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Aluminium zirconium (+3 and +4) heterometallic hydrido complexes of compositions $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ and $[(\eta^5\text{-}C_5H_5)_2ZrH(\mu\text{-}H)_2]_3Al$

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Abstract

The Zr(+3) complex of composition $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (**8**) and the Zr(+4) complex of composition $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (**9**) were isolated from solutions containing zirconocene(+4) and titanocene(+3) compounds and $LiAlH_4$ and characterized by X-ray structural analysis. The basic structural element of **8** is the six-atom ring Zr_2AlH_3, in which the metal atoms are linked by ordinary hydrogen bridges. In the structure of **9**, the H^b_{endo} atom is off the bisector plane of the Cp_2Zr fragment and the Al–H distances in the distorted octahedral environment of the aluminium atom are markedly different. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium; Titanium; Metallocenes; Aluminium; Hydrides; Reduction

1. Introduction

Hydrido complexes of zirconium and aluminium play an important role in many catalytic and stoichiometric reactions of unsaturated hydrocarbons [1]. A representative variety of hydrido and alumohydrido complexes of zirconocenes(+4) have now been synthesized and structurally characterized [2–7], but no zirconocene(+3) analogues of these compounds have been reported.

Here, we describe the structures of two new aluminium zirconium heterometallic hydrido complexes, one with Zr(+3) and the other with Zr(+4), both isolated from systems containing two transition metals, namely zirconium and titanium.

2. Results and discussion

2.1. Synthesis of hydrido complexes of zirconocene and aluminium

It is well known that Ti(+4) hydrido complexes are unstable and rapidly reduce to Ti(+3) complexes. As a consequence, the reactions of Cp_2TiCl_2 and $(Cp_2TiCl)_2$ with $LiAlH_4$ give titanocene(+3) derivatives only. In particular, these and similar reactions produce the trinuclear complexes $[Cp_2Ti(\mu\text{-}H)_2]_2AlX$ (**1**) (X = H, Hal, Alk, BH_4), which exhibit a high catalytic activity in olefin hydrogenation [8]. Unlike Ti(+4), Zr(+4) is not reduced rapidly by $LiAlH_4$.[2] According to earlier reports [5–7,9], the Cp_2ZrCl_2 ($Cp = C_5H_5$, C_5H_4R, C_5Me_5) compounds react with $LiAlH_4$ to yield hydrido and alumohydrido derivatives of zirconocene(+4) such as the trinuclear complex $[Cp'_2ZrH(\mu\text{-}H)_2]_2AlH$ ($Cp' = C_5H_4SiMe_3$) (**2**) [7].

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[2] Although zirconocene(+4) complexes are colourless, reaction mixtures of Cp_2ZrCl_2 and $LiAlH_4$ are usually red–purple. This fact is commonly explained by the partial reduction of Zr(+4) (see e.g. [5]).

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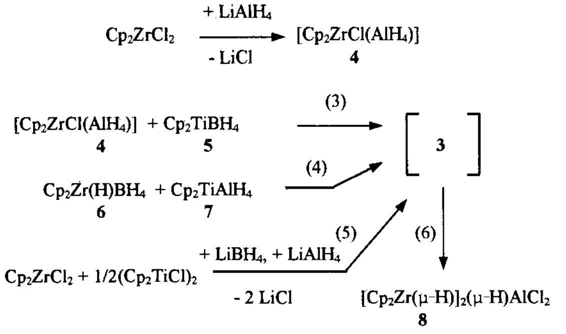
Encouraged by the fact that **1** and **2** contain analogous central metal hydride fragments, M(μ-H)$_2$Al(X)(μ-H)$_2$M, we attempted the synthesis of the trinuclear heterometallic complex Cp$_2$Zr(X′)(μ-H)$_2$Al(X)(μ-H)$_2$TiCp$_2$ (X, X′ = Cl, H, BH$_4$) (**3**). These complexes, containing transition-metal atoms in different oxidation states (Ti(+ 3) and Zr(+ 4)), would be expected to possess interesting structural and catalytic properties.

