

Preliminary communication

Synthesis of arene Ti and Zr complexes and their reactivity towards air:
crystal structure of $[(C_6H_3Me_3)_2Zr(\mu-Cl)_2AlCl_2](Al_2Cl_7)$ and $TiCl_3(OPh)$

Sergei Troyanov ^{*}, Alex Pisarevsky, Yuri T. Struchkov

Chemistry Department of Moscow State University, 119899 Moscow, Russia

Received 21 October 1994

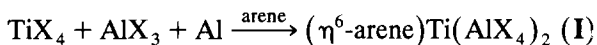
Abstract

The complex $[(C_6H_3Me_3)_2Zr(\mu-Cl)_2AlCl_2](Al_2Cl_7)$ has been prepared by reductive Friedel–Crafts synthesis. Its structure confirms remarkable differences in chemistry of arene complexes of Ti(II) and Zr(II). The crystalline complex $TiCl_3(OPh)$ was formed by slow oxidation of $(C_6H_6)TiAl_2Cl_8$ in air, whereas partial oxidation of Zr arene complexes gave the oxohalogenoaluminates containing cationic arene Zr(II) species.

Keywords: Zirconium; Titanium; Aluminium; Arene; Oxidation

It has been shown in a recent review [1] that the types and structure of titanium and zirconium arene complexes differ remarkably from each other for the same oxidation state of metal. For example, 16-electron neutral complexes of Ti(II) are known only, whereas most of the structurally characterized Zr(II) compounds are cationic with an 18-electron configuration of the Zr atom. We here describe the synthesis and structure of a new arene derivative of Zr(II) as well as the preliminary results on the oxidation experiments of some complexes in air.

The synthesis of Ti(II) arene complexes is simple if a full isolation of the reaction mixture from air and moisture is ensured. The preparation of Ti(II) complexes with benzene and its methylated derivatives have been described, the Friedel–Crafts reductive synthesis being used [2,3]:



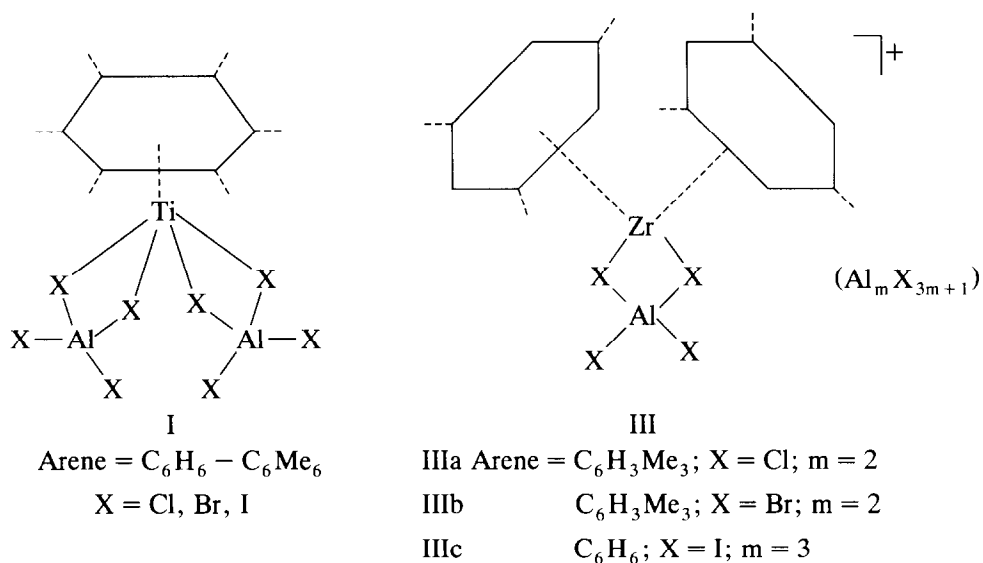
The molecular structure of I is essentially the same for different arene ligands and halogen atoms (X = Cl, Br or I) (Scheme 1). In the case of analogous reactions with zirconium(IV) halides, the formation of the intermediate triangular cluster compounds containing $[(\eta^6\text{-arene})_3Zr_3X_6]^{n+}$ cations ($n = 3, 2$) (II) is possible with

the mean Zr oxidation states of 3.00 and 2.67 respectively [4,5]. In such reactions, Zr(III) derivatives have been obtained when less active metals (Zn or Mg) were used as the reducing agents. The Zr(II) cationic 18-electron complexes $[(\eta^6\text{-arene})_2Zr(AlX_4)](Al_mX_{3m+1})$ (III) could be prepared using Al as a reducing metal. The preparation and structure of the bromide (IIIb) and iodide (IIIc) complexes have been described earlier [6,7], the arene ligands used being mesitylene and benzene respectively.

