mode of aggregation, tris(*tert*-butyldiphenylsiloxy)bismuth is associated into cyclic, centrosymmetric dimers in which each Bi atom interacts with one of the six phenyl groups of the partner molecule. The coordination mode is roughly η^6, and the Bi−centroid distance is 3.340 Å (**86**).[251]



(86)

These results support the ideas that (a) oxygen substituents at the Bi atom greatly enhance its acceptor properties and (b) substituents with flexible spacers between the aryl ring and the Bi atom allow the molecule to adopt a conformation which optimizes the Bi−arene interaction. On the basis of similar arguments, it is not unexpected that the Bi atom in diphenylbismuth phenylselenide ($Ph_2BiSePh$), with its poor acceptor properties, shows no affinity for the PhSe group of neighboring molecules in the crystal (Bi−arene distances of 3.67 and 3.84 Å).[252] The same reasoning applies to the structure of (2-(*tert*-butylsulfonyl)phenyl)di-*p*-tolylbismuth, with long average Bi−arene centroid distances of 3.55 Å. No such contacts are discernible in $(2\text{-}^tBuSO_2C_6H_4)(p\text{-}MeC_6H_4)BiCl$, where there is a coordination of the sulfone group to the metal atom instead.[253] In the description of the structure of the cluster anions contained in the dinuclear catecholato complex $(NH_4)_2[Bi_2(C_6H_4O_2)_4] \cdot 2C_6H_6O_2 \cdot 2H_2O$, the authors did not consider any Bi−arene contacts,[253] but these have later been calculated to be present, as shown by a contact distance of 3.49 Å.[248] In mesitylbismuth bis(dithiodiphenylphosphinate), $MesBi(S_2PPh_2)_2$,

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[246] Clegg, W.; Errington, R. J.; Fisher, G. A.; Flynn, R. J.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1993**, 637.

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[251] Mansfeld, D.; Mehring, M.; Schürmann, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1795.

[252] Calderazzo, F.; Morvillo, A.; Pelizzi, G.; Poli, R.; Ungari, F. *Inorg. Chem.* **1988**, *27*, 3730.

the Bi center shows intramolecular coordination by two extra sulfur atoms, and therefore no Bi−arene contacts are possible.[249]

5. Chemical Bonding in Arene Complexes of EX_3 Molecules. Chemical bonding in complexes of arenes with EX_3 molecules has been analyzed at various levels of theory, starting with simple charge transfer and donor−acceptor models.[135–138] The latter were refined using various types of orbital and hybrid orbital interactions.[132] The most popular model used the HOMO's of the aromatic system in symmetry-allowed combinations with E's atomic orbitals. For E = Bi in an η^6 position in particular, low-lying, relativistically contracted 6s states which are filled[140,226,248] and empty high-energy 5d states were neglected, leaving the 6p states as acceptor orbitals. For lower hapticities and symmetries, the appropriately modified combinations were chosen. In the more recent approaches ab initio and density functional methods were applied.

As mentioned above, for the hypothetical model complex $AsCl_3 \cdot C_6H_6$, DFT calculations gave a lower limit of the binding energy of 7.4 kcal mol^{-1} and have shown that the energy profile of the movement between different modes of hapticity (e.g. $\eta^3 \rightarrow \eta^6$) is very flat (<0.5 kcal mol^{-1}).[212,213]

Similarly, for the simplified model compound $BiX_3 \cdot C_6H_6$ with $X_3{}^{3-}$ representing an amine−tris(phenoxide) unit, the HOMO was found to be largely ligand-based, confirming the lowered position of the Bi $6s^2$ state. The LUMO of a symmetry is localized and antibonding with respect to Bi−X bonding. In total, a $\sigma + 2\pi$ mechanism has been proposed, for which the binding energy of the 1:1 adduct was estimated to be ca. 3.0 kcal mol^{-1}, whereas for the 2:1 adduct the value is 5.2 kcal mol^{-1}. Both values are probably underestimated, since the calculated geometries are not a perfect match for the experimental structures.[237] It should be noted that the calculated binding energies for the arsenic 1:1 compound (7.4 kcal) exceed the experimental results for the analogous antimony 2:1 compounds (ca. 5 kcal), while those for the bismuth 1:1 and 2:1 compounds were calculated to be significantly lower. Notwithstanding, the order of magnitude is generally consistent for experimental and theoretical data. The ample experimental evidence for an extreme directional flexibility of the E−arene bonding, which becomes obvious from the variety of hapticity patterns, and for the variability of the E−ring plane distances is also borne out by the calculations. However, it is probably fair to say that the state of theoretical treatment of the bonding phenomena is generally not yet really satisfactory. This is obvious, for example, from the fact that there is no explanation for the observation that the majority of antimony(III) complexes have the arene ligands in an off-center coordination (non-η^6), which on the other hand is rare for all other elements considered in this review.

