Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 252 (2008) 1564–1576
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Arene complexes of gallium: An effective tool for the synthesis of transition metal clusters and complexes

Mikhail Gorlov, Lars Kloo*

Inorganic Chemistry, Department of Chemistry, The Royal Institute of Technology (KTH), Stockholm, Sweden

Received 11 July 2007; accepted 18 November 2007
Available online 24 November 2007

Contents

Abstract

In this review, the interactions between gallium(III) halides or gallium(I) subvalent halides and aromatic hydrocarbons in solution and solid state are discussed. Such unique properties of gallium halides–arene mixtures as the ability to reduce metallic centers and accept halide atoms make them very efficient tool for the preparation of low-valent clusters and complexes of transition metals. Diverse mono- and polynuclear arene complexes of d- and f-elements, including coordination polymers, may be achieved by the reactions between transition metal halides and gallium(III) halides in arene media. The role of Lewis acidity of gallium halides, the nature of the substituents on the arene ring and the nature of transition metals are discussed in terms of coordination mode of arenes and resulting structure of the transition metal–arene complexes.

Keywords: Arenes; Gallium halides; Metal—metal bonds; Crystal structures

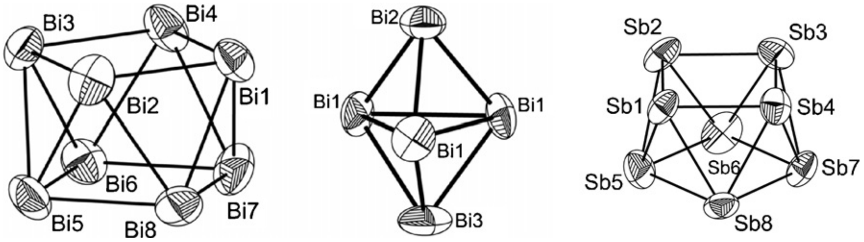
1. Introduction

It has been demonstrated that gallium(III) halides in arene media may be successfully used for the synthesis of cationic clusters of the p-block elements [1]. Thus, cationic clusters of bismuth and tellurium have been prepared by reduction of Bi

---

* Corresponding author.
E-mail address: Larsa@kth.se (L. Kloo).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.11.016



Scheme 1. Cationic bismuth and antimony clusters prepared in GaX_3–arene media.

or Te halides [2]. The first cationic antimony cluster was also synthesized in gallium(III) chloride–arene solution [3]. Some examples are given in Scheme 1.

The special properties of gallium(III) halides, i.e. 1, extremely high solubility in arenes (up to 50 mol% in benzene); 2, the Lewis acidity, the ability to accept halide ions from metal halides (to form anions such as GaX_4^-); 3, the reducing ability of GaX_3–arene mixtures with respect to more noble metal ions, make gallium(III) halides attractive candidates as reagent for the synthesis of low-valent complexes and clusters also of the d- and f-elements.

Similar properties of aluminium(III) halides were widely explored for the preparation of mononuclear low-valent iron complexes [4], binuclear palladium [5] and some f-element arene complexes [6]. Aluminium(III) halides, however, possess several disadvantages in comparison with the corresponding gallium(III) halides. Firstly, the solubility of aluminium(III) halides in arenes (benzene, toluene, *etc.*) is lower than that of gallium(III) halides. Secondly, aluminium(III) halides are very strong Lewis acids, which substantially limits the use of reagents possessing Lewis basic properties.

The inherent Lewis acidity of $GaCl_3$ causes the formation of stable dimers (Ga_2Cl_6), which dominate the chemistry of the pure substance in all aggregation states; it tends to be more molecular than that of the neighbors (Al and In) in Group 13. This property also causes a fairly high vapor pressure that has been utilized for inorganic synthesis, in which vapor transport reactions provide various transition metal gallates [7–9].

The chemistry and bonding in gallium cyclopentadienyl complexes are strongly related to those in gallium–arene compounds. Gallium may be coordinated to the cyclopentadienyl ligand through σ- [10] or π-bonding [11], including bridging mode [12], depending on the formal oxidation state and other ligands attached to the gallium coordination center. It is difficult to overestimate the importance of GaCp ($GaCp^*$) ligands in organometallic synthesis. Recently, an excellent review was published on the application of low-valent Group 13 organometallic compounds (most of them containing a Cp^* moiety) for the synthesis of transition metal clusters and complexes [13].

2. Interaction between gallium halides and arenes

Gallium halides may by divided into two groups depending on the formal oxidation state of the metal: gallium(III) halides and subvalent gallium(I) halides. In both cases, these halides are Lewis acids, and therefore the interaction with aromatic molecules, such as benzene and its derivatives, is vary favorable.

2.1. Gallium(I) halides

Historically, gallium–arene interactions were first studied for subvalent gallium(I) halides. In 1985 Schmidbaur published a review [14] covering the chemistry of $Ga^I(GaX_4)$ complexes (where $X^- = Cl^-, Br^-$) with wide range of arenes—from benzene and its alkylated derivatives to paracyclophane.

A number of gallium(I)–arene complexes were crystallographically characterized [15–22]. In the complex $[(C_6Et_6)(C_6H_5Me)GaGaCl_4]\cdot 1/2(C_6Et_6)$, see Fig. 1, gallium(I) is weakly coordinated (the Ga–C distances lie between 2.87 and 2.93 Å) to the hexaethylbenzene ligand in an η^6-mode [21]. Weak interactions (the shortest Ga–C distance is 3.33 Å) between Ga(I) and the toluene ligand as well as the $GaCl_4^-$ anions are also observed.

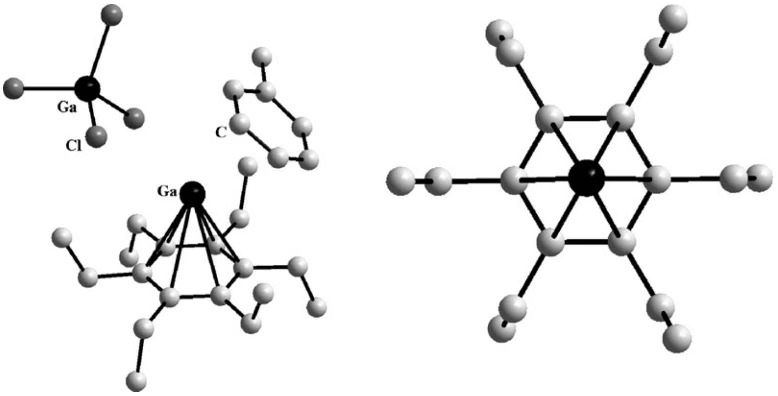


Fig. 1. Fragments of the crystal structure of $[(C_6Et_6)(C_6H_5Me)GaGaCl_4]\cdot 1/2(C_6Et_6)$ [21].

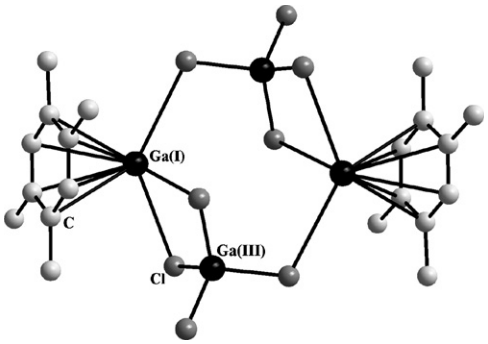


Fig. 2. Fragment of the crystal structure of $[(C_6Me_4)(C_6H_5Me)GaGaCl_4]_2$ [22].

An interesting structural feature is observed in the structure of $[(C_6Me_4)(C_6H_5Me)GaGaCl_4]_2$: two $GaCl_4$ groups connect Ga(I) atoms thus forming an eight-membered ring, as shown in Fig. 2; the tetramethylbenzene ligands are connected to Ga(I) atoms in an η^6-mode, and the toluene ligands are weakly coordinated to Ga(I) (the shortest Ga–C distance is 3.21 Å) [22]. It is notable that this octamembered fragment is very characteristic for Cu(I) and Ag(I) gallates containing arene ligands.

A theoretical investigation of bonding in subvalent gallium–arene complexes has been reported [23]. In this work, the electronic structures of model complexes $[Ga(benzene)]^+$ and $[Ga(benzene)_2]^+$ have been determined using the discrete variation Xα (DVXα) molecular orbital method. It was concluded that a weak dative bond is formed between benzene ligand and Ga(I), and charge is transferred from the π orbitals of the benzene to the three 4p orbitals of the Ga(I) atom [23].

The solution chemistry of $Ga^I(GaX_4)$ in arene media has been studied by different spectroscopic methods [24]. On the basis of NMR (^{13}C and ^{71}Ga), Raman spectroscopy and liquid X-ray scattering (LXS) data it was suggested that Ga^I forms a weak complex with benzene in solution (Ga^I–benzene distances are 2.70 Å). It was also proposed that in solution two benzene rings are coordinated to Ga^I in an η^6-mode. This is in agreement with structural data obtained for $Ga^I(GaX_4)$–arene complexes [15–22].

2.2. Gallium(III) halides

In contrast to relatively *soft* acceptor Ga^I, the Ga^{III} ion may be regarded as a *hard* acceptor, and therefore one may expect more strong interactions between Ga^{III} and arenes. Kochi and co-workers demonstrated that the charge-transfer concept is very useful for the interpretation of metal–arene bonding in transition metal–arene complexes, explaining both structural and chemical properties of this class of compounds [25].

The structure of concentrated solutions of $GaCl_3$ in benzene and mesitylene was studied by multinuclear NMR (^{13}C, ^1H, ^{71}Ga), Raman and UV/vis spectroscopy, including LXS as well as quantum chemistry calculations [26,27]. Gallium(III) chloride was found to be monomeric in mesitylene solution; there is some ambiguity regarding η^1- or η^6-coordination. In benzene, gallium(III) chloride exists as a mixture of different species containing terminal $GaCl_3$-groups, as indicated in Fig. 3 (right); the $GaCl_3$–benzene complex is best described in terms of interaction between the monobridged dimer and benzene.