On the contrary, an assumption was formulated in [8] that the arene derivatives of Zr(II) and Hf(II) in the chloride system have compositions and structures analogous to those of Ti(II) arene complexes (type I). In fact the crystalline substances and in particular single crystals are not easily obtainable in the chloride system owing to the great tendency to oil formation; so direct determination of the structure by diffraction methods is not possible. Nevertheless, we succeeded in obtaining single crystals in the chloride system using mesitylene as a ligand and a solvent [9]. The complex $[(\eta^6\text{-}C_6H_3Me_3)_2Zr(\mu-Cl)_2AlCl_2](Al_2Cl_7)$ has been studied by single-crystal X-ray diffraction [10].

The structure obtained (see Scheme 1) demonstrates unambiguously that, as in other Zr(II) derivatives, the Zr atom has an 18-electron configuration and coordinates two η^6 -bonded arene ligands and two Cl atoms from a tetrahedral $AlCl_4$ unit. The Zr atom in a singly

^{*} Corresponding author.



Scheme 1.

charged cation has a pseudotetrahedral environment with four ligands of average Zr–C distance 2.54 Å and average Zr–Cl distance 2.696 Å. It should be noted that the average Zr–C distances are virtually the same in all known complexes of type **III** with different arene lig-

ands and halogen atoms. For example, the Zr–C distance 2.53 Å was found in the bromide–mesitylene complex **IIIb** [6], and 2.54 Å in the iodide–benzene complex **IIIc** [7]. At the same time, the Zr–X distances increase regularly from 2.70 Å (X = Cl (**IIIa**)) to 2.82

