Arene Derivatives of Zirconium(II) and Hafnium(II) †

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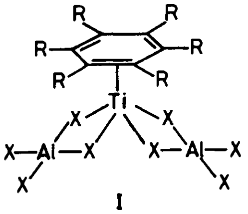
The anhydrous tetrahalides MX_4 (M = Zr or Hf, X = Br or I) were prepared by treating $M(BH_4)_4$ with dry HX in n-heptane as solvent, followed by sublimation under reduced pressure. The reaction of $ZrCl_4$ with Al–$AlCl_3$–aromatic hydrocarbon systems led to solutions containing zirconium(II)–arene complexes. For the case of benzene and hexamethylbenzene (in benzene), solid substances of composition $Zr(arene)(AlCl_4)_2$ were obtained. On the basis of spectroscopic properties, chemical reactivity, and other data these substances are believed to be zirconium(II) derivatives, with structures similar to those already established for the corresponding titanium(II) complexes. The hexamethylbenzene complex of zirconium(II) can also be obtained by a ligand-synthesis reaction from $[Zr(C_6H_6)(AlCl_4)_2]$ and but-2-yne. Spectroscopic evidence of the existence in solution of the corresponding hafnium(II)–η^6-arene complexes (arene = toluene or mesitylene) has been obtained. The trinuclear species $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]^{n+}$ (*n* = 1 or 2) were obtained either by Al–$AlCl_3$ reduction of $ZrCl_4$ (*n* = 2) or by treatment with water (*n* = 1) of the zirconium(II)–C_6Me_6–tetrachloroaluminate complex at low temperature.

Research in several laboratories is currently dealing with the isolation of zirconium and hafnium organometallics, especially because of their interest as olefin polymerization precursors.[1] It has already been shown on the basis of work carried out in our laboratories, that zirconium and hafnium complexes are less readily reduced than the corresponding titanium analogues.[2] The organometallic chemistry of zirconium and hafnium in oxidation states lower than IV thus presents challenging aspects. As far as the oxidation state II is concerned, several new systems have been reported in recent years.[3] A good example of the remarkable difference in stability of low oxidation state between titanium compounds and zirconium and hafnium compounds is the observation that while the η^6-arenetitanium(II) complexes of general formula $[Ti(\eta^6\text{-arene})\{(\mu\text{-}X)_2(AlX_2)\}_2]$ have been known for some decades[4] and their molecular structures established by *X*-ray diffraction methods [structure (I), R = H[4a,b] or Me[4d]] the corresponding zirconium- and hafnium- (II) derivatives have not yet been reported.



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In this paper the reactions of the tetrahalides of zirconium and hafnium with the Al–AlX_3–aromatic hydrocarbon system and the products obtained are described. Part of this work has been published in a preliminary form.[4k]

Results and Discussion

The study of the reactions of MX_4 with aluminium and aluminium halides needed to be preceded by a search for a readily accessible source of the pure‡ bromides and iodides. Since the method available requires the somewhat inconvenient use of the elements at high temperatures,[5] an alternative route from the tetrachloride was sought for. It was found that an intimate mixture of the tetrachloride of zirconium or hafnium with $LiBH_4$ was readily converted into the corresponding borohydrido complexes[6] if a small amount of diethyl ether was added to the solid reagents [equation (1), M = Zr or Hf; X = Br

$$MCl_4 + 4LiBH_4 \longrightarrow M(BH_4)_4 + 4LiCl \qquad (1)$$

or I].[7] The borohydrido complexes, after separation by sublimation at room temperature *in vacuo*, were treated with HX in n-heptane solution at room temperature, see equation (2), the precipitate of the crude MX_4 was then purified by

$$M(BH_4)_4 + 4HX \longrightarrow MX_4 + 2B_2H_6 + 4H_2 \qquad (2)$$

sublimation. Although the yields of MX_4 were moderate, the compounds were obtained in a sufficiently pure form for their further reactions. Treatment of MX_4 with tetrahydrofuran (thf) gave the corresponding thf adducts, see equation (3). The iodo

$$MX_4 + 2thf \longrightarrow [MX_4(thf)_2] \qquad (3)$$

complexes of zirconium- and hafnium-(IV) are new, as is the bromo derivative of hafnium (see Experimental section). The synthetic route to MX_4 *via* $M(BH_4)_4$ has been used previously[8] for the preparation of the zirconium and hafnium tetrafluorides.