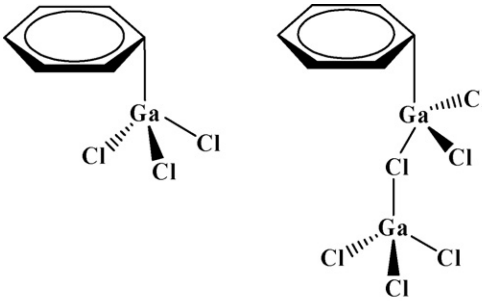


Fig. 3. $GaCl_3$–benzene complexes in solution.

Hydrolysis of a $GaCl_3$–C_6H_6 solution leads to the formation of mixture of poly(*p*-phenylene) and other polymeric species; it was suggested that the formation of polymers proceeds via protonated Wheland intermediates [26].

3. Gallium(III) halides in the synthesis of transition metal clusters and complexes

3.1. 3d-Elements

3.1.1. Iron

The synthesis of bis(arene)iron(II) cationic complexes was for the first time described by Fischer and Böttcher in 1956 [28]. Later, a new synthetic method based on aluminium(III) and iron(III) chlorides was proposed for the synthesis of the bis(benzene)iron(II) complex [4,29]. In spite of the profound interest in the chemistry and catalytic activity of Group VIII, metal–arene complexes [30–32], there are just a few examples of crystallographically characterized bis(arene)iron(II) and analogous bis(arene)ruthenium(II) cationic complexes reported [33–39]. It is important to note that almost all previously described compounds, containing bis(arene)iron(II) or bis(arene)ruthenium(II) cations, are donor–acceptor complexes in the crystalline state. Bis(arene)metal fragments may play the role of donor or acceptor depending on the anion nature. In contrast to bis(arene) complexes, half-sandwich compounds coordinating one arene ligand only, are well characterized by X-ray crystallography [40–42].

It was found [43] that the mixtures of gallium(III) halides and arenes represent a perfect tool for the synthesis of mononuclear bis(arene)iron(II) complexes. Thus, a series of mononuclear iron(II) complexes of the general formula $[Fe(\eta^6\text{-arene})_2](Ga_nX_{3n+1})_2$ (n = 1–3) have been synthesized by the simple reaction between FeX_3 and GaX_3 in arene solution [43]:

$$FeX_3 + GaX_3 + \text{arene} \rightarrow [Fe(\eta^6\text{-arene})_2](Ga_nX_{3n+1})_2 + \text{products of arene oxidation} \quad (1)$$

The structures of the compounds $[Fe(\eta^6\text{-benzene})_2](GaCl_4)_2$, $[Fe(\eta^6\text{-benzene})_2](Ga_3Cl_{10})_2$, $[Fe(\eta^6\text{-toluene})_2](Ga_2Cl_7)_2$, $[Fe(\eta^6\text{-toluene})_2](Ga_2Br_7)_2$ (see Fig. 4) have been confirmed by X-ray crystallography [43].

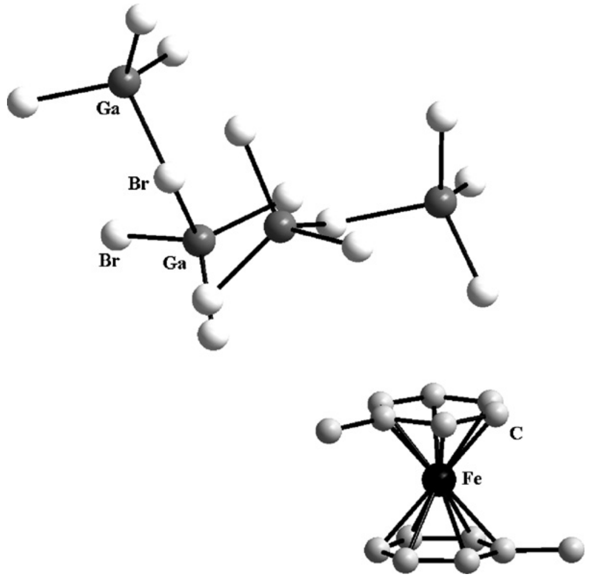


Fig. 4. X-ray structure of $[Fe(\eta^6\text{-toluene})_2](Ga_2Br_7)_2$ [43].

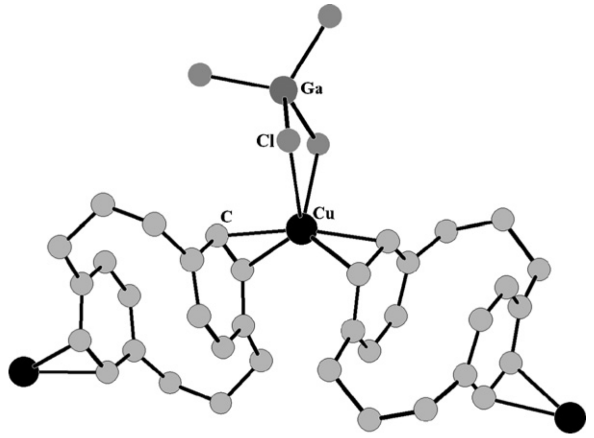


Fig. 5. Fragment of the structure of $[Cu(GaCl_4)\cdot(p\text{-}C_6H_4CH_2CH_2CH_2)_2]$ [45].

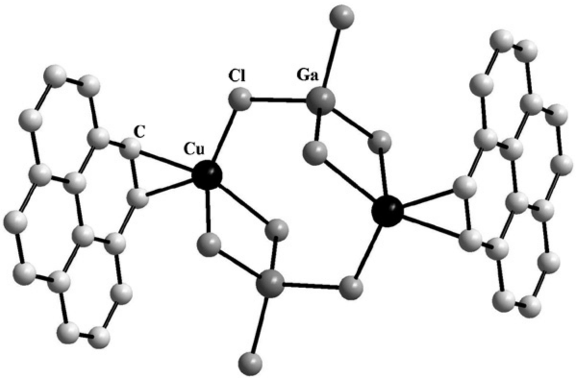


Fig. 6. Crystal structure of $[(Cu(GaCl_4)(pyrene))_2]$.

In these reactions gallium(III) halide–arene mixtures play two roles: 1, reducing agent with respect to iron(III) halides; 2, acceptor of halide ions, thus facilitating coordination of the arene to iron(II).

Crystallographically characterized mononuclear bis(arene) iron and related ruthenium complexes are listed in Table 1. It is important to note that gallium(III)-containing anions $Ga_nX_{3n+1}^-$ do not interact strongly with bis(arene) iron cations in the crystalline state, in stark contrast to the previously reported compounds. This indicates that additional stabilization of $[Fe(arene)_2]^{2+}$ cations is not necessary.

3.1.2. Copper

The first copper–benzene complex $[(C_6H_6)CuAlCl_4]$ was prepared and characterized by Turner and Amma [44]. The authors note that $AlCl_4^-$ anions play important role for the stability of this compound. Copper is bound to benzene in an η^2-manner; Cu–C distances are 2.15 and 2.30 Å, both ±0.03 Å.

The synthesis and crystal structures of polymeric [3.3]paracyclophane and [2.2]paracyclophane chlorogallate complexes $[Cu(GaCl_4)\cdot(p\text{-}C_6H_4CH_2CH_2CH_2)_2]$ (Fig. 5) and $[Cu(GaCl_4)\cdot(p\text{-}C_6H_4CH_2CH_2)_2]$ were reported [45]. In the former compound, copper is coordinated to two [3.3]paracyclophane ligands in an η^2-manner; Cu–C distances are between 2.14 and 2.28 Å [45]. The anion $GaCl_4^-$ is bound to one copper atom.

We have found that copper(I) chloride reacts with gallium(III) chloride in benzene or toluene solution to give arene-free copper(I) tetrachlorogallate $Cu(GaCl_4)$ [46]. This complex may be used as starting material for the synthesis of copper compounds with polycyclic aromatic hydrocarbons (PAHs). Thus, a binuclear copper(I)–pyrene complex $[(Cu(GaCl_4)(pyrene))_2]$, shown in Fig. 6, has been isolated and crystallographically characterized [47,48].

The pyrene ligands are bound to the copper in an η^2-manner (Cu–C distances are 2.14 and 2.13 Å). An interesting feature of this compound is the presence of an eight-membered ring

Table 1
Role of $M(arene)_2$ unit in iron and ruthenium bis(arene) complexes

Donor	Acceptor	Free
$[Fe(C_6Me_3H_3)_2]^{2+}$ $\{[C_3[C(CN)_2]_3]\}_2^{2-}$ [33]	$[Fe(C_6Me_3H_3)_2]^{2+}$ $[C_6(CN)_6]^{2-}$ [34]	$[Fe(C_6H_3Me_3)_2]^{2+}(PF_6^-)_2$ [38]
$[Fe(C_6Me_6)_2]^{2+}$ $[TCNQ^-]_2$ [37]	$[Ru(C_6Me_3H_3)_2]^{2+}$ $[C_6(CN)_6]^{2-}$ [34]	$[Fe(C_6Me_6)_2]^{2+}(PF_6^-)_2$ [35]
$[Ru(C_6Me_6)_2]^{2+}$ $[TCNQ^-]_2$ [37]	$[Fe(C_6Me_6)_2]^{2+}$ $[\mathit{Iso}\text{-}C_4(CN)_6]^{2-}$ [35]	$[Fe(C_6H_6)_2]^{2+}(GaCl_4^-)_2$ [43]
$[Fe(C_6Me_6)_2]^{2+}$ $[F_4\text{-}TCNQ^-]_2$ [37]	$[Ru(C_6Me_6)_2]^{2+}$ $[\mathit{Iso}\text{-}C_4(CN)_6]^{2-}$ [35]	$[Fe(C_6H_6)_2]^{2+}(Ga_3Cl_{10}^-)_2$ [43]
$[Ru(C_6Me_6)_2]^{2+}$ $[F_4\text{-}TCNQ^-]_2$ [37]	$[(C_6Me_4H_2)_2Fe^{2+}, Cp_2Fe](PF_6^-)_2$ [36]	$[Fe(C_6H_5Me)_2]^{2+}(Ga_2Cl_7^-)_2$ [43]
$[Fe(C_6Me_6)_2]^{2+}$ $[Cl_2\text{-}TCNQ^-]_2$ [37]	$[(C_6Me_6)_2Fe^{2+}, C_6Me_4H_2](PF_6^-)_2$ [36]	$[Fe(C_6H_5Me)_2]^{2+}(Ga_2Br_7^-)_2$ [43]
$[Ru(C_6Me_6)_2]^{2+}$ $[Cl_2\text{-}TCNQ^-]_2$ [37]	$[(C_6Me_6)_2Fe]^{2+}$ $(C(CN)_3)_2$ [39]	$[Ru(C_6H_5Me)_2]^{2+}(Ga_2Cl_7^-)_2$ [43]

