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Arene complexes of titanium and zirconium. Synthesis and structure

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Abstract

The synthetic methods and main structural types of arene complexes of titanium and zirconium in oxidation states from IV to 0 are reviewed. The synthetic possibilities of $MX_4/M'/AlX_3/$arene systems are discussed in some detail. In the Zr–Cl systems, the charge of triangular cluster cations $[(Arene)_3Zr_3Cl_6]^{n+}$ (2 or 3) controls the Zr–Zr distances.

In general, the stability of arene complexes increases for the more substituted arene ligands $C_6H_{6-m}Me_m$ and from the iodo to chloro derivatives, the M–C distances being independent of X within the known structural types. Distinctions between structural chemistry of titanium and zirconium arene complexes are determined by the different sizes of their atoms resulting in different coordination possibilities, and the most stable 16- and 18-electron valence configurations, respectively.

Key words: Titanium; Zirconium; Synthesis; Structure; Arene; π-Bonding; Cluster

1. Introduction

Since the discovery of the first bis-(arene) chromium complexes in 1955 many attempts have been made to synthesize similar derivatives for the most of the other transition metals, and among them, for titanium and zirconium. The first information concerning arene derivatives of titanium and zirconium is contained in the patents of Fisher and Hafner [1]. Later investigation by the same research group revealed that the reductive Friedel-Crafts reaction followed by partial hydrolysis and extraction of products does not result in bis-(arene) complexes [2]. Formation of trinuclear cationic species was suggested on the basis of electric conductivity and magnetic measurements.

As early as in 1959 using the same reaction type (but without hydrolysis) Natta and coworkers have synthesized a complex which they considered to be a Ti^{III} derivative $Cl_2Ti(\mu\text{-}Cl)_2AlCl(C_6H_5)$ containing a phenyl group [3]. Closer examination of this compound by chemical methods established its composition and suggested π-bonding of the benzene molecule to titanium (II). Analogous toluene and mesitylene complexes have also been obtained [4]. It was also found that such complexes catalyze the cyclotrimerization of butadiene to (*Z*,*E*,*E*)-1,5,9-cyclododecatriene [5], and that of substituted acetylene to benzene derivatives [6]. Some years later high catalytic activity of these complexes in nitrogen fixation in aprotic media under mild conditions was found [7]. The discovery of these interesting and important properties encouraged more systematic study both of the arene complexes and of the catalytic reactions. The first X-ray studies of this class of compounds were carried out in the laboratory of Prof. U. Thewalt. The structure of two titanium complexes $(\eta^6\text{-}arene)Ti[AlCl_4]_2$ have been determined [8]. The attempt to reproduce the first Fisher synthesis (though without hydrolysis) resulted in trinuclear zirconium complexes with a +2 positive charge on the cation [9] instead of +1, as suggested earlier [2].

Approximately at the same time a new synthetic method using metal vapours was successfully used for the preparation of arene phosphine complexes of zirconium(hafnium) (0) [10], and bis-(arene) complexes of titanium(0) [11]. Recently, the arene derivatives of M^{IV}, which seem to be less stable than other complexes, have been prepared [12].

In spite of some achievements, the arene complexes of Ti and Zr remain poorly studied in comparison with the derivatives of many transition elements. Since 1988 we have been deeply involved in this field of research working not only with Cl derivatives but also with Br and I ones as well. At present the experimental data are quite extensive and need some systematization. On

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the other hand, new types of complexes, which have been obtained in recent years, open up new opportunities for further development.

In this paper, we consider the methods of preparation, structure, and to some extent the reactions of arene complexes of titanium and zirconium. The structural chemistry of hafnium derivatives is, to date, rather too poorly investigated to be a subject for systematic consideration. Nevertheless, a few data concerning Hf compounds are invoked, if corresponding information on zirconium derivatives is lacking, taking into account that (with some exceptions) the structural chemistry of Zr and Hf is essentially similar.

2. Synthesis of complexes

The experimental methods of synthesis are different for the complexes in which the oxidation states of metals are IV, III–II, and 0. The most usual compounds (mainly halides) of the elements in the higher oxidation state IV are used, as a rule, for the preparation of arene complexes.

In complexes of M^{IV}, the coordination of arene ligand to metal atom is accomplished by the substitution of an electronegative ligand for a neutral arene molecule under formation of cationic complexes

$$3TiCl_4 + \text{arene} \longrightarrow [(\eta^6\text{-arene})TiCl_3](Ti_2Cl_9)\ \mathbf{I}\ [12a] \qquad (1)$$

(arene = hexamethylbenzene, HMB),

$$Cp^*MMe_3 + B(C_6F_5)_3 + \text{arene} \longrightarrow [Cp^*MMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3] \qquad (2)$$

[12b]

(M = Ti, Zr, Hf, arene = benzene, toluene, mesitylene, styrene),

or of zwitterions [12c]. Arenes are weakly bonded and can be easily removed or replaced by other donor ligands (*e.g.*. PR_3). These compounds are catalytically active in the olefin polymerization or alkyne trimerization although no reaction mechanisms have been suggested.