Before results on the reaction of MX_4 with Al–AlX_3 and the aromatic hydrocarbon are described, the earlier findings on closely related systems are discussed.

Fischer and Röhrscheid[9] have shown that the reduction of $ZrCl_4$ with Al (1:1.4 molar ratio) in the presence of AlX_3 and hexamethylbenzene in the melt, yields a zirconium complex of formula $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]X_n$ (X = Cl or PF_6); a bridged trinuclear structure (II) (*n* = 1 or 2) was assigned to the cation mainly on the basis of osmometric molecular weight and conductivity measurements. It is quite important to realize that

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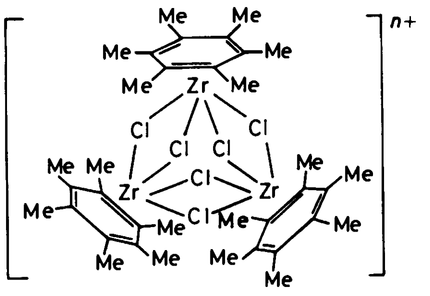
† *Non-S.I. unit employed:* mmHg = 133.322 Pa.

‡ This refers to the halide purity. The metal purity obviously depends on the source of the starting materials (see Experimental section).



(II)

Table. U.v.–visible data (nm) for $[M(\eta^6\text{-arene})(AlCl_4)_2]$ complexes

Arene	Ti*	Zr	Hf
Benzene	395	365	
	559	493	
	812		
Toluene	395	366	320
	548	495	482
	806		
1,3,5-Trimethylbenzene	390	374	332
	548	510	500
Hexamethylbenzene	388	362	
	554	508	
	854		

* H. Antropiusová, K. Mach, and J. Zelinka, *Transition Met. Chem.* (*Weinheim, Ger.*), 1978, **3**, 127; P. Biagini, F. Calderazzo, and G. Pampaloni, *J. Organomet. Chem.*, 1988, **355**, 99.

the Fischer and Röhrscheid product arises from hydrolytic treatment of the reaction mixture at low temperature (−20 °C).

Some years later, Stollmaier and Thewalt [10] reported that the reduction of $ZrCl_4$ with a large excess of aluminium and C_6Me_6 in benzene as solvent in the presence of $AlCl_3$ at 120 °C in a sealed tube, presumably without stirring, led to the formation of the compound $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3][Al_2Cl_7]_2$. An *X*-ray diffractometric experiment definitely established the existence of the trinuclear chloride-bridged zirconium species, as originally suggested by Fischer and Röhrscheid,[9] although the species isolated by Stollmaier and Thewalt carried a +2 charge. A pertinent result for our discussion is that reported by Pasynkiewicz and co-workers:[11] the hydrolytic treatment of the titanium(II)–hexamethylbenzene complex $[Ti(\eta^6\text{-}C_6Me_6)\{(\mu\text{-}Cl)_2AlCl_2\}_2]$ affords the $[Ti_3Cl_6(\eta^6\text{-}C_6Me_6)_3]^+$ cation[9] with dihydrogen evolution, thus suggesting that an electron transfer to the water proton occurred during the treatment with water.

With this background our own results with zirconium and hafnium complexes can be appropriately discussed.

The reaction of MX_4 with aluminium and aluminium halide produced dark red or violet to brown solutions, which are believed to contain the metal(II) complexes of the carbocyclic ligand, formed according to the stoicheiometry of equation (4).

$$3MX_4 + 4AlX_3 + 2Al + 3\text{arene} \longrightarrow 3[M(\text{arene})(AlX_4)_2] \quad (4)$$