By analogy with the synthesis of complexes **1** by reaction (1), we first attempted the synthesis of compounds **3** from stoichiometric amounts of reagents corresponding to reactions (2–4). Surprisingly, complexes **3** with any X and X′ appeared to be unstable, and their decomposition was accompanied by the reduction of Zr(+ 4).

$$Cp_2TiAlH_4 + Cp_2TiX \rightarrow \underset{\mathbf{1}}{[Cp_2Ti(\mu\text{-}H)_2]_2AlX} \qquad (1)$$



We were unable to determine the structure of the reduction product for X = Cl and X′ = BH$_4$. This product turned out to be the zirconocene(+ 3) complex of composition [Cp$_2$Zr(μ-H)]$_2$(μ-H)AlCl$_2$ (**8**). Note that **8** forms regardless of the metal to which Cl atoms or BH$_4$ and AlH$_4$ groups were initially bonded. For example, the reagents may be complexes **4** and **5** or complexes **6** and **7**. Furthermore, compound **8** can be obtained by reaction (5) by simply mixing the reactants. This fact seems to be direct evidence of the existence of complexes **3** in solution, which are at least intermediates in which ligand redistribution among metallic centres occurs. After mixing the reagents, Zr(+ 4) reduction starts even at room temperature but, as judged from the intensification rate of the purple colour of the solution, proceeds rather slowly. At 40°C, reaction (6) is complete in 2–3 h, yielding red needle crystals of complex **8**.

Because the yield of complex **8** is low (< 20%) and the transformation products of titanocene are unknown, it is impossible to make any well substantiated inferences as to the mechanism of reaction (6). The titanium compound may promote Zr(+ 4) reduction. It also is possible that, during decomposition of complex **3**, titanocene only binds some of the aluminium component, thus favouring the crystallization of complex **8** from the reaction solution. Anyway, using catalytic amounts of the titanium compound, we failed to produce a complex of zirconium in a lower oxidation state. For example, after treating a mixture of Cp$_2$ZrCl$_2$ and 5 mol% Cp$_2$TiCl$_2$ with LiBH$_4$ and LiAlH$_4$, we were only able to isolate a small amount of complex **9**, in which zirconium is in the oxidation state + 4:

$$Cp_2ZrCl_2 \xrightarrow{5\%[Ti],\ LiBH_4, LiAlH_4} \underset{\mathbf{9}}{[Cp_2ZrH(\mu\text{-}H)_2]_3Al} \qquad (7)$$

That is, reaction (7) proceeds similar to the formation of the complex [Cp$'_2$ZrH(μ-H)$_2$]$_3$Al (Cp′ = C$_5$H$_4$SiMe$_3$) (**10**) [7] and, in this case, it is reasonable to consider the compound of titanium and LiBH$_4$ to be an impurity.

Note that complex **8** can be formally considered an adduct of AlHCl$_2$ and (CpZrH)$_2$ or AlH$_3$ and (Cp$_2$ZrCl)$_2$. Relying on this model, we attempted the synthesis of a titanocene(+ 3) complex of a similar composition. However, our experiments demonstrated that this complex does not exist. At the reagent ratio corresponding to the stoichiometry of reaction (8), some of the (Cp$_2$TiCl)$_2$ was separated unchanged, and only the known [10] complex Cp$_2$Ti(μ-H)$_2$Al(H)Cl·OEt$_2$ was detected by EPR in solution.

$$(Cp_2TiCl)_2 + AlH_3 \nleftrightarrow [Cp_2Ti(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2 \qquad (8)$$

The reaction between (Cp$_2$TiH)$_2$ and AlHCl$_2$ also gave no trinuclear adduct. It afforded the dinuclear complex Cp$_2$Ti(μ-H)$_2$AlCl$_2$·OEt$_2$ [11], whose composition and structure are typical for this class of compound. The borohydrido analogue (see reaction (9)) was not obtained either.

$$^1/_2(Cp_2TiCl)_2 + Cp_2TiBH_4 + AlH_3 \nleftrightarrow$$
$$[Cp_2Ti(\mu\text{-}H)]_2(\mu\text{-}H)Al(Cl)BH_4 \qquad (9)$$

In this case, both the solution and the solid contained known [10] compounds only, among them the complex [Cp$_2$Ti(μ-H)$_2$]$_2$Al(μ-H)$_2$BH$_2$ (**1**), which formed in a nearly 100% yield.