The main preparative method for the arene complexes of titanium and zirconium in oxidation states from II to III is the Friedel-Crafts reductive synthesis (sometimes called the Fisher-Hafner method). The reduction of metal tetrahalide MX_4 (M = Ti, Zr) by active metal M′ is carried out in the presence of aluminium trihalide and arene ligand:

$$MX_4 + AlX_3 + M' + \text{arene} \longrightarrow M(\text{II–III})\ \text{complex} \qquad (3)$$

TABLE 1. Main structural features of arene titanium complexes

Composition of complexes				Distances, Å			Ref.
Type	Arene	X	Solvate molecule	Ti–C	Ti–X	Ti–Ti	
I	C_6Me_6	Cl	–	2.49	2.18		12
IIa	C_6H_6	Cl	–	2.49	2.60		8b
IIb	C_6H_6	Cl	C_6H_6	2.50	2.61		24
IIc	C_6Me_6	Cl	C_6H_6	2.50	2.62		8a
IId	$C_6H_2Me_4$	Cl, I	–	2.50	2.66, 2.90		27
IIe	C_6Me_6	Cl, Et	–	2.49	2.59–2.63		29
IIf	C_6H_6	Br	C_6H_6	2.49	2.73–2.77		25
IIg	C_6H_6	I	–	2.51	2.95–3.01		25
III	C_6H_6	I	C_6H_6	2.14; 2.40	2.86		17
				2.07; 2.27; 2.47	2.78	2.75–2.78	
IVa	C_6H_6	–		2.22–2.25			11
IVb	$C_6H_5CH_3$	–		2.24–2.27			11

The course of reaction (3) is essentially different for Ti and Zr systems. Titanium(II) complexes (η^6-arene)-$Ti[(\mu\text{-}X)_2AlX_2]_2$ **II** (Table 1) can be easily obtained if aluminium is used as a reducing metal M′ [4,5b,13,14]. The reaction is carried out under gentle heating. The reduction usually stops at this stage and the complex can be precipitated by addition of aliphatic hydrocarbon solvent.

A halogen exchange between Ti^{II} arene complex and aluminium halide provides an alternative way to bromo, or iodo derivatives of **II** [14]:

$$(\eta^6\text{-arene})Ti(AlCl_4)_2 + AlX'_3 \longrightarrow (\eta^6\text{-arene})Ti(AlX_4)_2 + AlCl_3 \qquad (4)$$

Apparently a driving force of reaction (4) is the low solubility of $AlCl_3$ in the hydrocarbons compared to that of $AlBr_3$ or AlI_3. One or two atoms in complexes **II** can be substituted by Et group using the reaction with $Et_{3-x}AlCl_x$ [15]. The reactivities of complexes **II** towards CO have been studied in some detail [13]. They are readily oxidized by cyclopentadiene to yield Cp derivative of Ti^{III} [16]

$$(\eta^6\text{-arene})Ti(AlCl_4)_2 + \longrightarrow (\eta^5\text{-}C_5H_5)Ti(AlCl_4)_2 + \text{arene} + H^{\cdot} \qquad (5)$$

Partial oxidation of HMB chloro complex by water followed by extraction with methylene chloride resulted in the isolation of a compound, which was suggested to be a trinuclear ionic complex $[(HMB)_3Ti_3Cl_6]Cl$ with a mean oxidation state of titanium 2.333 [2].

Only in one case, the interaction in the $TiX_4/AlX_3/Al/$arene system (X = I, arene = benzene, T = 130°C, reaction time one month) gave the complex **III** with oxidation state of titanium lower than 2 [17a].

Complex **III** $(\mu_2\text{-I})_3\text{Ti}_3\{1,3,5\text{-}[\mu_2\text{-I(I)}_2\text{Al}]_3\text{C}_6\text{H}_3\text{-}\mu_3,\eta^6;\eta^6\}\text{Ti}(\eta^6\text{-C}_6\text{H}_6)$ contains four Ti atoms, three of which can be considered as Ti^{II} and the fourth as Ti^0.

A more reliable synthetic method for titanium(0) derivatives makes use of co-condensation of metal and arene ligand vapours [10]

$$\text{arene(g)} + \text{Ti(g)} \longrightarrow (\eta^6\text{-arene})_2\text{Ti } \mathbf{IV} \qquad (6)$$

In this way the benzene, toluene [11] and 1,3,5-tris(^{t}Bu)-benzene derivatives of **IV** [18a] have been prepared. An alternative, synthetic, method is described in ref. 18b.