In general, the reaction occurred smoothly for zirconium at the reflux temperature of the starting aromatic hydrocarbon (benzene, toluene, or 1,3,5-trimethylbenzene). In the case of the more symmetric arenes benzene and hexamethylbenzene, products corresponding analytically to the formulation of equation (4) (X = Cl) were isolated as violet-brown microcrystalline solids.* For the toluene and the 1,3,5-trimethylbenzene derivatives, intractable oils were obtained. Nevertheless, in these cases, the formation of the arene derivative was established by u.v.–visible spectroscopy in solution (see below). Of specific interest is the product containing hexamethylbenzene. This compound was prepared by three different routes (*a*) by treatment of $ZrCl_4$ with Al–$AlCl_3$ and hexamethylbenzene at the reflux temperature of the reaction medium (benzene), (*b*) by the ligand-exchange reaction (5) from the benzene derivative,

$$[Zr(\eta^6\text{-}C_6H_6)(AlX_4)_2] + C_6Me_6 \longrightarrow [Zr(\eta^6\text{-}C_6Me_6)(AlX_4)_2] + C_6H_6 \quad (5)$$

and (*c*) by a ligand synthesis reaction consisting of treating the zirconium–benzene complex with but-2-yne. The third method of preparation is reminiscent of the cyclotrimerization reactions of alkynes recently found[12] to occur in the presence of the η^6-arene complexes of titanium(II).

The zirconium–halogen bond is expected to decrease in strength on going from the chloride to the bromide.[13] In agreement with this, $ZrBr_4$ was found to react with aluminium and aluminium bromide in the parent hydrocarbon (benzene or toluene) at room temperature to give red-violet solutions supposedly containing the zirconium(II)–arene complexes. However, the products could not be isolated (intractable oils were often obtained) and the extreme sensitivity to air and/or moisture of these solutions did not allow significant electronic spectra to be measured. Hafnium tetrachloride requires longer reaction times to be reduced; the corresponding solutions are believed to contain the hafnium(II)–η^6-arene complexes as suggested by the electronic spectra, see the Table. The spectra of the toluene and 1,3,5-trimethylbenzene derivatives show a shift of the two bands to higher energy with respect to the corresponding zirconium complexes. This is consistent with that expected for a change from 4*d* to a 5*d* central metal atom. No solid compounds could be obtained from the solutions containing the hafnium(II)–arene complexes.

The experimental data supporting the formulation of the products of equation (4) as being η^6-arene complexes of zirconium(II), similar to the corresponding crystallographically studied titanium(II) analogues,[4a,b,d] are as follows.

(*a*) The arene ligand of the benzene derivative $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]$ can be substituted by hexamethylbenzene in a reaction occuring at room temperature. This reaction suggests that the carbocyclic ligand is present around the central metal atom, and no oxidative-addition reactions across the C–H or the C–C bonds of the cyclic system have occurred.

(*b*) A molecular-weight determination by cryoscopy in benzene of the η^6-benzene complex yielded a value close to that for a monomeric formulation. The higher Δt observed may be attributed to a small amount of unavoidable decomposition.

(*c*) The electronic spectra, see Figure 1 and the Table, have a similar pattern to those of the corresponding titanium(II) complexes.[14] In particular, the zirconium complexes are characterized by two main absorption bands in the 360—365 and 490—510 nm regions, see Figure 1 and the Table. The band between 810 and 855 nm, generally observed for the titanium(II) complexes, is probably of too low intensity for the zirconium complexes to be observed. Although the molar absorption coefficients could not be determined due to the unavoidable presence of decomposition products, see Figure 2, the intensity of the absorption bands for zirconium appears to be considerably higher than for titanium.

(*d*) The +II oxidation state for the new zirconium complexes

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* The solids contained variable amounts of benzene, depending on the degree of drying *in vacuo*, in addition to that expected for the formation of equation (4). This is believed to be due to benzene retained in the lattice as suggested by the observation that also the C_6Me_6 complex prepared in benzene (see below) gave similar results.

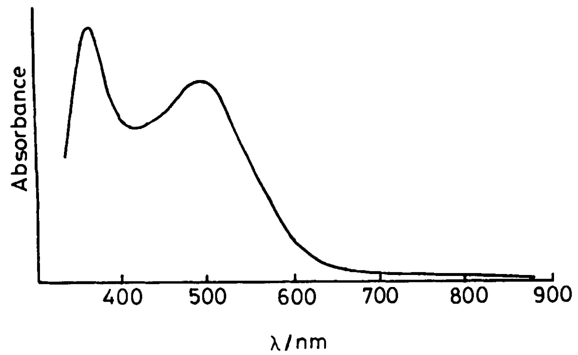

Figure 1. U.v.–visible spectrum of [Zr(η^6-C_6H_5Me)($AlCl_4$)$_2$] (toluene as solvent, crude reaction mixture)