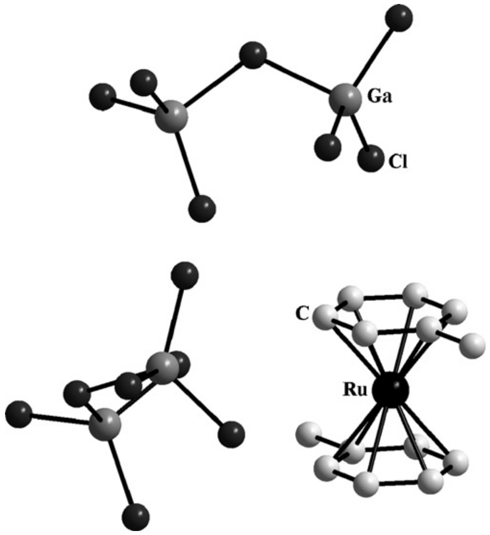


Fig. 7. Crystal structure of [Ru(η^6-toluene)$_2$(Ga_2Cl_7)$_2$].

(two $GaCl_4$-groups connect the copper atoms). We will highlight that this structural unit is typical for silver(I)–arene gallates in Section 3.2. In general, the easily available copper(I) tetrachlorogallate Cu($GaCl_4$) seems to be a promising starting material for the synthesis of copper(I) complexes with PAHs.

It should be noted that the benzene complex ((bz)$CuCl_3$)$_2$Zr (bz = η^2-benzene) was isolated from the CuCl–$ZrCl_4$–benzene system [49] similar to CuCl–$GaCl_3$–benzene system. This compound has a one-dimensional structure constructed from eight-membered rings Cu(bz)(μ-$ZrCl_3$)$_2$.

3.2. 4d-Elements

3.2.1. Ruthenium

Ruthenium(III) halides react with corresponding gallium(III) halides in arene media similarly to iron(III) halides. Thus, the mononuclear ruthenium(II) bis(toluene) complex [Ru(η^6-toluene)$_2$(Ga_2Cl_7)$_2$] was isolated and structurally characterized [43], see Fig. 7.

As in the case of the iron system, ruthenium(III) is reduced by the $GaCl_3$–toluene mixture, but metal–metal bond formation is not observed. It should be noted that ruthenium(II)–bis(arene) complexes have been described in literature [35,36,40,50,51], but synthetic routes to these compounds are more complicated in comparison with the one-step synthesis based on GaX_3–arene mixtures.

3.2.2. Palladium

Since the discovery of the first compound containing a direct single palladium–palladium bond [52], a large number of these complexes were synthesized and structurally characterized. The structure, chemistry and catalytic properties of clusters with Pd–Pd bonds were recently reviewed [53,54]. These compounds may take part in a wide range of catalytic reactions: isomerization of double C–C bonds [55,56], hydrogenation of multiple bonds [57–59], hydrogen-transfer reduction [60–62] and carbonylation [63–66].

Table 2
Palladium–palladium distances in binuclear palladium(I)–arene clusters

Compound	Pd–Pd (Å)	Reference
[$Pd_2(C_6H_6)_2(GaCl_4)_2$]	2.584	[69]
[$Pd_2(C_6H_6)_2(GaBr_4)_2$]	2.604	[70]
[$Pd_2(C_7H_8)_2(GaCl_4)_2$]	2.572	[69]
[$Pd_2(C_7H_8)_2(GaBr_4)_2$]	2.578	[70]
[$Pd_2(C_8H_6)_{10}(GaCl_4)_2$]	2.562	[70]
[$Pd_2(C_8H_{10})_2(GaBr_4)_2$]	2.578	[70]
[$Pd_2(C_6H_6)_2(Ga_2Cl_7)_2$]	2.562	[69]

Dipalladium clusters having arenes as ligands were prepared for the first time by Allegra et al., and crystal structures of two benzene compounds [$Pd_2(bz)_2X_2$] (X^- = $AlCl_4^-$ or $Al_2Cl_7^-$) were determined [5,67]. Later, it was found [68] that they could be used as catalysts for ethylene dimerization. For synthesis of these complexes, an $AlCl_3$/Al mixture was used; elemental aluminium formally reduces palladium(II) to palladium(I).

We have demonstrated that gallium(III) halides in arene media are very efficient reducing agents with respect to palladium(II) halides [69,70]. In these systems, no metallic gallium is needed. Binuclear palladium(I) complexes of the general formula [Pd_2^I(arene)$_2L_2$] have been isolated in high yield (up to 95%) under mild conditions:

$$PdX_2 + GaX_3 + \text{arene} \rightarrow [Pd_2^{I}(\text{arene})_2L_2] + \text{products of arene oxidation} \qquad (2)$$

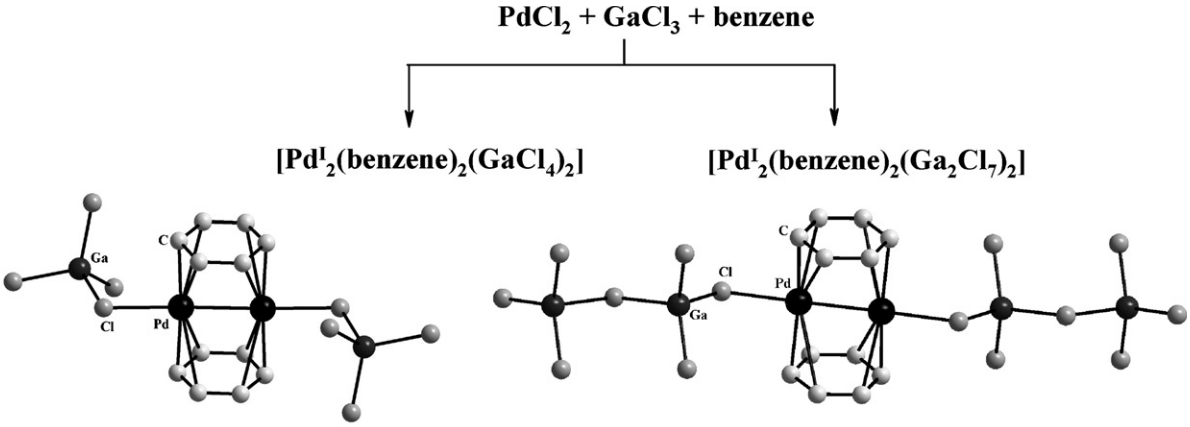
where X^- = Cl^-, Br^-; arene = benzene or alkylbenzenes; L^- = GaX_4^- or $Ga_2X_7^-$ groups connecting to the dipalladium unit via bridging halide atoms. The series of dipalladium compounds that has been prepared and characterized by single crystal X-ray diffraction is shown in Table 2.

Palladium–palladium distances lie within 2.5–2.6 Å, which is in agreement with structural data obtained for other Pd(I)–Pd(I) complexes with single Pd–Pd bonds [53].

Gallium halides act as acceptors of halide atoms; different groups like GaX_4^- or $Ga_2X_7^-$ may be bound to the dipalladium unit, as highlighted in Scheme 2. Thus, in the case of the $PdCl_2$–$GaCl_3$–benzene system, both complexes may be isolated in crystalline form. In general, gallium(III) halides tend to form polynuclear anions $Ga_nX_{3n+1}^-$; as it was shown for iron and platinum systems, also compounds with $Ga_3X_{10}^-$ may be formed [43,71].

The coordination mode of the arene ligands in binuclear palladium(I) arene complexes may be described as η^3:μ:η^3, but the Pd–C distances vary within one molecule (for example, between 2.21 and 2.93 Å for [$Pd_2(bz)_2(Ga_2Cl_7)_2$]). Normally, palladium forms two short contacts and one long contact with one arene ligand. For example, in [$Pd_2(bz)_2(GaCl_4)_2$] the Pd–C distances between palladium and one benzene ligand are 2.23, 2.37 and 2.78 Å, and 2.22, 2.41 and 2.74 Å.

The nature of the Lewis acids GaX_3 (X^- = Cl^-, Br^-, I^-) plays an important role in reaction (2). Thus, in the case of a strong Lewis acid like $GaCl_3$, the major products are binuclear compounds [Pd_2^I(arene)$_2L_2$], whereas using $GaBr_3$, a mixture of [Pd_2^I(arene)$_2L_2$] and [Pd^{II}($GaBr_4$)$_2$] complexes are formed



Scheme 2. Binuclear Pd(I) clusters isolated from $PdCl_2$–$GaCl_3$–benzene system.

[70,72]. In the analogous iodide system, representing a weaker Lewis acid, only $[Pd^{II}(GaI_4)_2]$ was isolated and no products containing palladium(I) complexes can be observed [72]. This trend is illustrated in Scheme 3.

A very interesting extension of this chemistry was reported by Kurosawa and co-workers in their studies of the catalytic effects of directly metal–metal-bonded dimeric transition metal aggregates, including palladium dimers [73,74]. As noted by the authors, the stabilization of dimeric, subvalent Pd units could be extended using polyene ligands [75,76], displaying linear chains of up to four Pd atoms (see Fig. 8). Typical Pd–Pd distances are 2.6–2.7 Å.