The same Fisher-Hafner method (reaction (3)) used with zirconium tetrahalides gives different complexes depending on some factors, the main ones of which are the nature of halogen ligand X (Cl, Br, or I), of metal M′ (M′ = Al, Mg, or Zn), or arene ligand $\text{C}_6\text{H}_{6-m}\text{Me}_m$, and the duration of interaction. A mixture of different products is often formed and, if their solubility in arene ligand is not high enough, an oily phase is separated. The crystallization of compounds from such an oily layer is extremely difficult. It may be concluded from the results obtained that, for the systems with the same arene and M′, the degree of reduction increases in the sequence Cl < Br < I. For example, reduction in benzene system (X = Cl) is found to be very slow even on heating; the bromo derivative of Zr^{III} (type **V**, Table 2) was formed at ordinary temperature, whereas the use of iodides gave zirconium(II) complexes of type **VIII** [19]. On the other hand, the zirconium complexes with oxidation states from 3 to 2 can be synthesized for the same arene and halogen X by variation of metal M′ and reaction time. So, in the system $\text{ZrCl}_4/\text{AlCl}_3/\text{Al}/$mesitylene, zirconium complexes were isolated with the oxidation states of Zr 3.0 (type **VIa**), 2.667 (type **VIIa,b**), and 2.0 (type **VIIIa**) [20]. If metals less active than Al are used (*e.g.* Zn, or Mg), the final oxidation state of Zr in the complexes is not lower than 3 (type **VIa,b**) [20].

An additional factor contributing to the variety of complexes in the same systems is the amount (concentration) of AlX_3 which affects the composition of an anion in the ionic complexes. The most usual anionic species are Al_2X_7^-: Al_2Cl_7^- in **VIa**, **VIIa–c**, **VIIIa**, and Al_2Br_7^- in **VIIIb** [21]. The lower concentration of AlX_3 (Al_2Cl_6) in the solution results in the lower anion nuclearity (*e.g.* AlCl_4^- in **VIIa**, or even Cl in $[(\text{HMB})_3\text{Zr}_3\text{Cl}_6]\text{Cl}$ after extraction with methylene chloride [2]). An increase of AlX_3 content can cause a formation of anion of greater nuclearity (*e.g.* $\text{Al}_3\text{I}_{10}^-$ in **VIIId** [19]). It is interesting to note that a partial hydrolysis of Zr^{II} complex **VIIIb** (in the presence of reducing metal M′) gives the derivative of Zr^{II}, **VIIIc** with aluminium partially hydrolyzed in anion $\text{Al}_3\text{OBr}_8^-$ [21].

The use of a stoichiometric amount of the stronger reducing agent makes possible the achievement of specified oxidation state of metal M. So, the complexes of Hf^{II} were prepared by the reduction with sodium amalgam [22]

$$\text{HfI}_4 + \text{Na(Hg)} + \text{arene} + \text{PMe}_2\text{Ph} \longrightarrow$$

$$\underset{\mathbf{X}}{(\mu\text{-}\eta^{12}\text{-arene})\text{Hf}_2\text{I}_4(\text{PMe}_2\text{Ph})_4} \qquad (7)$$

The metal vaporization technique is also used for the preparation of $(\text{arene})_2\text{M}$ complexes (M = Zr, Hf; arene = 1,3,5-tris(^{t}Bu)benzene) [18a]. Furthermore,

TABLE 2. Main structural features of arene zirconium (hafnium) complexes

Composition of complexes					Distances, Å			Ref.
Type	Arene	X	$n+$ *	Anion	M–C	M–X	Zr–Zr	
V	C_6H_6	Br	1	Al_2Br_7^-	2.69	2.71; 2.82	3.19	19
VIa	$\text{C}_6\text{H}_3\text{Me}_3$	Cl	3	Al_2Cl_7^-	2.61	2.52	3.27	20
VIb	$\text{C}_6\text{H}_3\text{Me}_3$	Cl	3	$\text{Mg(AlCl}_4)_3^-$	2.61	2.52	3.28	20
VIIa	$\text{C}_6\text{H}_3\text{Me}_3$	Cl	2	AlCl_4^-, Al_2Cl_7^-	2.60	2.54	3.33	20
VIIb	$\text{C}_6\text{H}_3\text{Me}_3$	Cl	2	Al_2Cl_7^-	2.59	2.54	3.32	20
VIIc	C_6Me_6	Cl	2	Al_2Cl_7^-	2.59	2.55–2.56	3.35	9
VIIIa	$\text{C}_6\text{H}_3\text{Me}_3$	Cl	1	Al_2Cl_7^-	2.54	2.70		21b
VIIIb	$\text{C}_6\text{H}_3\text{Me}_3$	Br	1	Al_2Br_7^-	2.54	2.82		21a
VIIIc	$\text{C}_6\text{H}_3\text{Me}_3$	Br	1	$\text{Al}_3\text{OBr}_8^-$	2.53	2.82		21a
VIIId	C_6H_6	I	1	$\text{Al}_3\text{I}_{10}^-$	2.54	2.98–3.01		19
IX(Hf)	$\text{C}_6\text{H}_5\text{CH}_3$	–	–	–	2.48			23
X(Hf)	C_6H_6	I	–	–	2.28–2.55	2.88–2.92		22
	$\text{C}_6\text{H}_5\text{CH}_3$	I	–	–				

* $n+$: positive charge for the cationic complexes.