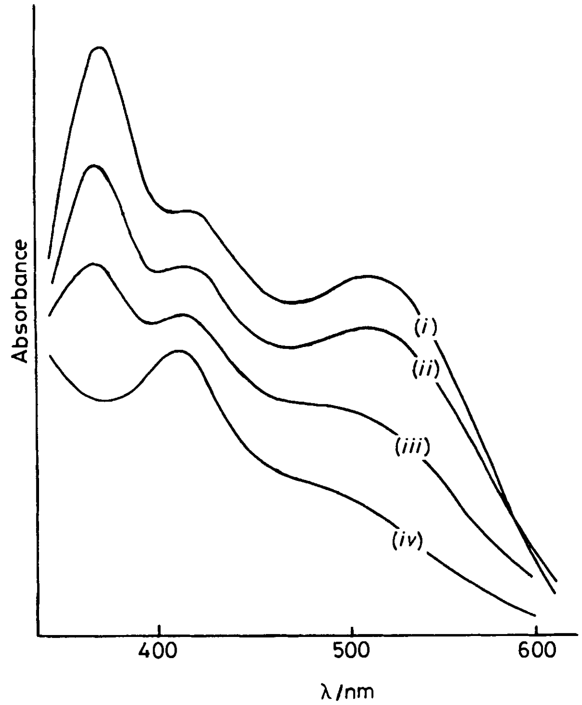

Figure 2. U.v.–visible spectra of [Zr(η^6-C_6Me_6)($AlCl_4$)$_2$] (benzene solution, crude reaction mixture) immediately after the transfer of the solution to the cuvette (*i*), after 10 min (*ii*), after 35 min (*iii*), and after exposure to air for 2 s (*iv*)

is also suggested by the fact that the benzene–chloro derivative was found to be substantially diamagnetic, which is consistent with the presence of a magnetically diluted d^2 system, the two electrons being coupled in a low-lying molecular orbital.[15] It is interesting in this connection that a member of the η^6-arene–titanium(II) complexes was found to be substantially diamagnetic, as suggested by the sharpness of the ^{1}H n.m.r. peaks.[4g]

(*e*) A solution of the zirconium(II)–bromo complex [Zr(η^6-C_6H_6)($AlBr_4$)$_2$], reacts at room temperature with $ZrBr_4$ to give a 77% yield of $ZrBr_3$, obtained according to the *syn*-proportionation of equation (6). This reaction occurred in the

$$[Zr(\eta^6\text{-}C_6H_6)(AlBr_4)_2] + ZrBr_4 \longrightarrow 2ZrBr_3 + C_6H_6 + 2AlBr_3 \quad (6)$$

parent hydrocarbon as medium, where $AlBr_3$ is quite soluble.

Although proof could not be provided by an *X*-ray diffraction study, due to the low tendency of these systems to crystallize or, in most cases, even to solidify, it is believed that the zirconium–arene complexes described in this paper have a structure similar to that already established for the corresponding titanium(II) systems, *i.e.* structure (**I**).

Presumably there is a redox connection between some of the zirconium(II)–arene complexes of suggested structure (**I**) and the trinuclear chloride-bridged compounds of structure (**II**). Low-temperature hydrolysis of the zirconium(II)–C_6Me_6 derivative leads to the presumably trinuclear chloride-bridged complex [Zr_3Cl_6(η^6-C_6Me_6)$_3$]Cl, according to reaction (7).

$$3[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2] + 18H_2O \longrightarrow [Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]Cl + \tfrac{1}{2}H_2 + 17HCl + 6Al(OH)_3 \quad (7)$$

This corresponds to previous findings by Pasynkiewicz and coworkers[11] on the corresponding titanium(II)–arene complex containing the same carbocyclic ligand. Although no *X*-ray diffraction study has been made it is reasonable to assume that complexes with structure (**II**) should exist for titanium as well. In the chloride-rich medium in which the hydrolysis was carried out the trinuclear cation was extracted as the chloride. Moreover, the [Zr_3Cl_6(η^6-C_6Me_6)]$^{2+}$ cation, formally containing the Zr^{III}–Zr^{III}–Zr^{II} sequence of metal centres, and structurally characterized by Stolmeier and Thewalt[10] as the heptachlorodialuminate derivative [Zr_3Cl_6(η^6-C_6Me_6)$_3$][Al_2Cl_7]$_2$, was obtained in the present study by reducing $ZrCl_4$ with the stoicheiometric amount of aluminium and aluminium chloride, according to equation (8). The doubly charged

$$9ZrCl_4 + 9C_6Me_6 + 4Al + 8AlCl_3 \longrightarrow 3[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3][Al_2Cl_7]_2 \quad (8)$$

trinuclear cation was also isolated as the chloride derivative in the chloride-rich medium generated by the low-temperature treatment of the heptachlorodialuminate complex with water (no dihydrogen evolution was observed during this reaction).