The synthetic route to this family of compounds was typical organometallic; a Pd^I dimer with labile nitrile ligands was reacted with a Pd^0 compound in presence of the polyene ligand in organic solution. Late findings involve the fascinating “sheet-like” sandwich compounds of Pd_3 and Pd_5 entities with PAHs [77]. Formally, the Pd aggregates have an oxidation state lower than +I.

Mono-arene dipalladium(I) complexes are also known [78–80]. Thus, the synthesis and chemistry of unusual binuclear complexes $[Pd_2X(\mu\text{-}X)P^tBu_2Bph]$ ($X^- = Cl^-$, Br^-, Bph = biphenyl) with an intramolecular coordination of a phenyl group to the dipalladium unit have been reported [78,79]. These complexes are catalytically active in the reactions of amination of aryl chlorides [79]. Not only six-membered aromatic ligands may be coordinated to the dipalladium(I) center; the structure and solution chemistry of indenyl complexes $[Pd_2(\mu\text{-}Cl)(\mu, \eta^3\text{-}indenyl)(PR_3)_2]$ have recently also been reported [80].

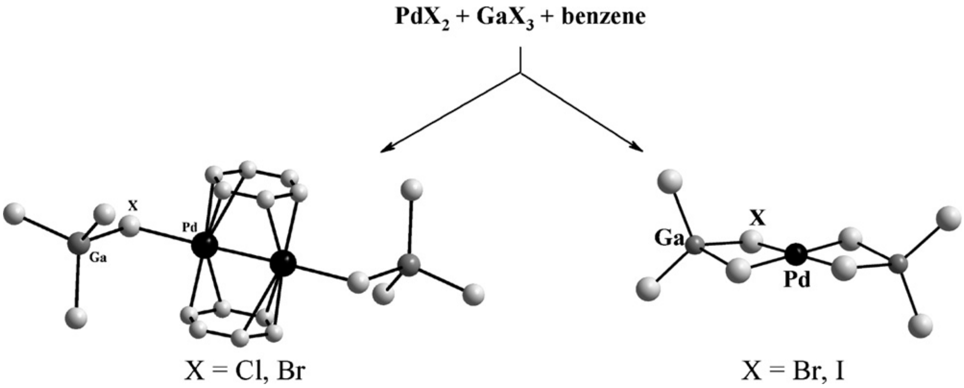
3.2.3. Silver

Arene complexes of silver are known since 1958, when the $[Ag(ClO_4)(benzene)]$ complex was prepared and characterized [81]. Later, a large number of mono- and polynuclear compounds containing alkylbenzenes or PAHs coordinated to silver(I) have been described [45,82–90]. The chemistry of multilayer silver(I) complexes with PAHs was recently reviewed [86]. It was shown that one-, two- and three-dimensional compounds can be designed. The authors note that the coordinative versatility of aromatic ligands and the nature of the anions play a crucial role with respect to the resulting structure of the compound [86].

Silver gallates, like $Ag(GaCl_4)$, were also studied as precursors for the synthesis of silver–arene complexes [45]. As a consequence, [2.2]paracyclophane complexes $[Ag(GaX_4)\cdot(p\text{-}C_6H_4CH_2CH_2)_2]$ ($X^- = Cl^-$, Br^-), shown in Fig. 9, were isolated [45].

Silver atoms are coordinated to two [2.2]paracyclophane ligands in η^2- and η^3-manner. The Ag–C distances in $[Ag(GaCl_4)\cdot(p\text{-}C_6H_4CH_2CH_2)_2]$ vary from 2.43 to 2.66 Å.

In our lab, the reactions between silver(I) halides and gallium(III) halides in arene media have been investigated [91–93]. It was observed that the nature of the substituents on the arene



Scheme 3. The role of Lewis acidity of GaX_3 in PdX_2–GaX_3–arene systems.

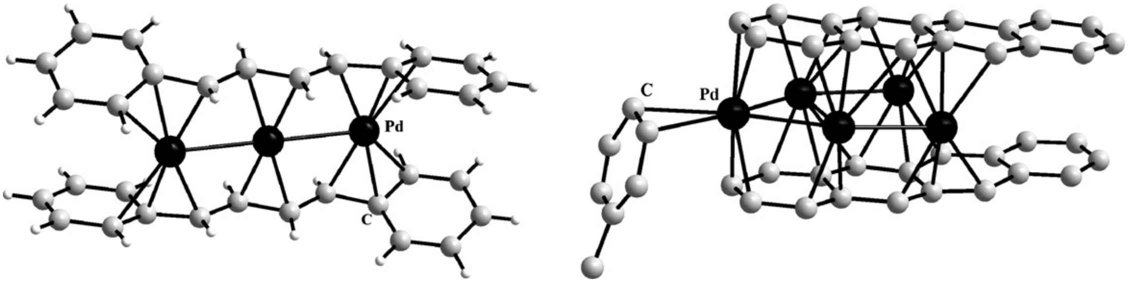


Fig. 8. The Pd_3 chains [76] and Pd_5 “sheets” isolated [77].

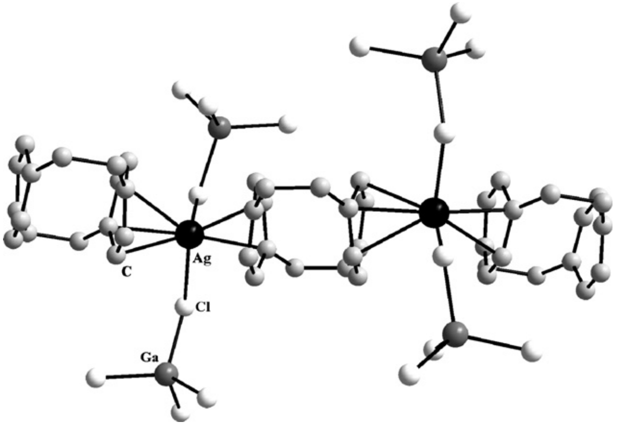


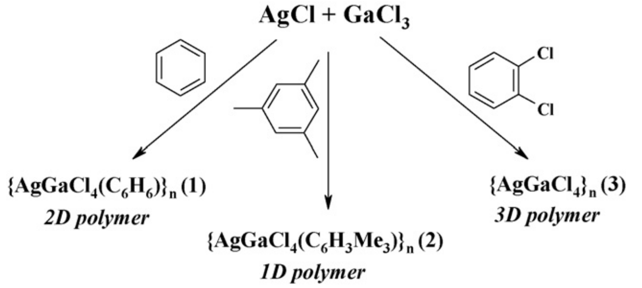
Fig. 9. Fragment of the structure of $[Ag(GaX_4)\cdot(p\text{-}C_6H_4CH_2CH_2)_2]$.

ring play a determinant role with respect to the eventual structure of the products.

As shown in Scheme 4, one-, two- and three-dimensional compounds have been isolated depending on the electron-donor properties of the substituents on the arene ring.

In the crystal structure, the benzene complex $\{Ag(GaCl_4)(bz)\}_n$ (Figs. 10 and 11) forms infinite sheets, composed of two organic layers separated by an inorganic layer. The silver atoms are connected to three carbon atoms; Ag–C distances are 2.87, 2.48 and 2.84 Å [91].

The corresponding mesitylene compound $\{Ag(GaCl_4)(C_6H_3(CH_3)_3)\}_n$ was prepared in a similar way as the benzene complex through the reaction between AgCl and $GaCl_3$ in mesitylene [92]. As in the case of the benzene system, gallium(III) chloride plays the role of Lewis acid, thus accepting chloride ions from the silver ions. One can conclude that the presence of electron-donor substituents on the arene molecule facilitates the formation of silver–arene bonds. This is in agreement with literature data: all π-bonded silver(I)–arene complexes isolated so far are based on alkyl- or cycloalkyl- substituted arenes [45,81–90]. In the crystal structure, eight-membered rings in $\{Ag(GaCl_4)(C_6H_3(CH_3)_3)\}_n$ form one-dimensional polymeric chains, as seen in Fig. 12; in contrast to $\{Ag(GaCl_4)(bz)\}_n$, where eight-membered rings compose a two-dimensional sheet structure. The Ag–C distances in $\{AgGaCl_4(C_6H_3(CH_3)_3)\}_n$ are 2.86, 2.43 and 2.86 Å. In general, the Ag–C distances are 0.3–0.7 Å longer than in the Cu–C ones in copper gallates. It is important to note the difference in metal–arene coordination mode (η^2 for Cu and η^3 for Ag).



Scheme 4. Synthesis of polymeric silver(I) gallates in arene media.

The presence of electron-acceptor groups on the arene ring precludes the coordination of arenes to silver atoms. Thus, the reaction between AgCl and $GaCl_3$ in 1,2-dichlorobenzene leads to the formation of the inorganic 3D-polymeric $\{Ag(GaCl_4)\}_n$ compound [93] (Fig. 13).

Interestingly, the eight-membered rings seem to constitute a very stable structural unit; it is present in all silver gallates. A similar unit is also characteristic for copper(I) and gallium(I) gallates.

3.3. 5d-Elements

3.3.1. Platinum

In contrast to palladium, only one binuclear π-bonded platinum(I)–(η^6-arene) complex has been crystallographically

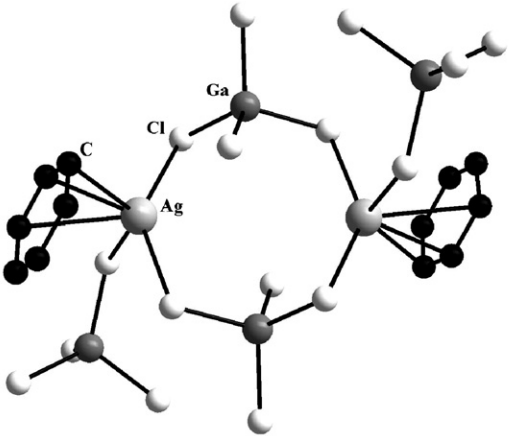


Fig. 10. Fragment of the structure of $\{Ag(GaCl_4)(bz)\}_n$.