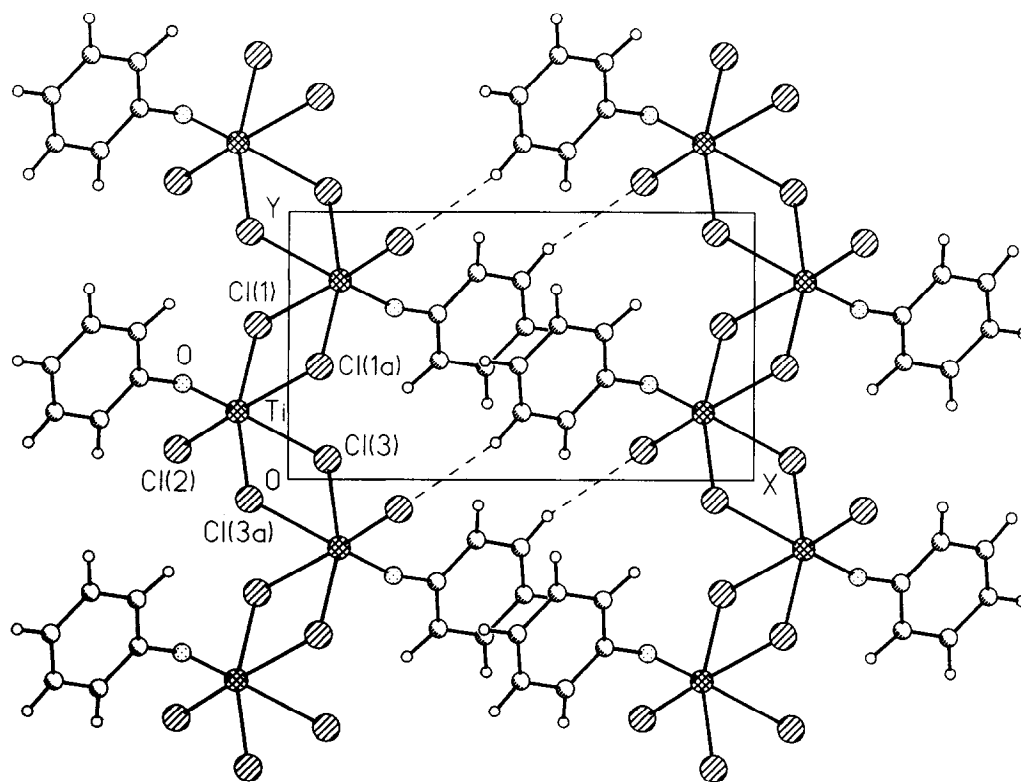


Fig. 1. Part of the Oxy projection of the TiCl₃(OPh) structure. The neighbouring chains at the same z level are connected by weak H bonds of type C–H···Cl with the following distances and angle: C···Cl, 3.69 Å; H···Cl, 2.85 Å; C–H···Cl, 155°.

Å ($X = \text{Br}$ (**IIIb**)), and to 3.00 Å ($X = \text{I}$ (**IIIc**)) corresponding to the atom radii of the halogen atoms. In a similar way, the Al–X(bridge) and Al–X(terminal) distances increase from 2.19 Å and 2.10 Å (**IIIa**) to 2.33 Å and 2.23 Å (**IIIb**), and to 2.56 Å and 2.50 Å (**IIIc**) respectively. The average Al–Cl distances in the Al_2Cl_7^- anion in **IIIa** were determined to be 2.28 Å for Al–Cl(b) and 2.10 Å for Al–Cl(t).

The results of some experiments on the oxidation of the Ti(II) and Zr(II) arene complexes were unexpected. In one case a solid Ti(II) complex ($\eta^6\text{-C}_6\text{H}_6$)Ti(AlCl₄)₂ was separated from the air by a porous glass filter so that air could diffuse slowly into system. Pale yellow crystals were formed at the site of the initial compound. The X-ray study showed that the oxidation of Ti(II) to Ti(IV) is accompanied by oxidation of benzene to a phenol derivative, giving trichlorophenoxytitanium(IV) catena-[(C₆H₅O)Ti(μ-Cl)₂Cl] (**IV**) [11]. A solid substance of the same composition has been described in [12] as red crystals.

The crystal structure of **IV** consists of infinite chains parallel to the *y* axis (Fig. 1). Two of the three Cl atoms are of a bridging nature and the third is terminal corresponding to pseudo-octahedral coordination of the Ti atom by five Cl atoms and one oxygen atom. The shortest Ti–Cl distance of 2.219(2) Å to the terminal Cl(2) atom falls into the narrow range 2.21–2.22 Å found in the dimeric structures of dichlorodialkoxytitanium(IV) [TiCl₂(OR)₂]₂ (R≡Et [13] or Ph [14]). Both Ti–Cl–Ti bridges are asymmetrical owing to the *trans* effect in the Ti environment, the longer distances 2.559(2) Å (Cl(3)) and 2.517(2) Å (Cl(1a)) having a short Ti–O or Ti–Cl(t) bond in the *trans* position, and the shorter distances 2.382(2) Å (Cl(1)) and 2.372(2) Å (Cl(3a)) being in the *trans* position to each other. Similar bond distance relationships have also been found in other *cis*-chain structures such as TiCl₃(N₃) [15] and ZrI₄ [16]. The Ti–O distance of 1.746(4) Å corresponds exactly to the value of 1.774(10) Å found for the terminal phenoxy group in the dimer [TiCl₂(μ-OPh)(OPh)]₂ [14].

Quite a different oxidation process took place by the slow diffusion of air into the system containing zirconium complexes of type **IIIb** and an excess of metallic Al. After some weeks, a new complex was obtained with the same cation, and the oxobromoaluminate anion instead of bromoaluminate anion, before oxidation [6]. No oxidation of Zr(II) occurred in this case apparently owing to the presence of strong reducing metal. Similar processes seem to occur in the system containing Zr(III) cluster complex of type **II**. Slow oxidation by air resulted in the formation of a Zr(III) complex with Al₃OBr₈[−] anions. However, the difference found for the oxidation of Ti(II) and Zr(II) complexes by air could be caused by the absence or presence of a reducing metal

in the system. For a more definite conclusion a detailed investigation is required.

Acknowledgement

The research described in this publication was made possible in part by Grant MPK000 from the International Science Foundation.