These findings show that the [Zr_3Cl_6(η^6-C_6Me_6)$_3$]$^{n+}$ ($n = 1$ or 2) cations are not affected by water over short reaction times under the conditions used in the course of this investigation, see Experimental section. It can be suggested also that the reaction mixture of Fischer and Röhrscheid[9] did in fact contain the zirconium(II)–C_6Me_6 complex, undergoing oxidation by water to the Zr^{III}–Zr^{II}–Zr^{II} trinuclear system, according to equation (7).

The zirconium(II)–arene derivatives reported in this paper would appear to be good starting materials to obtain the dichloride $ZrCl_2$.[16] Thermal decomposition of the benzene–chloro complex under reduced pressure has not led to tractable or to defined products. Attempts are now being made to displace $AlCl_3$ from its combination with zirconium(II) by chemical means.

Experimental

Unless otherwise stated, all operations were carried out under an atmosphere of prepurified argon. The reaction vessels were oven dried before use. Solvents were dried by conventional methods.

Infrared spectra were recorded with a Perkin-Elmer model 283 instrument equipped with grating on solutions or Nujol mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. U.v.–visible spectra were measured on a Perkin-Elmer model Lambda 15 instrument. Gas chromatographic analyses were performed with a Dani model 8400 instrument equipped with a Carbowax 20 M column.

Commercially available zirconium tetrachloride (Fluka) and hafnium tetrachloride (Fluka) were purified by treatment with boiling $SOCl_2$ followed by sublimation at 200 °C (10^{-2} mmHg). Zirconium and hafnium partially substitute each other in their compounds, the metal purity usually not exceeding 98%. Hafnium tetrachloride with a low (<0.5%) zirconium content (CESUS Chimie, France) has been used for some of the reactions, as specified. Aluminium trichloride (C. Erba) and aluminium tribromide (Fluka) were commercial products sublimed *in vacuo* prior to use. Aluminium tri-iodide was prepared according to the literature method.[17]

Preparation of MX_4 (M = Zr *or* Hf, X = Br *or* I).—The compounds $ZrCl_4$ (10.7 g, 46 mmol) and $LiBH_4$ (3.7 g, 170 mmol) were vigorously shaken in a Schlenk tube in the presence of Et_2O (1 cm^3). An exothermic reaction took place. The Schlenk tube was connected to a vacuum line and the borohydrido complex was distilled into a flask (maintained at about −78 °C) and dissolved in n-heptane (200 cm^3). Anhydrous HBr was bubbled into the clear solution for 6 h at room temperature which caused the separation of a colourless solid. The suspension was stirred for an additional 12 h under an HBr atmosphere. The solid was filtered off, washed with n-heptane (2 × 25 cm^3), dried *in vacuo* at room temperature, and sublimed at 190 °C (10^{-2} mmHg) over a period of 18 h giving $ZrBr_4$ in the form of a microcrystalline colourless solid (5.98 g, 32% with respect to $ZrCl_4$) (Found: Br, 77.1; Zr, 22.8. Br_4Zr requires Br, 77.8; Zr, 22.2%).

In a similar way, the following compounds were obtained [reaction time (h), sublimation conditions, yield (%)]: ZrI_4, 17, 200 °C (10^{-2} mmHg), 20.5 (Found: I, 83.9; Zr, 15.3. I_4Zr requires I, 84.8; Zr, 15.2%); $HfBr_4$, 15, 190 °C (10^{-2} mmHg), 44.5 (Found: Br, 64.2; Hf, 36.3. Br_4Hf requires Br, 64.2; Zr, 35.8%); HfI_4, 15, 170 °C (10^{-2} mmHg), 37 (Found: I, 73.1; Hf, 26.7. HfI_4 requires I, 74.0; Hf, 26.0%).