6. Potentials of the Chemistry of Arene π Complexes of As, Sb, and Bi Compounds. Recent work in this area has shown that π complexation of neutral arenes by EX_3 units, with E = As, Sb, Bi and X = halogen, chalcogen, etc., is a widespread phenomenon which dependably occurs if it is not opposed by other, stronger forces. Thermodynamic data for the complex formation are only available for SbX_3 adducts, and these indicate that the enthalpies of formation are generally in the range of typical "weak forces" (5−10 kcal mol^{-1}) comparable to hydrogen bonding, aggregation of weak σ donors and acceptors, and metallophilic bonding between closed-shell atoms. Aromatic hydrocarbons with low oxidation potentials and hence high donor strengths (such as the polyalkylated benzenes $C_6H_xR_{6-x}$) form the strongest complexes. The acceptor properties of the EX_3 units can be strongly enhanced by employing an auxiliary acceptor for X^-: for example, as demonstrated for the system $C_6Me_6/BiCl_3/AlCl_3$, in which the cation $BiCl_2{}^+$ becomes attached more tightly to the hexamethylbenzene ring than did the $BiCl_3$ units in $(BiCl_3)_n \cdot C_6Me_6$.

The E−arene plane distances are generally in the range of 2.9−3.4 Å, the heavier element (Bi) counterintuitively having the shorter distances, probably largely due to relativistic effects. The coordination is not really "regioselective" regarding the positioning above the arene ring. The energy profile of moving the E element above the rings appears to be very flat, and the hapticity can be anywhere from η^1 to η^6, with the preference for the latter again being most pronounced for the heaviest element (Bi).

Complexation occurs predominantly in the solid state, whereas in solution the arene−EX_3 interactions are overruled by solvation. This and other observations make it obvious that the arene complexation is readily reversible, and that the adducts are components of delicate equilibria, a feature also closely resembling the properties of systems with hydrogen bonds. Finally, EX_3 molecules can become attached to the arene rings from only one or from both sides, yielding 1:1 or 1:2 complexes, respectively. This should also apply to allotropes of carbon, but as yet there is no hard experimental evidence for this type of surface−molecule interaction.

The above characteristics indicate that compounds containing freely accessible arene rings together with compounds featuring EX_3, $-EX_2$, or $EX_2{}^+$ functionalities can be employed as very flexible building blocks for crystal engineering. The examples already documented in the literature clearly show this potential in that not only a plethora of isolated molecular complexes but also one-, two-, and three-dimensional arrays have been discovered, which are readily assembled and exhibit considerable thermal stability. Aromatic hydrocarbons were found to be soluble in liquid (or molten) EX_3 or mixed systems EX_nY_{3-n}. The polar EX_3 compounds are soluble in nonpolar aromatic hydrocarbons through the efficient coverage of their E functions. Clearly, new ideas are required to exploit further the potential offered by these quite unusual general characteristics.

V. Summary

Three triads of the immediate post-transition-metal elements, viz. Ga−In−Tl, Ge−Sn−Pb, and As−Sb−Bi, in their low oxidation states, have all been shown to produce stable arene complexes. Arenes appear to function as electron donors, while the metal compounds or salts are electron acceptors. Complex formation is supported by electron-donating substituents on the arenes, by electron-withdrawing substituents or anions on the metal atom or cation, and by auxiliary anion acceptors. The energies of formation are in the range of those characteristic of *weak forces*, and therefore the assembly of the supramolecular aggregates is generally reversible even under mild conditions. Nevertheless, the multidimensional arrays in the solid state are robust structures with considerable thermal stability. Aggregation is also operative in melts of the binary or ternary systems of arene donor, metal salt acceptor, and auxiliary acceptor, as shown by the extremely low arene vapor pressures. However, solvation in solution leads to extensive disintegration of the molecular or multidimensional aggregates into the solvated components. The phenomena observed in structural investigations throughout the three triads suggest that the ns^2 lone

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(253) Suzuki, H.; Murafuji, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1169.

pair of electrons ($n = 4-6$) typical for the immediate post-transition-metal elements in their lower oxidation states plays an essential role in determining the mode of bonding. For this reason, relativistic effects which most strongly affect ns orbitals cause noncontinuous behavior among each triad, favoring arene binding to the heaviest elements, Tl, Pb, and Bi, which are also distant post-lanthanide elements. For these elements, centric η^6 hapticity is most common, while for some of the lighter elements (Sn, Sb) lower hapticities (mainly η^3) predominate. There are as yet no simple valence rules, such as the 18-electron rule for arene complexes of the transition metals, which can safely predict the number and hapticity of ligands that can be bound to a low-valent post-transition-metal atom. For some of the nine elements under consideration, mainly In and Ge, the knowledge about arene complexation is still very limited, but some key examples have been detected which suggest that a rich chemistry can also be expected for these poorly developed areas.

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