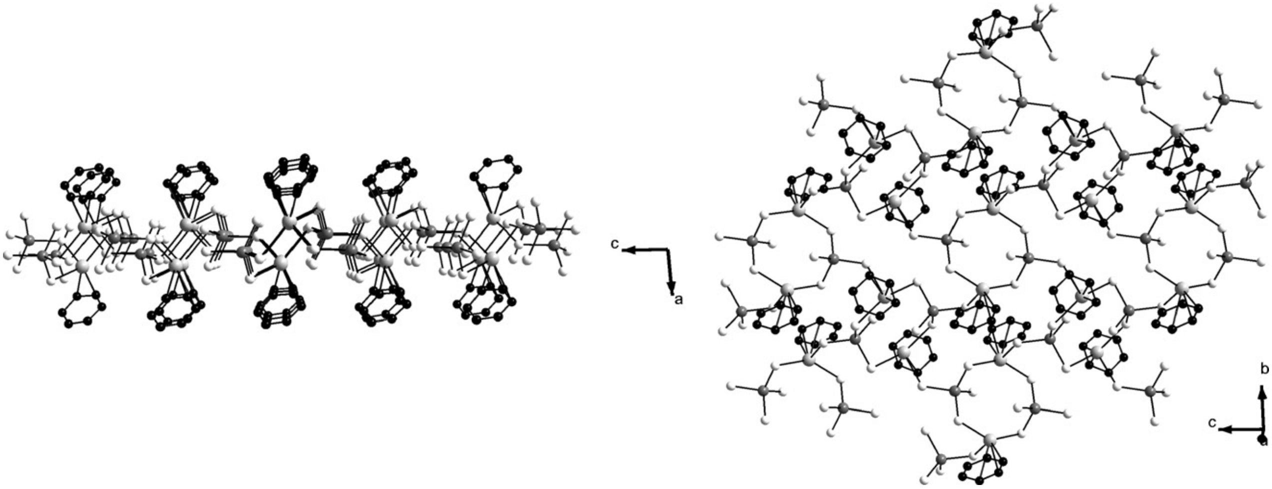


Fig. 11. 2D-structure of $\{Ag(GaCl_4)(bz)\}_n$.

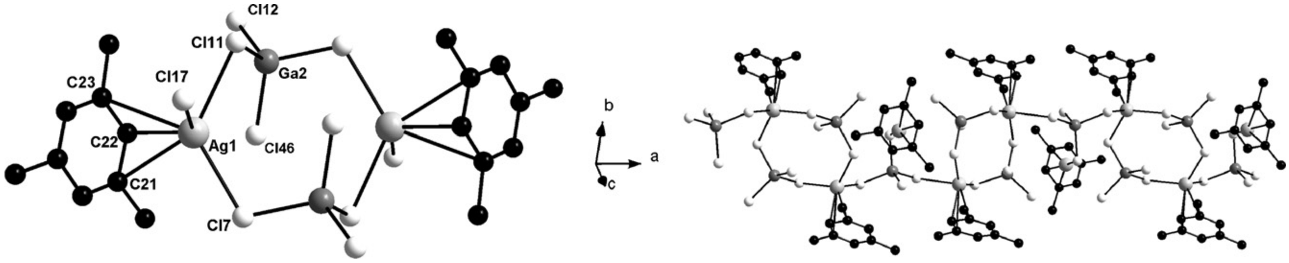


Fig. 12. Structure of $\{Ag(GaCl_4)(C_6H_3(CH_3)_3)\}_n$.

characterized [69]. The use of GaX_3–arene mixtures seems to be efficient way for the preparation of these compounds. Thus, a binuclear platinum(I) naphthalene complex $[Pt_2(C_{10}H_{10})_2(GaCl_4)_2]\cdot 2C_6H_6$ has been prepared by the reaction between $K_2[PtCl_4]$, $GaCl_3$ and naphthalene in benzene solution [69], as displayed in Fig. 14. Each platinum atom is connected to two carbon atoms of the naphthalene ligand; Pt–C distances range 2.17–2.25 Å.

A similar platinum(I) *p*-xylene compound, $[Pt_2(p\text{-xylene})_2(Ga_2Br_7)_2]$, was isolated from the $K_2[PtBr_4]$–$GaBr_3$ system in *p*-xylene solution, also shown in Fig. 14; Pt–C distances lie between 2.21 and 2.24 Å [94]. The important difference between platinum(I) and palladium(I) complexes (Section 3.2) is the coordination mode of the arene ligands: in the case of platinum, arenes are coordinated to the Pt_2^{2+} unit in a $\eta^2{:}\mu{:}\eta^2$ mode, whereas in palladium complexes the coordination mode of the arenes to the Pd_2^{2+} unit may be described as $\eta^3{:}\mu{:}\eta^3$.

An unusual binuclear platinum(0) complex was isolated in the reaction between platinum(II) chloride, gallium(III) chloride

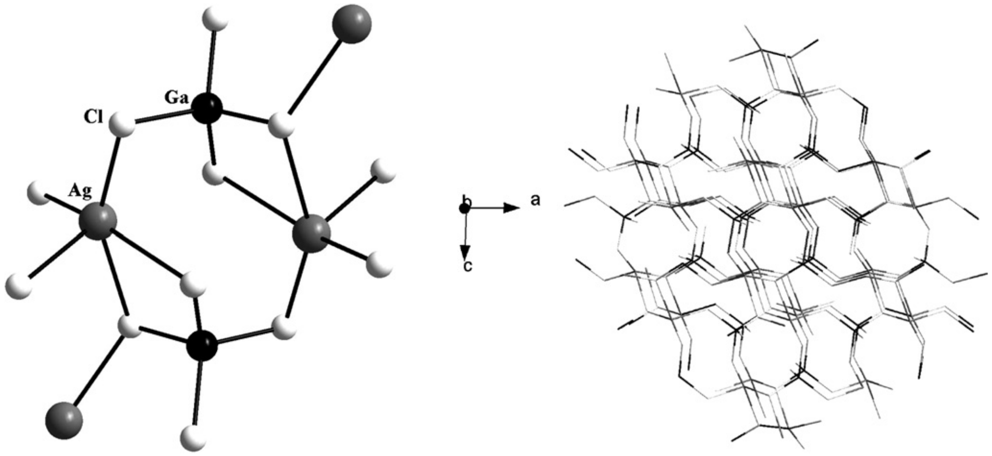


Fig. 13. Structure of $\{Ag(GaCl_4)\}_n$.

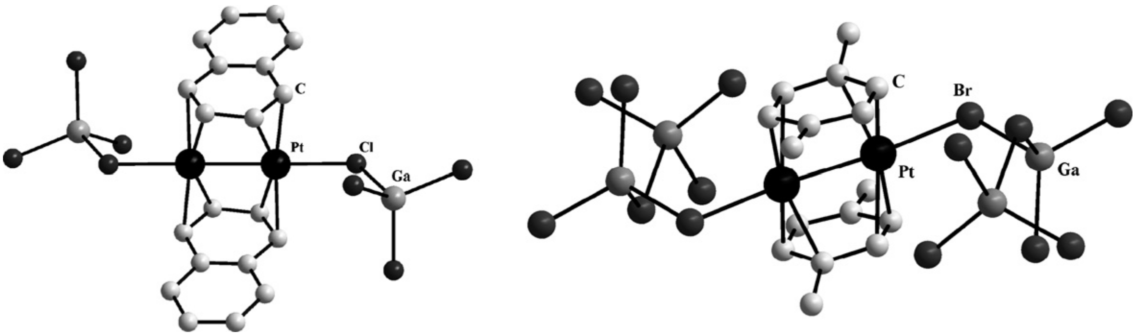


Fig. 14. Crystal structures of $[Pt_2(C_{10}H_{10})_2(GaCl_4)_2]\cdot 2C_6H_6$ and $[Pt_2(p\text{-xylene})_2(Ga_2Br_7)_2]$.

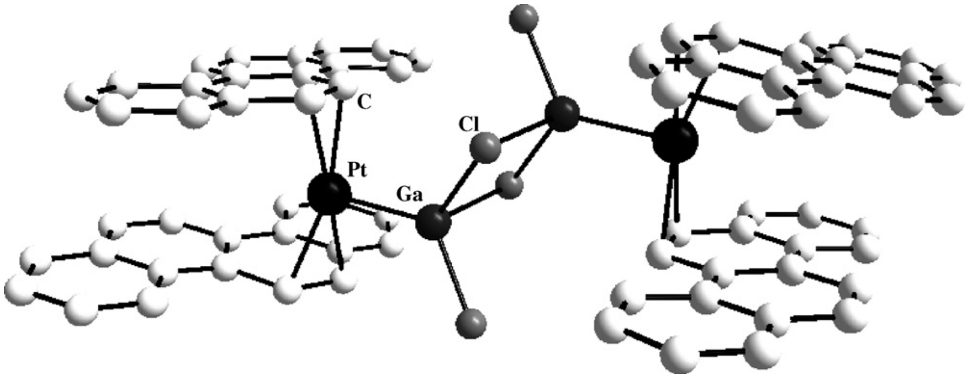


Fig. 15. Structure of the cation $[Pt_2(Ga_2Cl_2(\mu\text{-}Cl)_2)(chrysene)_4]^{2+}$.

and chrysene in 1,2-dichlorobenzene solution [71]:

$$PtCl_2 + GaCl_3 + chrysene \rightarrow [Pt_2(Ga_2Cl_2(\mu\text{-}Cl)_2)(chrysene)_4](Ga_3Cl_{10})_2 \qquad (3)$$

In this reaction (3), two direct Pt–Ga bonds are formed (2.34 Å). The structure of the cation is shown in Fig. 15. The platinum–gallium distance is comparable to those in platinum(0)–gallium(I) complexes, previously described in literature [95–99].It should be emphasized that the isolation of this compound demonstrates diversity of reaction routes based on platinum or palladium halides in combination with gallium halides in arene media.