2.2. Structure of [Cp$_2$Zr(μ-H)$_2$](μ-H)AlCl$_2$ (**8**)

The central structural element of complex **8** (Fig. 1, Tables 1 and 2) is a Zr$_2$AlH$_3$ ring, where the metal atoms are each coordinated to two bridging hydrogens. The Zr(1)–Al and Zr(2)–Al distances in **8** are identical (2.904–2.906 Å) and are 0.04 to 0.10 Å shorter than those in zirconium(+ 4) alumohydrides [5–7]. The Zr(1)···Zr(2) distance (3.483 Å), Cp–Zr–Cp angles (131.3°), and Cp–Zr distances (2.18–2.19 Å) are similar

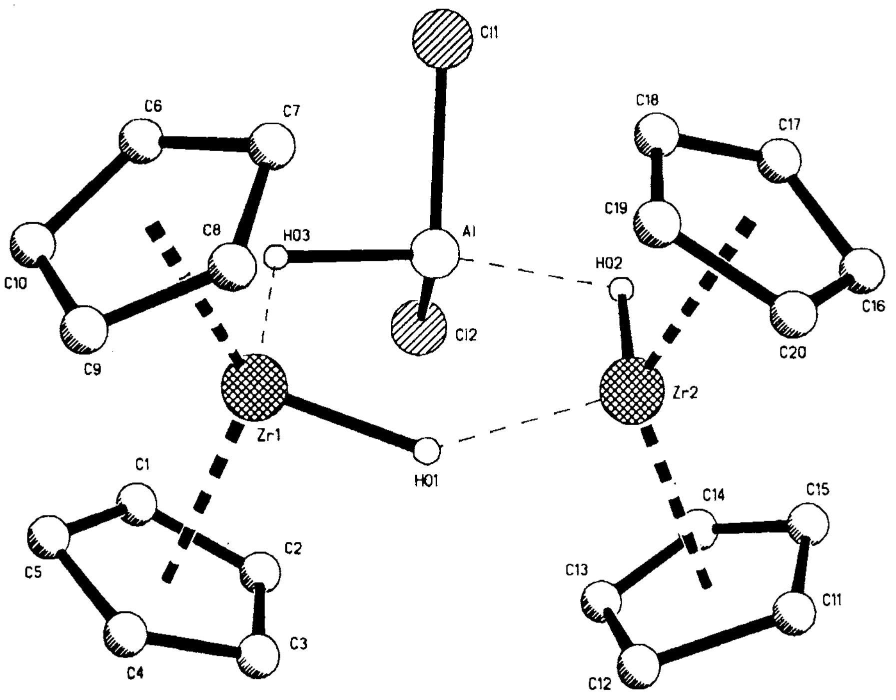


Fig. 1. The structure of $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (**8**).

to the respective parameters of Zr(+ 4) complexes such as the hydride $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ [2] and adducts $Cp_2ZrH(\mu\text{-}H)_2AlH_2\cdots L$ [5].

Although in **8** the Zr(1) and Zr(2) atoms are coordinated to the same ligands and the Cp–Zr–Cp angles are equal, the metal hydride ring is markedly asymmetric: the Zr(1)–H(3) and Zr(2)–H(2) distances are equal (both 1.84 Å), but there is a great difference between the Zr(1)–H(1) and Zr(2)–H(1) distances (1.69 and 2.02 Å) as well as between the Al–H(2) and Al–H(3) distances (1.90 and 1.67 Å). Note that, besides complex **8**, only one compound with such a metal hydride ring, namely, the Natta–Tebbe complex $(C_{10}H_8)[CpTi(\mu\text{-}H)]_2(\mu\text{-}H)AlEt_2$ [12] was reliably identified (see below). The structures of hydrido complexes of transition metals and aluminium, and the structures of titanocene(+ 3) and zirconocene(+ 4) complexes in particular (Table 3), most typically contain an $M(\mu\text{-}H)_2Al$ double bridge and a five-coordinate aluminium atom rather than an M_2AlH_3 ring [8].