arene phosphine complexes of Zr(Hf)(0) have been obtained by this method [10a]

$$\mathrm{Zr(Hf)(g)} + \text{arene} + \mathrm{PMe_3} \longrightarrow$$

$$(\eta^6\text{-arene})_2\mathrm{M(PMe_3)_2} \qquad (8)$$

$$\text{arene} = \mathrm{C_6H_6}\ (\mathrm{Hf}),\ \mathrm{C_6H_5CH_3}\ (\mathrm{Zr, Hf}).$$

Bimetallic Zr(Hf)-Sn compounds have been prepared by the interaction of phosphine complexes with hexamethylditin [23]

$$(\eta^6\text{-arene})_2\mathrm{M(PMe_3)_2} + \mathrm{Sn_2Me_6} \longrightarrow$$

$$(\eta^6\text{-arene})_2\mathrm{M(SnMe_3)_2} + \mathrm{PMe_3} \qquad (9)$$

$$\mathbf{IX}\ (\text{arene} = \mathrm{C_6H_5CH_3}).$$

In concluding this section it may be said again that the preparative work with arene complexes of titanium and zirconium is difficult due to their high sensitivity to oxidation and hydrolysis. Therefore some special experimental techniques should be developed not only for preparation and isolation but also for investigation of these compounds.

3. Structures of complexes

Although there are many methods for studying structure we restrict our consideration only to the results of the direct structure determinations by means of X-ray diffraction. An attempt was made to find out and to explain some regularities of structures, and, in some cases, to establish a link between structure and properties of the complexes.

3.1. Titanium complexes

The only known structure for titanium(IV) arene derivatives contains cationic (η^6-HMB)TiCl$_3^+$ species (type **I** Fig. 1, Table 1) and dimeric anions Ti$_2$Cl$_9^-$ [12a]. The titanium atom in a cation is approximately tetrahedrally coordinated by three Cl atoms at short distances 2.17–2.18 Å and one π-bonded HMB ligand at Ti–C distances ranging from 2.46 to 2.52 Å, which are close to those in neutral arene complexes of titanium(II) of type **II**, 2.50 Å.

The structure of 16-electron arene complexes of titanium(II) (η^6-arene)Ti[(μ-X)$_2$AlX$_2$]$_2$ (type **II**) has been studied most extensively due to their interesting catalytic properties. The overall geometry of the complex can be described as a four-legged piano stool with four halogen atoms on the base, X(1)X(2)X(5)X(6) (Fig. 1). The pairs of halogen X(1)X(2) and X(5)X(6) belong to two distorted tetrahedral AlX$_4$ groups. Some geometrical features of molecules are given in Table 1. The fine differences in the geometry of inorganic framework, *e.g.* non-planar displacement of four bridging X atoms and the configurations of $\overline{\text{Ti–X–Al–X}}$ cycles, were discussed elsewhere [25].

The catalytic activity of the complexes in the trimerization of butadiene varies considerably depending on arene and X (Cl, Br, or I). Progressive decrease of activity has been found for the chloro complexes with successive increase of the number of methyl substituents in the arene ligand up to HMB, to which may be attributed the increase of donor ability and stability of complexes in the same rank order. It is notable that such differences in the stability are at variance with the virtually equal Ti–C distances in benzene (**IIa,b**) and HMB (**IIc**) complexes.

The nature of the halogen atom has also a pronounced effect on the catalytic activity. It has been found that bromo as well as mixed chloro-bromo complexes showed the highest initial rate of butadiene consumption, while the iodo ones were practically inert [26]. The structural investigation of complexes with X other than Cl (**IIf,g**) as well as with mixed Cl-I halogen did not show any appreciable variations in their structure, because Ti–C distances in all molecules are constant within narrow limits, 2.49–2.51 Å [25,27]. It is possible that the catalytic activity is also controlled by the shielding degree depending on the number of

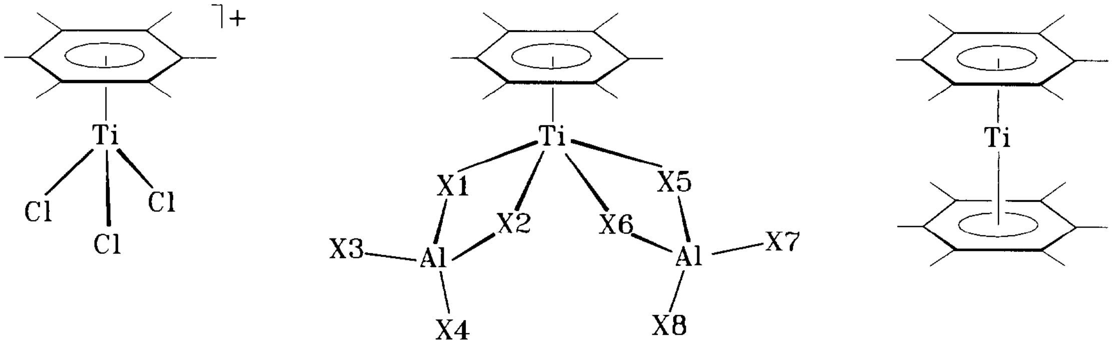

Fig. 1. Structures of arene titanium complexes of types I, II, and IV.

methyl substituents in the ligand and slight non-equivalence of the Ti–X bonds. A study of the halogen mixed complexes revealed an important fact that the different halogen ligands are not randomly distributed between bridge and outer positions [28], Cl atoms occupying predominantly bridge position (X1, X2, X5, X6), whereas I atoms are located mainly in the outer ones (X3, X4, X7, X8) in the structure of chloro-iodo complex **IId** [27]. This fact can account for the high stability of halogen mixed complexes in the course of catalysis.