References and notes

- [1] S. Troyanov, *J. Organomet. Chem.*, 475 (1994) 139.
- [2] H. Martin and F. Vohwinkel, *Chem. Ber.*, 94 (1961) 2416.
- [3] S.I. Troyanov and V.B. Rybakov, *Metalloorgn. Khim.*, 1 (1988) 1282.
- [4] F. Stollmaier and U. Thewalt, *J. Organomet. Chem.*, 208 (1981) 327.
- [5] S.I. Troyanov, *Izv. Akad. Nauk RAN*, 1 (1994) 134.
- [6] S.I. Troyanov and V.B. Rybakov, *Metalloorgn. Khim.*, 5 (1992) 1082.
- [7] S.I. Troyanov and V.B. Rybakov, *Metalloorgn. Khim.*, 2 (1989) 1382.
- [8] F. Calderazzo, P. Pallavicini and G. Pampaloni, *J. Chem. Soc., Dalton Trans.*, (1990) 1813.
- [9] Preparation of [(C₆H₃Me₃)₂Zr(AlCl₄)](Al₂Cl₇): one of the sections of a two-section ampoule was charged with about 3 mmol (0.7 g) of ZrCl₄, 6 mmol (0.8 g) of AlCl₃, about 3 mmol (0.05 g) of metallic Al, and 30–35 ml of mesitylene. After the evacuation, the ampoule was sealed, heated for 2–3 h in a water bath at 80–90°C (the mesitylene solution turned red) and then cooled to room temperature. The interaction was virtually complete in a week, and a red crystalline substance was separated from solution and dried in the same ampule. The yield was about 1.7 g (70%).
- [10] The extremely hygroscopic crystals were placed into capillaries in a glove-box under argon. Crystal structure determination of **IIIa** (Siemens P3/PC four-circle diffractometer; Mo Kα, graphite monochromator; $\theta(\text{max}) = 24^\circ$; $T = 157 \text{ K}$): C₁₈H₂₄Al₃Cl₁₁Zr; $M = 802.5$; monoclinic; space group, $P2_1/c$; $a = 9.482(2)$, $b = 11.707(3)$ and $c = 28.377(8)$ Å; $\beta = 90.06(2)^\circ$; $V = 3150.1 \text{ \AA}^3$; $Z = 4$; $D_c = 1.692 \text{ g cm}^{-3}$; $\mu = 13.76$; dark red prism; approximately $0.3 \times 0.3 \times 0.3 \text{ mm}$; 5905 raw data; 3780 unique observed reflections with $I \geq 4\sigma(I)$. The structure was solved using Siemens SHELXTL PLUS (PC version) by a combination of direct methods and Fourier difference techniques and refined by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The positions of hydrogen atoms were not determined or calculated. The final residuals were $R = 0.037$ and $R_w = 0.050$. The atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- [11] Structure determination of **IV** (same diffractometer and methods were used for structure solution as for **IIIa** (see [10]); $\theta(\text{max}) = 30^\circ$; $T = 153 \text{ K}$ (the crystals decomposed under X-ray irradiation at room temperature)): C₆H₅OCl₃Ti; $M = 247.4$; monoclinic, space group, $P2_1/n$; $a = 10.731(6)$, $b = 5.980(2)$ and $c = 14.476(6)$ Å; $\beta = 104.56(2)^\circ$; $V = 899.1 \text{ \AA}^3$; $Z = 4$; $D_c = 1.828 \text{ g cm}^{-3}$; $\mu = 17.8 \text{ cm}^{-1}$; yellow needles; approximately $0.2 \times 0.2 \times 0.7 \text{ mm}$; 3213 raw data; 1557 unique observed reflections with $I \geq 3\sigma(I)$. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all atoms

- except H (which were refined isotropically) to the final $R = 0.050$ and $R_w = 0.060$. The atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.
- [12] R.W. Crowe and C.N. Caughlan, *J. Am. Chem. Soc.*, **72** (1950) 1694.
- [13] W. Haase and H. Hoppe, *Acta Crystallogr. Sect. B*, **324** (1968) 281.
- [14] K. Watenpaugh and C.N. Caudhlan, *Inorg. Chem.*, **5** (1966) 122.
- [15] H.-O. Wellern and U. Müller, *Chem. Ber.*, **109** (1976) 3039.
- [16] S.I. Troyanov, *Kristallografiya*, **31** (1986) 446.