Preparation of $MX_4(thf)_2$ (M = Zr *or* Hf, X = Br *or* I).—The tetrahydrofuran complex $[ZrBr_4(thf)_2]$ was prepared according to a modified literature procedure.[18] A suspension of $ZrBr_4$ (2.72 g, 6.6 mmol) in CH_2Cl_2 (45 cm^3) was treated dropwise with thf (0.89 g, 12.3 mmol) dissolved in CH_2Cl_2 (20 cm^3). A colourless solution was obtained which was filtered and cooled overnight at about −30 °C. The crystalline colourless solid which separated was filtered off at low temperature, washed at room temperature with n-heptane (2 × 25 cm^3), dried *in vacuo*, and identified as $[ZrBr_4(thf)_2]$ (1.62 g, 44%) (Found: Br, 56.7; Zr, 16.9. $C_8H_{16}Br_4O_2Zr$ requires Br, 57.6; Zr, 16.4%).

The following new compounds were isolated in a similar way: $[ZrI_4(thf)_2]$, yellow, 66.2% (Found: I, 66.9; Zr, 12.2. $C_8H_{16}I_4O_2Zr$ requires I, 68.3; Zr, 12.3%); $[HfBr_4(thf)_2]$, colourless, 87% (Found: Br, 49.1; Hf, 28.2. $C_8H_{16}Br_4HfO_2$ requires Br, 49.8; Hf, 27.8%); $[HfI_4(thf)_2]$, yellow, 58% (Found: I, 60.7; Zr, 21.9. $C_8H_{16}HfI_4O_2$ requires I, 61.1; Zr, 21.5%).

Preparation of $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]\cdot nC_6H_6$.—A suspension of aluminium powder (3.7 g, 137.1 mmol) in benzene (300 cm^3) was treated with $AlCl_3$ (5.4 g, 40.5 mmol) and $ZrCl_4$ (7.1 g, 30.5 mmol). The mixture was stirred at reflux temperature and a violet suspension was obtained after 24 h. A dark red oily substance was present together with unreacted aluminium powder. The hot mixture was filtered and, after cooling at room temperature, the volume was reduced to 70 cm^3 *in vacuo* at room temperature and n-heptane (100 cm^3) was added. The solid which formed after 24 h at 4 °C was filtered off, washed with n-heptane (2 × 30 cm^3) and dried *in vacuo* at room temperature for 2 h giving $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]\cdot 1.3C_6H_6$ (5.5 g, 30%) as a dark brown solid (Found: Al, 8.8; Cl, 46.3; Zr, 14.8; C_6H_6, 29.3. $C_{13.8}H_{13.8}Al_2Cl_8Zr$ requires Al, 8.9; Cl, 46.6; Zr, 15.0; C_6H_6, 29.5%*).

The described procedure was repeated several times and compounds containing variable amounts of lattice benzene (0.3—1.3 mol per Zr) were obtained. Yields as high as 70% were secured by extracting the dark red oily substance admixed with excess of aluminium with hot benzene for 2—3 h.

A molecular-weight determination by cryoscopy in benzene for a 1.14×10^{-2} mol dm^{-3} solution gave a Δt of 0.07 °C corresponding to a molecular weight of 421 {Calc. for $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]$ 506.9}.

Preparation of $[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]\cdot nC_6H_6$.—(*a*) *From* $ZrCl_4$–$AlCl_3$–C_6Me_6 *in benzene.* A suspension of aluminium powder (1.2 g, 44 mmol) in benzene (100 cm^3) was treated with $AlCl_3$ (2.5 g, 18.7 mmol), C_6Me_6 (3.9 g, 24 mmol), and $ZrCl_4$ (3.4 g, 14.6 mmol). After 10 min of stirring at room temperature, the suspension turned deep violet. The mixture was stirred at room temperature for 24 h and then at reflux temperature for 4 h. After filtration of the reaction mixture while still hot, the slightly soluble materials were extracted with boiling benzene for 16 h. From the benzene extract the upper layer was discarded and the remaining deep brown oily substance was maintained for 3 h at 60 °C *in vacuo*. The residue was treated with n-heptane (100 cm^3) and kept at room temperature for 15 h. The solid was filtered off, washed with n-heptane (2 × 30 cm^3), and dried *in vacuo* at room temperature affording $[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]\cdot 0.5C_6H_6$ (2.87 g, 31%) (Found: Al, 8.4; Cl, 44.2; Zr, 14.3; C_6H_6, 4.4; C_6Me_6 25.2. $C_{15}H_{21}Al_2Cl_8Zr$ requires Al, 8.6; Cl, 45.0; Zr, 14.5; C_6H_6, 6.2; C_6Me_6, 25.8%).