More active complexes of type **II** are produced in the (arene)$TiAl_2X_8$-Et_2AlX systems resulting in the substitution of a few X for Et groups. Our X-ray investigation of such a mixed Cl-Et complex **IIe** reveals that just the end position X4 and X8 undergo the substitution by Et groups [29].

16-Electron bis-(arene) titanium (0) complexes **IVa,b** (Fig. 1) are characterized by a sandwich structure with eclipsed conformation of arene ligands (benzene, toluene) [11]. The Ti–C distances 2.22–2.27 Å are significantly shorter than those in the complexes of Ti^{II} (type **II**).

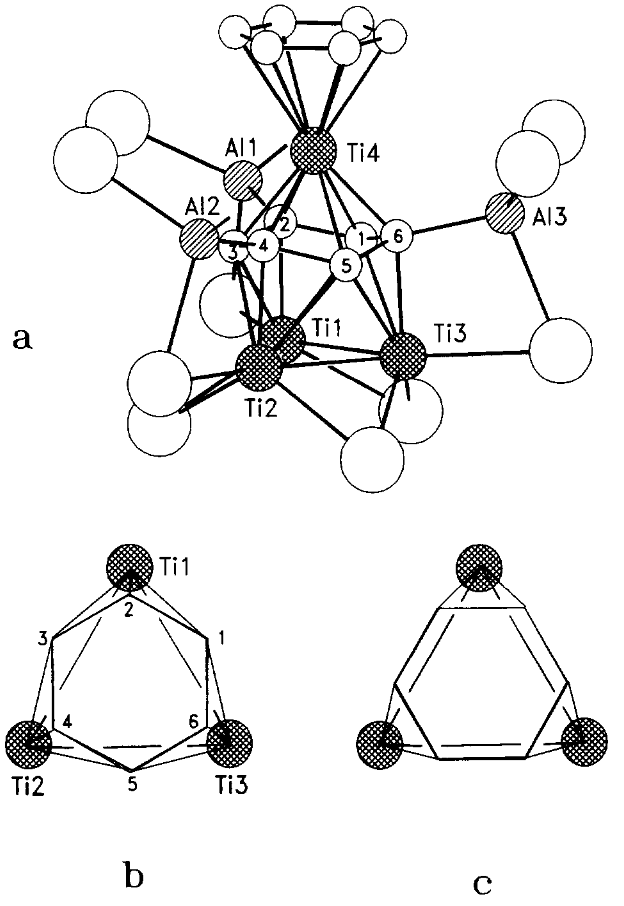

Fig. 2. (a) Structure of complex **III**. The coordination of benzene molecule on: (b) triangular titanium cluster in **III**; (c) triangular metallic fragments of clusters (Os_3 [30a,b], Ru_6 [30a]), or metallic surface (Rh [30c]).

A fragment analogous to dibenzenetitanium is present in the structure of complex **III** containing Ti^0 and three Ti^{II} atoms (Fig. 2) [17a]. A special feature of this structure is coordination of one benzene molecule (the lower base of dibenzenetitanium fragment) by titanium triangular cluster additionally connected with three C atoms of benzene through Ti–I–Al–C bridges. The rigid orientation of benzene molecule relative to Ti cluster (Fig. 2b) causes a disruption of the aromatic system so that the ring C(1)–C(6) becomes strongly puckered (∠CCC 116°). On the other hand all C–C bonds are geometrically equivalent and have approximately the same (although enlarged) length, 1.48 Å. Therein lies a difference from the coordination mode of "free" benzene molecules on triangular metallic clusters [30a,b] or on the surface of metals [30c] (Fig. 2c). In such complexes benzene molecule remains flat (planar) but the bonds alter in length so that the molecule has a triene-like structure. The puckering of benzene molecule in **III** leads to an appreciable difference in the length of Ti(4)–C bonds (to the lower ring) 2.07 and 2.27 Å, whereas the bonds to the upper ring have all approximately the same length 2.47 Å, which is close to that in complexes of type **II**, 2.50 Å [17b].

3.2. Zirconium complexes

A wide variety of different oxidation states of Zr atom occurs in the known zirconium arene complexes compared to those of titanium. It is of interest that presumably ionic zirconium arene complexes have been obtained, which are generally characterized by 18-electron configuration of Zr atom.