Interesting structural features of complex **8** can be revealed by comparing the angles between metal–hydrogen bonds in titanium and zirconium complexes. As seen from Table 3, the H^b–M–H^b angles in zirconocene(+ 4) complexes (d^0) are nearly equal to those in titanocene(+ 3) complexes (d^1). According to Alcock [19], the H^b–Ti–H^b angle cannot be much larger than 75° (this rule is obeyed by titanocene(+ 3) complexes) and the unpaired electron is localized in the bisector plane of the Cp_2Ti fragment, outside the H^b–Ti–H^b angle. This model suggests the following explanation

Table 1

Crystal data and structure refinement for $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (**8**) and $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (**9**)

	8	**9**
Empirical formula	$C_{20}H_{23}AlZr_2Cl_2$	$C_{30}H_{39}AlZr_3$
Formula weight	543.69	699.66
Colour	Red	White
Crystal size (mm)	0.4 × 0.3 × 0.24	0.3 × 0.15 × 0.15
Unit cell dimensions		
a (Å)	11.495(2)	15.858(2)
b (Å)	15.780(3)	15.858(2)
c (Å)	11.971(2)	23.542(5)
β (°)	99.55(2)	90
γ (°)	90	120
Wavelength (Å)	0.71069	0.71073
Radiation type	Mo–K_α (β-filter)	Mo–K_α (β-filter)
Crystal system	Monoclinc	Trigonal
Space group	$P2_1/c$	$R3c$
Z	4	6
Volume (Å^3)	2141.3(7)	5127.1(14)
Density (calculated)	1.682	1.477
Diffractometer	CAD-4	CAD-4
Collection method	$\theta/2\theta$	$\theta/2\theta$
θ range for data collection (°)	1.80–24.89	3.65–24.90
Absorption coefficient (mm^{-1})	0.124	0.944
Reflections collected	1335	1163
Independent reflections	1260	514
Goodness-of-fit on F^2	1.086	1.146
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0415$ $wR_2 = 0.1162$	$R_1 = 0.0215$ $wR_2 = 0.0496$

Table 2
Bond lengths (Å) and angles (°) for $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (**8**)

Zr(1)–Cp(1)	2.20(1)	Cp(1)–Zr(1)–Cp(2)	131.3
Zr(1)–Cp(2)	2.18(1)	H(1)–Zr(1)–Cp(1)	100.3
Zr(1)–H(1)	1.69(1)	H(1)–Zr(1)–Cp(2)	116.3
Zr(1)–H(3)	1.84(1)	H(3)–Zr(1)–Cp(1)	105.8
Zr(1)···Al	2.906(5)	H(3)–Zr(1)–Cp(2)	94.3
Zr(1)···Zr(2)	3.483(3)	H(3)–Zr(1)–H(1)	106.0
Zr(1)–C_{av}	2.49(1)	Cp(3)–Zr(2)–H(2)	94.9
Zr(2)–H(2)	1.84(1)	Cp(4)–Zr(2)–H(2)	97.4
Zr(2)–Cp(3)	2.19(1)	Cp(4)–Zr(2)–Cp(3)	131.3
Zr(2)–Cp(4)	2.19(1)	H(1)–Zr(2)–H(2)	109.4
Zr(2)–H(1)	2.02(1)	H(1)–Zr(2)–Cp(3)	102.4
Zr(2)···Al	2.904(6)	H(1)–Zr(2)–Cp(4)	117.1
Zr(2)–C_{av}	2.48(1)	Cl(2)–Al–Cl(1)	106.2
Al–Cl(1)	2.163(7)	H(3)–Al–Cl(1)	95.4
Al–Cl(2)	2.166(7)	H(3)–Al–Cl(2)	106.5
Al–H(3)	1.67(1)	H(2)–Al–Cl(1)	99.2
Al–H(2)	1.90(1)	H(2)–Al–Cl(2)	98.1
		H(2)–Al–H(3)	146.4

for the fact that zirconocene(+4) and titanocene(+3) complexes are often similar in structure and composition: the H^t atom in zirconocene(+4) and the unpaired electron in titanocene(+3) occupy the same MO, namely, the $1a_1$ orbital of the Cp_2M fragment [19–21].