Other preparations were carried out similarly and products containing variable amounts of clathrated benzene (*n* ranging from 0.2 to 1.0) were obtained.

(*b*) *From* $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]$ *and* C_6Me_6 *in benzene.* A solution of $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]\cdot 0.7C_6H_6$ (0.85 g, 1.5 mmol) in benzene (150 cm^3) was treated at room temperature with C_6Me_6 (0.36 g, 2.2 mmol). Immediate reaction took place and the solution turned brown with separation of a dark brown oily substance. After stirring for 18 h at room temperature, the upper layer was discarded and the product was isolated as in (*a*) affording $[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]\cdot 0.3C_6H_6$ (0.46 g, 48%) (Found: Al, 9.8; Cl, 46.7; Zr, 16.6. $C_{13.8}H_{19.8}Al_2Cl_8Zr$ requires Al, 8.8; Cl, 46.2; Zr, 14.8%).

(*c*) *From* $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]$ *and but-2-yne in benzene.* A solution of $[Zr(\eta^6\text{-}C_6H_6)(AlCl_4)_2]\cdot 0.6C_6H_6$ (0.27 g, 0.5 mmol) in benzene (50 cm^3) was treated at 0 °C with but-2-yne (0.34 g, 6.3 mmol). A violet solution formed instantaneously. While the mixture warmed to room temperature, its colour quickly changed to brown and a dark brown oil separated. After 15 h of stirring at room temperature, the upper layer was separated and the remaining oil treated as in (*a*) affording $[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]\cdot nC_6H_6$ (0.064 g) identified by i.r. spectroscopy. The benzene solution was hydrolysed at room temperature, the organic layer was collected, and the aqueous layer was extracted several times with benzene. The combined benzene extracts were dried over $MgSO_4$ and, after evaporation of the solvent *in vacuo* at room temperature, the residue was identified at C_6Me_6 (0.16 g, 47% with respect to the starting but-2-yne) by i.r. and ^1H n.m.r. spectroscopy.

Hydrolytic Treatment of $[Zr(\eta^6\text{-}C_6Me_6)(AlCl_4)_2]$.—A known amount (0.76 g, 1.2 mmol of zirconium) of the hexamethylbenzene complex prepared according to (*a*) was added to a mixture of water (25 cm^3) and CH_2Cl_2 (30 cm^3) cooled at about

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* Determined by gas chromatography after hydrolysis at room temperature and extraction with n-heptane (decalin as internal standard).

−30 °C. Gas evolution was noted. After a few minutes the organic layer became dark brown; it was collected and evaporated to dryness *in vacuo*. The residue was dissolved in dry CH_2Cl_2 (20 cm^3) and concentrated to a small volume; addition of n-heptane (25 cm^3) caused the precipitation of $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]Cl$ (0.24 g, 59%) (Found: Cl, 24.4; Zr, 26.5. $C_{36}H_{54}Cl_7Zr_3$ requires Cl, 24.6; Zr, 27.1%).

In a gas volumetric experiment carried out at 24.6 °C under an atmosphere of dihydrogen the volume of H_2 evolved (reaction time 0.5 h) was found to correspond to 97% of the expected amount for the oxidation of three zirconium centres to the Zr^{III}–Zr^{II}–Zr^{II} system.

Preparation of $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3][Al_2Cl_7]_2$.—This preparation is similar to that reported earlier by Stollmaier and Thewalt [10] but differs in the molar ratio of the reagents and the reaction temperature.

Zirconium tetrachloride (10.54 g, 45.2 mmol) was magnetically stirred with aluminium (0.585 g, 21.7 mmol) and aluminium chloride (5.74 g, 43.1 mmol) in benzene (150 cm^3) in the presence of C_6Me_6 (7.9 g, 48.7 mmol) at 24.8 °C for 48 h. The reaction mixture was then refluxed for 6 h. After cooling at room temperature, the solvent was decanted and the brown reaction mixture was dried *in vacuo*. Addition of n-heptane (100 cm^3) led to the formation of a brown solid which was collected by filtration and dried *in vacuo* (16.6 g, 70%). The compound gave satisfactory elemental (Cl, Zr, and Al) analyses corresponding to the title composition.