3.3.2. *Mercury*

Barron and co-workers described the synthesis and crystal structures of a series of mercury(II) complexes of the general formula $Hg(arene)(MCl_4)_2$, where M = Al or Ga; arene = mono- or dialkylbenzenes [100–103]. These compounds were prepared by the reaction between $HgCl_2$ and $GaCl_3$ in arene media:

$$HgCl_2 + GaCl_3 + arene \rightarrow Hg(arene)(GaCl_4)_2 \qquad (4)$$

Notably, in these reactions gallium(III) chloride plays the role of acceptor of chloride ions, but no reduction of mercury(II) was observed in arene media in spite of the strong reducing ability of $GaCl_3$–arene mixtures and the high stability of the Hg_2^{2+} unit.

The authors note [101] that compounds of the type $Hg(arene)(MCl_4)_2$ may exist in two forms: neutral $[Hg(arene)(MCl_4)_2]$ or ionic $[Hg(arene)(MCl_4)](MCl_4)$ depending on the nature of the arene molecules. The mercury–arene bonding may be described as of highly asymmetric η^2-type. Thus, the Hg–C distances in the toluene compound $[Hg(toluene)(GaCl_4)_2]$ are 2.35 and 2.71 Å. The structure is shown in Fig. 16.

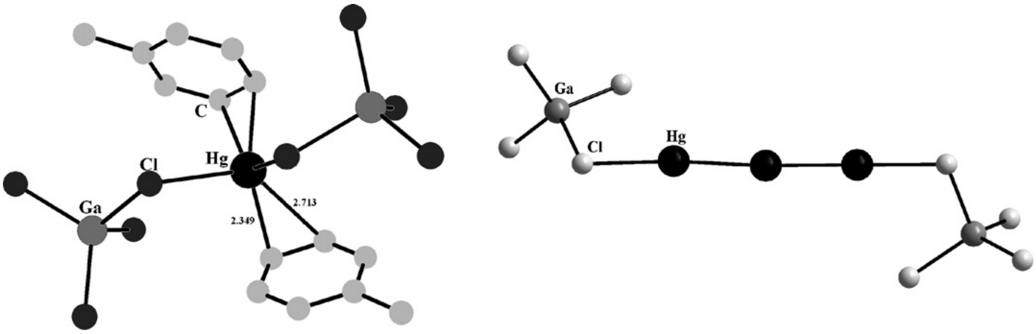


Fig. 16. Crystal structures of $Hg(toluene)(GaCl_4)_2$ [101] and $Hg_3(GaCl_4)_2$ [104].

Table 3
Selected bond lengths (Å) in lanthanide–arene complexes

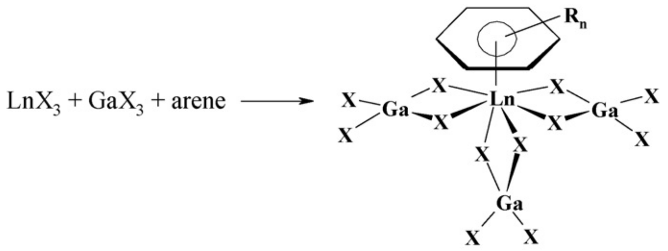
Complex	Ln–C	Ln–X	Ga–(η–X)	Ga–X
$[Ce(C_6H_5Me)(GaCl_4)_3]$	2.89–3.03	2.81–2.91	2.21–2.24	2.10–2.12
$[Ce(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$	2.94–2.96	2.85–2.91	2.22–2.23	2.10–2.12
$[Yb(C_6H_5Me)(GaCl_4)_3]$	2.77–2.94	2.66–2.80	2.22–2.25	2.10–2.12
$[Yb(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$	2.82–2.88	2.70–2.80	2.23–2.24	2.10–2.11
$[Dy(C_6H_5Me)(GaBr_4)_3]$	2.79–2.96	2.85–2.98	2.36–2.39	2.25–2.27
$[Ce(naphthalene)(GaCl_4)_3]$	2.91–3.00	2.83–2.91	2.22–2.24	2.08–2.12
$[Ce(pyrene)(GaCl_4)_3]\cdot 0.5(pyrene)$	2.91–3.03	2.83–2.91	2.21–2.24	2.10–2.12

Gallium(III) chloride activates the mercury towards the coordination of arenes. It was found that complexes like $Hg(arene)(GaCl_4)_2$ catalyze the H/D exchange reaction of C_6D_6 with arenes [103].

In our lab the chemical reactivity of mercury(I) halides with respect to gallium(III) halides in arene media has been studied [104,105]. It was found that mercury(I) chloride reacts with gallium(III) chloride in benzene/1,2-dichlorobenzene solution to give the binuclear complex $Hg_2(GaCl_4)_2$. Reduction of mercury(I) chloride with mercury metal in gallium(III) chloride–benzene mixture leads to the trinuclear compound $Hg_3(GaCl_4)_2$. It is notable that the arenes play a role in the further reduction of mercury, since the analogous reaction in absence of arenes in molten salts does not reduce Hg_2^{2+} any further. Based on spectroscopic and LXS data from the arene solution, it can be concluded that the arenes are coordinated to the subvalent, cationic mercury chains in an end-on mode, rather than in a sandwich mode [105]. However, in the crystalline compounds isolated no coordination of arene to the mercury was observed [105]. It should be noted that in similar system with aluminium, complex $[Hg_2(C_6Me_6)](AlCl_4)_2$ was isolated and structurally characterized [106] displaying an end-on coordination mode, where the aluminates take the sandwiching coordination site. This is an interesting difference with respect to the analogous Pd^I dimers, in which the arenes primarily are found in the sandwiching coordination site.

3.4. f-Elements

Arene complexes of the f-block elements have been of constant interest over the last two decades [6,107–122]. In general, lanthanide–arene complexes described in literature can be divided into two groups: mono(arene) and bis(arene) complexes [107]. The oxidation state of the lanthanide atoms varies from +3 to 0 [108–120]; coordinated arene ligands may be present in neutral as well as in anionic forms [111–113].



Scheme 5. Reaction of gallium(III) halides with f-block element halides in arenes.

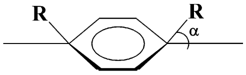
One of the most simple and effective synthetic routes to lanthanide–mono(arene) complexes, containing arene ligands coordinated to the metal in η^6-mode, is the reaction of a lanthanide halide with aluminium(III) halide in arene solution. Employing this method, a series of mononuclear complexes of Sm [108,114–116], La [111], Nd [111,115], Gd [115], Yb [115], Y [121], Pr [121], Eu [122] and U [108,120] has been prepared. As arene ligands, benzene and its alkylated derivatives have been used.

We have found that mononuclear arene complexes $[Ln(\eta^6\text{-}arene)(GaX_4)_3]$ may be easily prepared by the reaction between LnX_3 (where Ln = Ce, Yb, Dy; $X^- = Cl^-$, Br^-) and excess of the corresponding GaX_3 in toluene or *p*-xylene [43], as shown in Scheme 5.

The X-ray structures of $[Ce(C_6H_5Me)(GaCl_4)_3]$, $[Ce(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$, $[Yb(C_6H_5Me)(GaCl_4)_3]$, $[Yb(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$ and $[Dy(C_6H_5Me)(GaBr_4)_3]$ were determined [43].

In all cases, the arene ligands are coordinated to the lanthanide ion in η^6-mode. Selected interatomic distances are listed

Table 4
The deviation of the methyl groups out of the aromatic plane in $[Ln(\eta^6\text{-}arene)(GaX_4)_3]$

Complex	α (°)	
$[Ce(C_6H_5Me)(GaCl_4)_3]$	2.7	
$[Ce(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$	8.4; 4.1	
$[Yb(C_6H_5Me)(GaCl_4)_3]$	2.5	
$[Yb(p\text{-}C_6H_4Me_2)(GaCl_4)_3]\cdot 0.5(p\text{-}C_6H_4Me_2)$	11.3; 5.0	
$[Dy(C_6H_5Me)(GaBr_4)_3]$	5.1	

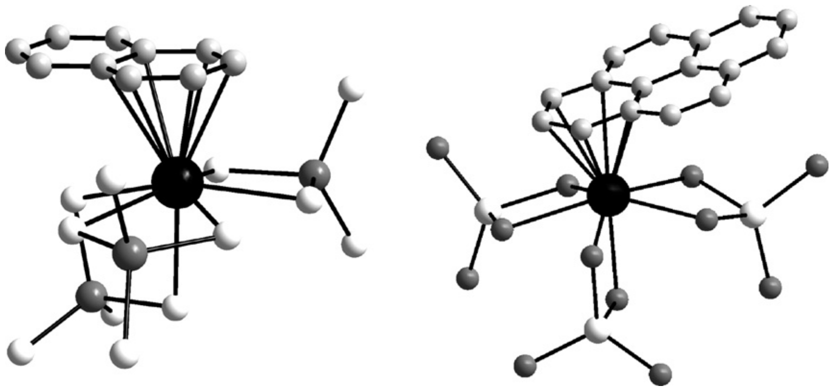
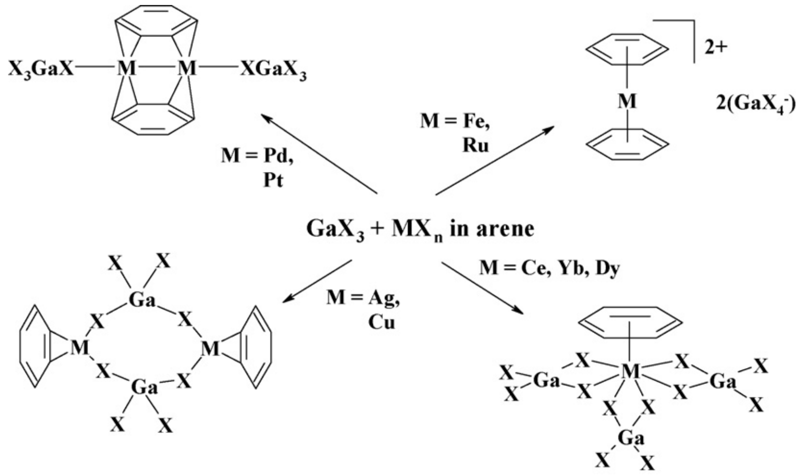


Fig. 17. Molecular structures of [Ce(naphthalene)$(GaCl_4)_3$] and [Ce(pyrene)$(GaCl_4)_3$]·0.5(pyrene).