3.2.1. The ionic complex V

$\{(\mu\text{-Br})_3[\eta^6\text{-}C_6H_6]Zr(\mu\text{-Br})_2AlBr_2]_2\}(Al_2Br_7)$ containing Zr^{III} occupies a somewhat special position because this type of complex has been prepared in the bromide system only [19] (Fig. 3, Table 2). The relatively short Zn–Zr distance 3.19 Å corresponds to an ordinary bond, which is also in agreement with a total count of 18 valence electrons for both Zr atoms. A considerable elongation of the average Zr–C distance 2.69 Å (compared to that in other zirconium arene complexes) may be explained by some overcrowding of the coordination sphere of Zr atoms. This complex has a close structural analogy with the neutral Nb complex $[(\eta^6\text{-HMB})Nb(\mu\text{-Br}_4)Nb(\eta^6\text{-HMB})]$, in which the availability of the Nb–Nb bond has been also postulated assuming an 18-electron configuration of Nb atoms [31a,b].

The ionic complexes **VI** and **VII** [(arene)$_3$-Zr_3Cl_6]$(Al_mCl_{3m+1})_n$ have approximately the same geometry of cations (Fig. 3) containing a triangular zirconium cluster with pairs of Cl atoms bridging each Zr–Zr side, and three arene ligands (Mes or HMB) each π-bonded to Zr atom [9,20]. An important difference of **VI** and **VII** types consists in the different charge of cation. In the case of **VI**, the charge n is +3 which corresponds to the mean oxidation state of Zr +3, whereas the oxidation state of Zr in **VII** with a charge of cation +2 is 2.667. It has been found that the addition of one electron into triangular cluster cation of the complex **VI** affects essentially the Zr–Zr distance. It increases from 3.27–3.28 Å in **VIa,b** to 3.32–3.33 Å in **VIIa,b** for mesitylene complexes, and to 3.35 Å in **VIIc** for HMB derivative, apparently due to the enhanced donor ability of HMB (Table 2). It means that the additional electron occupies a weak antibonding orbital in **VII**. Other changes in the geometry of the cluster cation: a slight increase of mean Zr–Cl bond lengths (from 2.52 to 2.54–2.56 Å) and Zr–Cl–Zr angles (from 81.2° (**VIb**) to 81.9° (**VIIa**), and 82.0 (**VIIc**)) are mainly dictated by the increase of Zr–Zr distances. Recently, an appropriate Br derivative of type **VI** (n = 3) was obtained and investigated by X-ray analysis: $[(Mes)_3Zr_3Br_6](Al_3OBr_8)_3$ with Zr–Zr distances 3.39–3.44 Å [31c].

The question concerning existence of analogous cluster cations with a charge +1 (*e.g.* with oxidation state of Zr atom 2.333) has not been clarified until now. Their formation by the partial oxidative decomposition (by water [2]) of complexes would indicate the lower oxidation state of Zr (probably 2) in the complexes which were synthesized in the first step according to Scheme (3). The fact that it is possible is suggested by the preparation of complex **VIII** through reduction with aluminium. The existence of such arene zirconium complexes with positive charge of cation 1–3 would demonstrate an enhanced stability of triangular zirconium clusters with 45–47 electrons instead of 48e$^-$, which corresponds to the 18-electron rule.

In a singly charged cation $[(\eta^6\text{-arene})_2Zr(\mu\text{-}X)_2AlX_2]^+$ of the complexes **VIII**, the zirconium(II) atom coordinates two arene ligands, mesitylene (**VIIIa–c**), or benzene (**VIIId**), and two bridging X atoms of the AlX_4 group, so that its coordination by four ligands may be considered as pseudotetrahedral (Fig. 3, Table 2). Thus the 18-electron rule applies also