Hydrolytic Treatment of $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3][Al_2Cl_7]_2$: *Preparation of* $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]Cl_2$.—A mixture of dichloromethane (50 cm^3) and water (30 cm^3) was cooled to about −50 °C and treated with $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3][Al_2Cl_7]_2$ (2.1 g, 1.3 mmol). The mixture was allowed to warm slowly (2 h) to room temperature affording a dark brown organic phase in the presence of a colourless aqueous solution. The organic phase was separated and washed with water; the aqueous phase was washed with dichloromethane and discarded, the combined organic extracts were filtered, and the volume of the brown solution was reduced to *ca.* 20 cm^3. Heptane (100 cm^3) was added to give large brown crystals which were collected by filtration and dried *in vacuo* affording 0.6 g, (43% yield) of $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)_3]Cl_2$ (Found: Cl, 27.0; Zr, 26.7. $C_{36}H_{54}Cl_8Zr_3$ requires Cl, 27.2; Zr, 26.2%).

Preparation of Solutions of $[M(\eta^6\text{-arene})(AlCl_4)_2]$ (*arene* = *Toluene or Mesitylene*, M = Zr *or* Hf).—Only the preparation of $[Zr(\eta^6\text{-}C_6H_5Me)(AlCl_4)_2]$ is reported in detail, the others being performed in a similar way.

A suspension of aluminium powder (1.1 g, 40.8 mmol) in toluene (100 cm^3) was treated with $AlCl_3$ (1.1 g, 8.2 mmol) and $ZrCl_4$ (1.4 g, 6.0 mmol) and heated at reflux temperature for 8 h. A suspension of a dark violet oily substance in a violet solution was obtained. The crude reaction mixture was decanted and the upper layer transferred *via* cannula to a u.v. cell for spectral measurements, see Figure 2.

In the case of the hafnium derivatives the reaction time at the reflux temperature of the medium was increased to 24 h. The solutions were characterized spectroscopically, see the Table. The use of $HfCl_4$ with an unusually high metal purity (<0.5%) did not lead to results different from those obtained with the commercially available tetrahalide.

Reaction of $[Zr(\eta^6\text{-}C_6H_6)(AlBr_4)_2]$ *with* $ZrBr_4$. *Preparation of* $ZrBr_3$.—A suspension of aluminium powder (0.51 g, 18.9 mmol) in benzene (100 cm^3) was treated with $AlBr_3$ (1.29 g, 4.8 mmol) and $ZrBr_4$ (1.48 g, 3.6 mmol) and stirred at room temperature for 24 h. The reaction mixture was heated at reflux temperature for 1 h and filtered when hot. A suspension of a dark violet oily substance in a violet solution was obtained. The violet solution was transferred *via* cannula to a flask containing $ZrBr_4$ (1.24 g, 3.0 mmol). The mixture was then stirred at room temperature for 48 h affording a blue solid in an almost colourless solution. The solid was filtered off, washed with benzene, and dried *in vacuo* affording 1.52 g (77% yield with respect to the $ZrBr_4$ added in the second stage of the reaction) of $ZrBr_3$ (Found: Br, 72.4; Zr, 27.6. Br_3Zr requires Br, 72.4; Zr, 27.6%).*

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* *Note added at proof:* After submission of this paper, we learnt that two zirconium η^6-benzene complexes, obtained from the reaction of ZrX_4 with Al–AlX_3–C_6H_6, have been isolated and structurally characterized (S. I. Troyanov and V. B. Ribakov, *Metalloorg. Khim.*, 1989, **2**, 1382). $[\{Zr(\eta^6\text{-}C_6H_6)(Br_2AlBr_2)\}_2(\mu\text{-}Br)_3]^+[Al_2Br_7]^-$ and $[Zr(\eta^6\text{-}C_6H_6)_2(I_2AlI_2)]^+[Al_3I_{10}]^-$. The occurrence of the zirconium (II) complex is in accord with our general conclusions about the reduction of zirconium to the oxidation state II.

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