Scheme 6. Gallium(III) halide–arene mixtures for the synthesis of transition metal complexes.

in Table 3. The lanthanide–carbon distances lie between 2.8 and 3.0 Å, and they do not significantly depend on the nature of the lanthanide atom (for cerium compounds Ln–C distances are slightly longer). Ga–(μ–X) distances are longer than those between gallium and non-bridging halide ions.

An interesting structural feature observed in these complexes is the distortion of the planarity of the arene ligands. In all cases the methyl groups are bent out of the aromatic plane. The deviation angle α varies between 2.7° and 11.3° (Table 4). Hubig et al. noted [25] that “there is a trend between bending angle α and the degree of charge transfer from the arene donor to the coordinated acceptor”.

The benzene or toluene ligands in [Ln(η^6-arene)$(GaX_4)_3$] may be substituted by PAHs. Thus, the reactions between [Ce(C_6H_5Me)$(GaCl_4)_3$] and naphthalene or pyrene yield crystalline compounds [Ce(naphthalene)$(GaCl_4)_3$] and [Ce(pyrene)$(GaCl_4)_3$]·0.5(pyrene), respectively [43]. The products are shown in Fig. 17.

4. Concluding remarks and future prospects

The contents of the present review show that gallium(III) halide–arene systems constitute a versatile tool for the preparation of different classes of complexes and clusters of the d- and f-elements. The ability to reduce metal centers exhibited by gallium(III) halide–arene mixtures may be used for the preparation of low-valent compounds or clusters supported by metal–metal bonds. In addition, the use of easily available starting materials (anhydrous metal halides) and one-step synthetic procedures make this strategy very attractive for practical work. An indication of this versatility is shown in Scheme 6.

The potential of compounds, containing simple arene ligands, like benzene or alkylbenzenes, coordinated to the metal centers, may be used for the further formation of more complex molecular aggregates. Indeed, weakly coordinated arenes may be easily substituted by polycyclic aromatic hydrocarbons or P-donor ligands.

Activation of arene ligands coordinated to mono- or bimetallic centers is another attractive direction in which to explore the chemical reactivity of such compounds. Moreover, many of these compounds may be prepared *in situ*, which means that simple mixtures gallium(III) halide-transition metal halide in arene media may possess catalytical activity with respect to activation of C–H bonds. Such catalytical properties of GaX_3/MX_n/arene systems are under current investigation in our group.

Acknowledgements

This work was supported by the Swedish Research Council and the Göran Gustafsson Foundation.

References

[1] S. Ulvenlund, A. Wheatley, L.A. Bengtsson, J. Chem. Soc., Chem. Commun. (1995) 59.

[2] A.N. Kuznetsov, B.A. Popovkin, K. Stahl, M. Lindsjö, L. Kloo, Eur. J. Inorg. Chem. 24 (2005) 4907.

[3] M. Lindsjö, A. Fischer, L. Kloo, Angew. Chem. Int. Ed. 43 (2004) 2540.

[4] J.F. Helling, S.L. Rice, D.M. Briatsch, T. Mayer, J. Chem. Soc. Chem. Commun. (1971) 930.

[5] G. Allegra, G.T. Casagrande, A. Immirzi, L. Porri, G. Vitulli, J. Am. Chem. Soc. 92 (1970) 289.

[6] M.N. Bochkarev, Chem. Rev. 102 (2002) 2089.

[7] H. Schäfer, Z. Anorg. Allgem. Chem. 426 (1976) 113.

[8] H. Schäfer, J. Nowitski, Z. Anorg. Allgem. Chem. 435 (1977) 49.

[9] H. Schäfer, J. Nowitski, Z. Anorg. Allgem. Chem. 437 (1977) 10.

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

[11] B. Buchin, C. Gemel, T. Cadenbach, R. Schmid, R.A. Fischer, Angew. Chem. Int. Ed. 45 (2006) 1074.

[12] S. Scholz, J.C. Green, H. Lerner, M. Botle, M. Wagner, Chem. Commun. (2002) 36.

[13] C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R.A. Fischer, Eur. J. Inorg. Chem. (2004) 4161.

[14] H. Schmidbaur, Angew. Chem. 97 (1985) 893.

[15] H. Schmidbaur, U. Thewalt, T. Zafiropoulos, Organometallics 2 (1983) 1550.

[16] M. Uson-Finkenzeller, W. Bublak, B. Huber, G. Mueller, H. Schmidbaur, Z. Naturforsch. B 41B (1986) 346.

[17] H. Schmidbaur, W. Bublak, B. Huber, G. Mueller, Helv. Chim. Acta 69 (1986) 1742.

[18] H. Schmidbaur, W. Bublak, B. Huber, G. Mueller, Z. Naturforsch. B 42 (1987) 147.

[19] H. Schmidbaur, R. Nowak, W. Bublak, P. Burkert, B. Huber, G. Mueller, Z. Naturforsch. B 42 (1987) 553.

[20] H. Schmidbaur, R. Hager, B. Huber, G. Mueller, Angew. Chem. 99 (1987) 354.

[21] H. Schmidbaur, R. Nowak, B. Huber, G. Mueller, Z. Naturforsch. B 43 (1988) 1447.

[22] H. Schmidbaur, R. Nowak, B. Huber, G. Mueller, Polyhedron 9 (1990) 283.

[23] G.A. Bowmaker, H. Schmidbaur, Organometallics 9 (1990) 1813.

[24] S. Ulvenlund, A. Wheatley, L.A. Bengtsson, J. Chem. Soc., Dalton Trans. (1995) 245.

[25] S.M. Hubig, S.V. Lindeman, J.K. Kochi, Coord. Chem. Rev. 200–202 (2000) 831.

[26] S. Ulvenlund, A. Wheatley, L.A. Bengtsson, J. Chem. Soc., Dalton Trans. (1995) 255.

[27] L. Bengtsson-Kloo, S. Ulvenlund, Spectrochim. Acta A 53A (1997) 2129.

[28] E.O. Fischer, R. Böttcher, Chem. Ber. 89 (1956) 2397.

[29] J.F. Helling, D.M. Braitsch, J. Am. Chem. Soc. 92 (1970) 7207.

[30] J.L. Atwood, S.D. Christie, M.D. Clerk, D.A. Osmond, K.C. Sturge, M.J. Zaworotko, Organometallics 11 (1992) 337.

[31] M.-H. Delville, Inorg. Chim. Acta 291 (1999) 1.

[32] T.G. Kotch, A.J. Lees, S.J. Fuerniss, K.I. Papathomas, Chem. Mater. 7 (1995) 801.

[33] J.S. Miller, M.D. Ward, J.H. Zhang, W.M. Reiff, Inorg. Chem. 29 (1990) 4063.

[34] M.D. Ward, Organometallics 6 (1987) 754.

[35] M.D. Ward, J.C. Calabrese, Organometallics 8 (1989) 593.

[36] R.E. Lehmann, J.K. Kochi, J. Am. Chem. Soc. 113 (1991) 501.

[37] M.D. Ward, D.C. Johnson, Inorg. Chem. 26 (1987) 4213.

[38] T.S. Cameron, A. Linden, K.C. Sturge, M.J. Zaworotko, Helv. Chim. Acta 75 (1992) 294.

[39] J.K. Kochi, C.H. Wei, J. Organomet. Chem. 451 (1993) 111.

[40] J.R. Hamon, J.Y. Saillard, A. Le Beuze, M.J. McGlinchey, D. Astruc, J. Am. Chem. Soc. 104 (1982) 7549.

[41] A.R. Koray, T. Zahn, M.L. Ziegler, J. Organomet. Chem. 291 (1985) 53.

[42] E.P. Kündig, P. Jeger, G. Bernardinelli, Inorg. Chim. Acta 357 (2004) 1909.

[43] M. Gorlov, L. Kloo, submitted for publication.

[44] R.W. Turner, E.L. Amma, J. Am. Chem. Soc. 88 (1966) 1877.

[45] H. Schmidbaur, W. Bublak, B. Huber, G. Reber, G. Müller, Angew. Chem. Int. Ed. 25 (1986) 1089.

[46] Synthesis of $Cu(GaCl_4)$: benzene (3 ml) was added to the solid CuCl (99 mg, 1 mmol) and $GaCl_3$ (176 mg, 1 mmol). The mixture was heated for 2 h at 60 °C and then cooled to room temperature. Colorless crystals formed within 1–2 days on the walls of the reaction vessel.

[47] Synthesis of $[(Cu(GaCl_4)(pyrene))_2]$: $Cu(GaCl_4)$ (200 mg, 0.727 mmol) was dissolved in benzene (10 ml) and pyrene (606.75 mg, 3.0 mmol) was added. The mixture was stirred for 1–2 h without heating. Yellow needles formed within 1 week.

[48] Crystallographic data for $[(Cu(GaCl_4)(pyrene))_2]$: monoclinic, space group $P21/c$, $a = 10.802(7)$, $b = 7.074(9)$, $c = 21.525(10)$ Å, $\beta = 93.05(6)^\circ$, $V = 1642.5(2)$ Å^3, $Z = 4$, $T = 293(2)$ K, $R_{\mathrm{all}} = 0.0684$. The diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å.

[49] A.M. Dattelbaum, J.D. Martin, Inorg. Chem. 38 (1999) 6200.

[50] D. Braga, A. Abati, L. Scaccianoce, B.F.G. Johnson, F. Grepioni, Solid State Sci. 3 (2001) 783.

[51] L.C. Porter, J.R. Polam, J. Mahmoud, Organometallics 13 (1994) 2092.

[52] A.D. Gel'man, E. Meilakh, Dokl. Akad. Nauk SSSR 36 (1942) 188.

[53] T. Murahashi, H. Kurosawa, Coord. Chem. Rev. 231 (2002) 207.