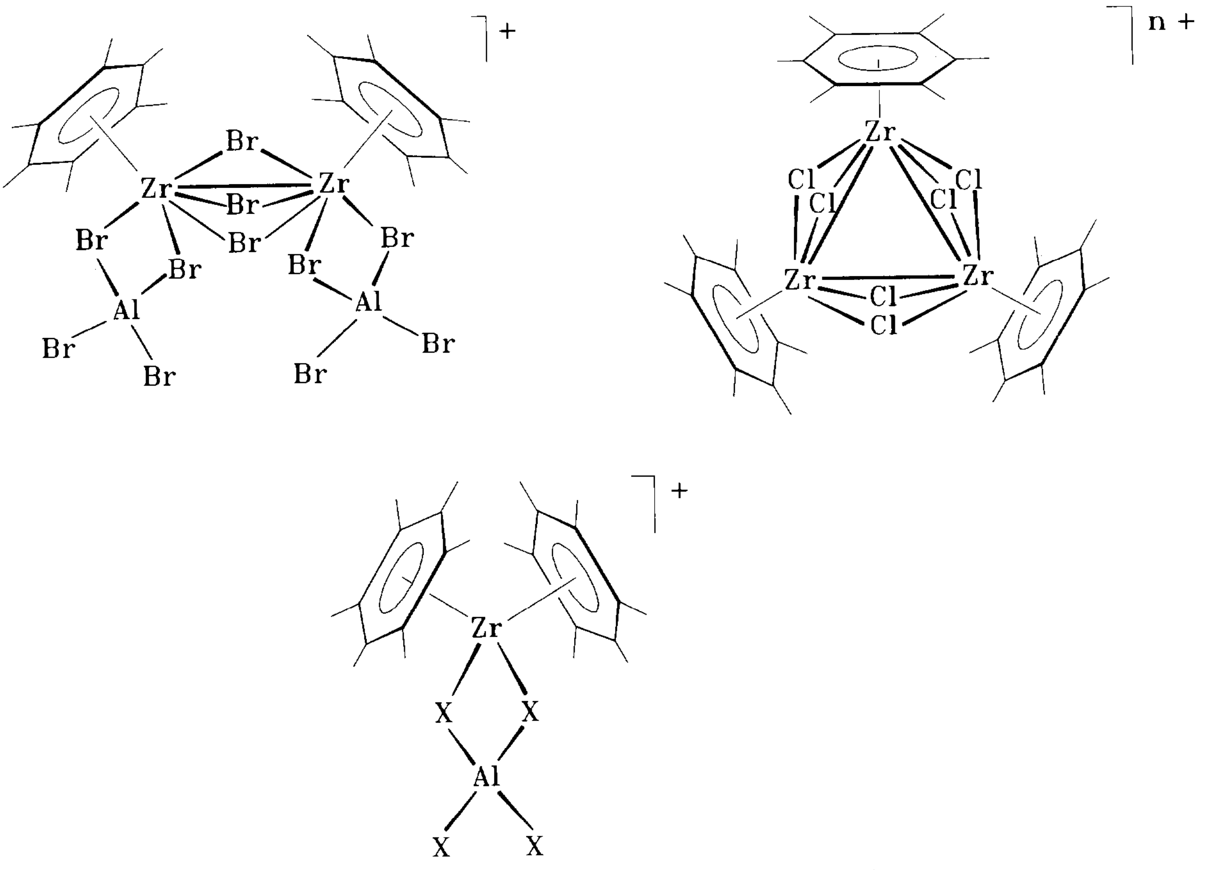

Fig. 3. Structures of the cationic arene zirconium complexes of types V, VI (n = 3), VII (n = 2), and VIII.

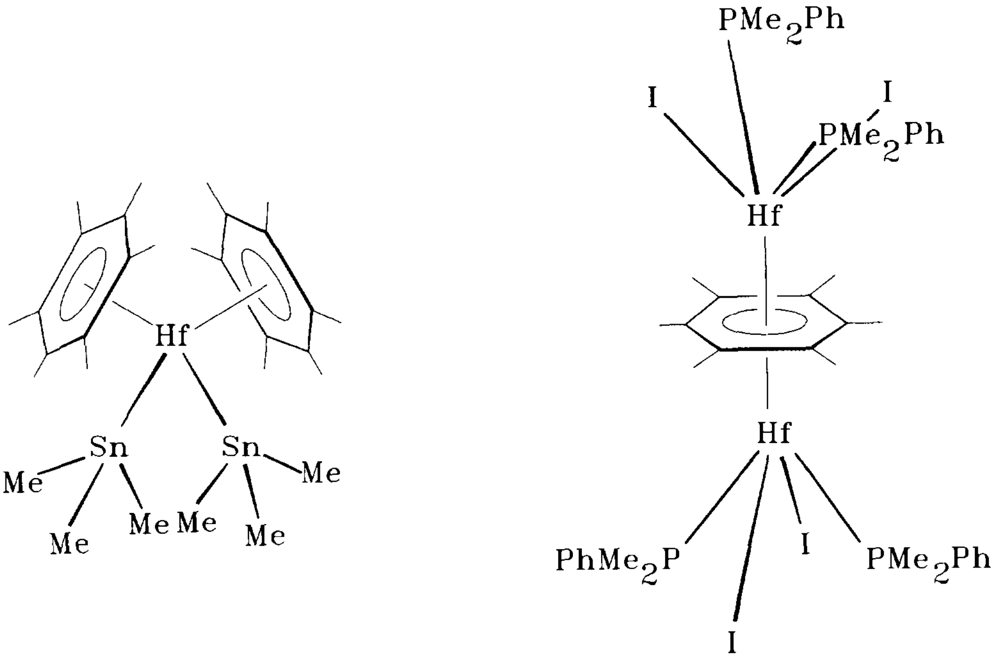

Fig. 4. Structures of neutral complexes of types **IX** (Zr, Hf), and **X** (Hf).

for the complexes **VIII**. The Zr–C(arene) distances, 2.54 Å are unaffected by the nature of X (Cl, Br, or I), as well as in the complexes of type **II**. The Zr–X distances in **VIII** are significantly longer than those in **VI** and **VII** because the bridging Cl atom joins Zr and Al atoms, which are not connected by direct interaction. The Zr–X bonds in **VIII** are not much ($\approx$ 0.1 Å) longer than Ti–X bonds in the corresponding complexes **II** (**VIIIa** — **IIa–c**; **VIIIb,c** — **IIb**; and **VIIId** — **IId**). Such a small difference is probably conditioned by the presence of one AlX_4 group in **VIII** (when compared with two such groups in **II**) resulting in a more covalent character of Zr–X bonds.

In the pseudotetrahedral Zr(Hf) complexes **IX** (η^6-arene)$_2$M(SnMe$_3$)$_2$ (arene = toluene) (Fig. 4), the metal atom has 18 valence electrons [23]. Two arene ligands form a bent sandwich with average Hf–C distance 2.48 Å (X-ray study was carried out for Hf derivative only). Even taking into account the somewhat (*ca.* 0.01 Å) smaller size of the Hf atom than that of Zr we can point out that the M–C distances in complexes of type **IX** are very short, probably, due to the weakness of the $Sn(CH_3)_3$ group as a donor, and to relatively long M–Sn distance (Hf–Sn 2.95 Å).

A still shorter Hf–C average distance, 2.42 Å has been found in an electron-poor complex of hafnium(II) **X** with coordination of two Hf atoms on both sides of the arene ligand (benzene, toluene) (Fig. 4) [22]. Such a mode of coordination disrupts the stability of the π-system so that there are some deviations from planarity, although they are small and not regular in contrast to much more appreciable deviations in complex **III**. A rotation of arene ligand in **X** about the Hf $\cdots$ Hf axis, which has been found at room temperature, appears to be possible due to the position of arene inside the complex molecule. In most of the other cases, arene ligands occupy the outer positions so that their rotation (or libration) is hindered by intermolecular contacts in the crystal. In the case of complex **III**, the inner benzene molecule is fixed by three Ti–I–Al–C bridges.

4. Conclusions

The experimental results on synthesis and structure of titanium and zirconium arene complexes presented above provide an opportunity to make some general remarks. Arene complexes of Ti and Zr(Hf) are known for different oxidation states of metals both for the highest +4 (rare), and for the lower ones up to 0; the former seems to be thermodynamically less stable although they are all extremely sensitive to oxidation and hydrolysis.

In the reductive Friedel-Crafts reactions titanium(IV) can be more easily reduced (or to the lower oxidation state) compared with zirconium(IV). The reducibility of tetrahalides is the highest for iodides and the lowest for chlorides. The stability of complexes formed is dependent on the nature of arene ligand. More methylated benzene derivatives have the higher donor ability, which enhances the stability of complexes, makes their preparation easier, and reduces their catalytic activity.

The distinctions between the structures of titanium and zirconium complexes are determined by the difference of the atomic sizes and thus of the coordination abilities. Due to its lower size, the Ti atom seldom achieves the 18-electron configuration. In the most of the known complexes, the Ti atom has 16 valence electrons (types **II** and **IV**). By contrast, the Zr atom is large enough for coordination of ligands providing the 18-electron valence shell, which is often attained in the cationic complexes. For the same reason, the formation of M–M bonds is more typical for zirconium complexes (at the distances 3.19–3.35 Å) than for titanium ones. Still, as the early transition element, Zr can possess less than 18 valence electrons, for example, in the triangular cluster cations $[(\eta^6\text{-arene})_3Zr_3X_6]^{n+}$ ($n = 1–3$) which is also known for the analogous clusters of niobium [32].

The existence of pseudotetrahedral zirconium(II) complexes of type **VIII** coupled with the 18-electron valence configuration make unreliable the assumption of close analogy in the structure of Ti^{II} and Zr^{II} complexes [6c,33]. The synthesis and structure determination of the seven membered metallocyclic complexes $[\overline{Ti{-}CPh{-}(CPh)_4{-}CPh}]Br_2$ [34a] and $[\overline{Zr{-}CPh{-}(CPh)_4{-}CPh}]\,[(\mu\text{-}Cl)_2AlCl_2]_2$ [34b] provides a further demonstration of the different coordination abilities of Ti and Zr atoms. 16-Electron zirconium complexes can be stable enough in the case of special bulk ligands providing steric hindrance. Thus, the bis-(arene) complexes $[\eta^6\text{-}1,3,5\text{-tris}({}^tBu)benzene]_2M$ have been synthesized both for Ti and for Zr.

For the elements of Group IVB Ti, Zr, and Hf, the nearest similarity of the structures and properties of arene complexes has been found for the oxidation states IV and O, while there are essential differences for the oxidation states II, III, and intermediate not only between Ti and Zr, but also between Zr and Hf. This latter difference is known also for lower halides and can serve as a basis for an effective separation of Zr and Hf [35]. The preparation of some unusual arene complexes *e.g.*. those with both side π-coordination of arene ligand, or with the puckered benzene fragment coordinated on triangular Ti cluster, demonstrates new challenging aspects and a great potential gain in this field of the early transition metal chemistry.

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