[54] I.I. Moiseev, M.N. Vargaftik, New J. Chem. (1998) 1217.

[55] I.I. Moiseev, M.N. Vargaftik, in: R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di- and Polynuclear Metal Cluster Complexes, VCH–Wiley, New York, 1998.

[56] S.V. Pestrikov, I.I. Moiseev, Izv. Akad. Nauk SSSR Ser. Khim. (1964) 349 (in Russian).

[57] G. Schmid, Chem. Rev. 92 (1992) 1709.

[58] R. Wyman, in: B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1980.

[59] L.N. Lewis, Chem. Rev. 93 (1993) 2693.

[60] B.R. James, Homogeneous Hydrogenation, Wiley, New York, 1973.

[61] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.

[62] I.I. Moiseev, G.A. Tsirkov, A.E. Gekhman, M.N. Vargaftik, Mendeleev Commun. 7 (1997) 1.

[63] F. Ragaini, S.J. Cenini, J. Mol. Catal. A. 109 (1996) 1.

[64] J.S. Lee, C.W. Lee, K.H. Park, J. Mol. Catal. 61 (1990) L15.

[65] T. Satoh, M. Ikeda, Y. Kushino, M. Miura, M. Nomura, J. Org. Chem. 62 (1997) 2662.

[66] E. Drent, P. Arnoldy, P.H.M. Budzelaar, J. Organomet. Chem. 475 (1994) 57.

[67] G. Allegra, A. Immirzi, L. Porri, J. Am. Chem. Soc. 87 (1965) 1394.

[68] P. Pertici, G. Vitulli, Tetrahedron Lett. 20 (1979) 1897.

[69] M. Gorlov, A. Fischer, L. Kloo, Inorg. Chim. Acta. 350 (2003) 449.

[70] M. Gorlov, A. Fischer, L. Kloo, J. Organomet. Chem. 689 (2004) 489.

[71] M. Gorlov, A. Fischer, L. Kloo, Angew. Chem. Int. Ed. 44 (2005) 3906.

[72] M. Gorlov, A. Fischer, L. Kloo, Z. Anorg. Allg. Chem. 630 (2004) 324.

[73] T. Murahashi, E. Mochizuki, Y. Kai, H. Kurosawa, J. Am. Chem. Soc. 121 (1999) 10660.

[74] T. Murahashi, H. Nakashima, T. Nagai, Y. Mino, T. Okuno, M.A. Jalil, H. Kurosawa, J. Am. Chem. Soc. 128 (2006) 4377.

[75] T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, Angew. Chem. Int. Ed. 46 (2007) 3509.

[76] Y. Tatsumi, T. Naga, H. Nakashima, T. Murahashi, H. Kurosawa, Chem. Commun. (2004) 1430.

[77] T. Murahashi, M. Fujimoto, M.-A. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, Science 313 (2006) 1104.

[78] U. Christmann, R. Vilar, A.J.P. White, D.J. Williams, Chem. Commun. (2004) 1294.

[79] U. Christmann, D.A. Pantazis, J. Benet-Buchholz, J.E. McGrady, F. Maseras, R. Vilar, J. Am. Chem. Soc. 128 (2006) 6376.

[80] C. Sui-Seng, G.D. Enright, D. Zargarian, J. Am. Chem. Soc. 128 (2006) 6508.

[81] G.H. Smith, R.E. Rundle, J. Am. Chem. Soc. 80 (1958) 5075.

[82] E.A.H. Griffith, E.L. Amma, J. Am. Chem. Soc. 96 (1974) 5407.

[83] R.W. Turner, E.L. Amma, J. Am. Chem. Soc. 88 (1966) 3243.

[84] E.A.H. Griffith, E.L. Amma, J. Am. Chem. Soc. 93 (1971) 3167.

[85] I.F. Taylor Jr., E.A. Hall, E.L. Amma, J. Am. Chem. Soc. 91 (1969) 5745.

[86] M. Munakata, L.P. Wu, G.L. Ning, Coord. Chem. Rev. 198 (2000) 171.

[87] M. Munakata, L.P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, K. Sugimoto, Inorg. Chem. 36 (1997) 4903.

[88] M. Munakata, L.P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, G.L. Ning, T. Kojima, J. Am. Chem. Soc. 120 (1998) 8610.

[89] M. Munakata, L.P. Wu, G.L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Maeno, J. Am. Chem. Soc. 121 (1999) 4968.

[90] G.L. Ning, L.P. Wu, K. Sugimoto, M. Munakata, T. Kuroda-Sowa, M. Maekawa, J. Chem. Soc., Dalton Trans. (1999) 2529.

[91] Synthesis of $\{AgGaCl_4(C_6H_6)\}_n$: benzene (2–3 ml) was added to the solid mixture of AgCl (100 mg, 0.697 mmol) and $GaCl_3$ (123 mg, 0.697 mmol). The mixture was heated for 10–15 min (80 °C) without stirring. After cooling, a colourless solution was transferred into a 5-mm NMR tube and layered with *n*-heptane. Colourless, transparent crystals were separated within 2–3 weeks. The crystals are unstable in the absence of mother solution, probably because of loss of the coordinated benzene ligands.

[92] The compound $\{AgGaCl_4(C_6H_3(CH_3)_3)\}_n$ was prepared in a manner similar to that of $\{AgGaCl_4(C_6H_6)\}_n$, but using mesitylene instead of benzene. Colourless crystals were grown within 1 week.

[93] Synthesis of $\{AgGaCl_4\}_n$: $GaCl_3$ (1.310 g, 7.44 mmol) was dissolved in 7–8 g of 1,2-dichlorobenzene at room temperature. After addition of AgCl (1.02 g, 7.11 mmol), the mixture was heated for 1 h under stirring and then left overnight. The solvent was removed; white crystals were washed with *n*-heptane and dried in vacuo. Yield 82%.

[94] Synthesis of $[Pt_2(p\text{-xylene})_2(Ga_2Br_7)_2]$: *p*-xylene (3 ml) was added to the solid mixture of $K_2[PtBr_4]$ (0.04 g, 0.067 mmol) and $GaBr_3$ (0.125 g, 0.405 mmol). The mixture was stirred for 1–2 h without heating. The resulting brown solution was placed in a 5-mm NMR tube, and *n*-heptane was carefully layered above the reaction solution. Red needles formed within 3 months.

[95] C. Gemel, T. Steinke, D. Weiss, M. Cokoja, M. Winter, R.A. Fischer, Organometallics 22 (2003) 2705.

[96] D. Weiss, M. Winter, K. Merz, A. Knufer, R.A. Fischer, N. Frohlich, G. Frenking, Polyhedron 21 (2002) 535.

[97] D. Weiss, T. Steinke, M. Winter, R.A. Fischer, N. Froehlich, J. Uddin, G. Frenking, Organometallics 19 (2000) 4583.

[98] D. Weiss, M. Winter, R.A. Fischer, C. Yu, K. Wichmann, G. Frenking, Chem. Commun. (2000) 2495.

[99] R.A. Fischer, H.D. Kaesz, S.I. Khan, H.J. Muller, Inorg. Chem. 29 (1990) 1601.

[100] A.S. Borovik, S.G. Bott, A.R. Barron, Angew. Chem. Int. Ed. 39 (2000) 4117.

[101] A.S. Borovik, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 123 (2001) 11219.

[102] A.S. Borovik, A.R. Barron, J. Am. Chem. Soc. 124 (2002) 3743.

[103] C.S. Branch, A.R. Barron, J. Am. Chem. Soc. 124 (2002) 14156.

[104] J. Rosdahl, M. Gorlov, A. Fischer, L. Kloo, Z. Anorg. Allg. Chem. 630 (2004) 760.

[105] S. Ulvenlund, J. Rosdahl, A. Fischer, P. Schwerdtfeger, L. Kloo, Eur. J. Inorg. Chem. (1999) 633.

[106] W. Frank, B. Dincher, Z. Naturforsch., B 42 (1987) 828.

[107] G.B. Deacon, Q. Shen, J. Organomet. Chem. 506 (1996) 1.

[108] F.A. Cotton, W. Schwotzer, Organometallics 6 (1987) 1275.

[109] Y.K. Gun’ko, P.B. Hitchcock, M.F. Lappert, Organometallics 19 (2000) 2832.

[110] J.G. Brennan, F.G.N. Cloke, A.A. Sameh, A. Zalkin, Chem. Commun. (1987) 1668.

[111] B. Fan, Q. Shen, Y. Lin, J. Organomet. Chem. 377 (1989) 51.

[112] M.C. Cassani, D.J. Duncalf, M.F. Lappert, J. Am. Chem. Soc. 120 (1998) 12958.

[113] K.-H. Thiele, S. Bambirra, J. Sieler, S. Yelonek, Angew. Chem. Int. Ed. 37 (1998) 2886.

[114] F.A. Cotton, W. Schwotzer, J. Am. Chem. Soc. 108 (1986) 4657.

[115] H. Liang, Q. Shen, J. Guan, Y. Lin, J. Organomet. Chem. 474 (1994) 113.

[116] H. Nakamura, Y. Nakayama, H. Yasuda, T. Maruo, N. Kanehisa, Y. Kai, Organometallics 19 (2000) 5392.

[117] G.B. Deacon, C.M. Forsyth, P.C. Junk, B.W. Skelton, A.H. White, Chem. Eur. J. 5 (1999) 1452.

[118] G.B. Deacon, T. Feng, C.M. Forsyth, A. Gitlis, D.C.R. Hockless, Q. Shen, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2000) 961.

[119] W.J. Evans, N.T. Allen, J.W. Ziller, J. Am. Chem. Soc. 122 (2000) 11749.

[120] G.C. Campbell, F.A. Cotton, J.F. Haw, W. Schwotzer, Organometallics 5 (1986) 274.

[121] P. Biagini, G. Lugli, R. Millini, Gazz. Chim. Ital. 124 (1994) 217.

[122] H. Liang, Q. Shen, S. Jin, Y. Lin, J. Chem. Soc., Chem. Commun. (1992) 480.