In complex **8** (also a d^1-configuration), the angles H(1)–Zr(1)–H(3) (106°) and H(1)–Zr(2)–H(2) (109.4°) are too large for the Alcock model [19] and are nearly equal to the H^t–Zr–H^b_{exo} angles in zirconocene(+4) complexes **11** (108°) and **2** (109.7°). It is, therefore, reasonable to assume that the unpaired electron in **8**, like the H^b_{endo} atom in $Cp_2Zr(+4)$ complexes, occupies the $2a_1$ orbital of the Cp_2Zr fragment. In other words, complex **8** differs from titanocene(+3) complexes in that the bridging hydrogen atoms and the unpaired electron in its molecule form a Balhgausen and Dahl AB_2 system[3] [20]. On this assumption, the shortened Zr···Al distance and the unusual, pseudotetrahedral $\{H_2Cl_2\}$ surrounding of the aluminium atom in **8** can be explained by the extra interaction of unpaired electrons with the vacant orbitals of the aluminium atom.

The above considerations are apparently valid for the Natta–Tebbe complex $(C_{10}H_8)[CpTi(\mu\text{-}H)]_2(\mu\text{-}H)AlEt_2$ [12]. This compound is isoelectronic to complex **8**, and its H^b–Ti–H^b angles (which are, unfortunately, not reported in [12]) must be similar to those in **8**. It is likely that the fulvalene ($C_{10}H_8$) ligand stabilizes the Natta–Tebbe complex, because we failed to obtain a titanocene(+3) complex with the Zr_2AlH_3 fragment. It is noteworthy that, unlike the $\{Zr_2AlH_3\}$ ring in **8**, the Ti_2AlH_3 ring in the Natta–Tebbe complex has a symmetry plane. We will dwell only on one possible cause of these differences.

Many properties of Zr(+3) organometallic compounds, including their instability, can be explained by the occurrence of reaction (10)[4]:

$$2Zr(+3) \rightleftarrows Zr(+4) + Zr(+2) \qquad (10)$$

In the light of this reaction, the asymmetry of the metal–hydrogen ring in **8** appears to reflect the tendency of this complex to disproportionation by reaction (11). In other words, the complex is about to disproportionate, its hydrido hydrogens are already displaced from their regular positions, but the heavy structural fragments remain in their original, symmetric positions.

$$\underset{\mathbf{8}}{[Cp_2Zr(\mu\text{-}H)_2](\mu\text{-}H)AlCl_2} \underset{-L\ (12)}{\overset{+L\ (11)}{\rightleftarrows}}$$

$$\underset{\mathbf{12}}{Cp_2Zr^{(+4)}H(\mu\text{-}H)_2AlCl_2\cdot L} + \underset{\mathbf{13}}{Cp_2Zr^{(+2)}\cdot L_n} \qquad (11\text{–}12)$$

It is reasonable to assume the occurrence of the back process (reaction (12), in which complex **12**, a 'normal' zirconocene(+4) complex, binds intermediate **13**. Anyway, reaction (12) seems to be a possible route for the formation of **8**.

2.3. Structure of $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (9)

The general structural motif of **9** (Fig. 2, Table 4) is similar to that of the complex $[Cp'_2ZrH(\mu\text{-}H)_2]_3Al$ ($Cp' = C_5H_4SiMe_3$) (**10**) [7], which is known to cocrystallize with the complex $[Cp'_2ZrH(\mu\text{-}H)_2]_2AlH$ (**2**). The Zr–H distance in **9** (1.93–2.06 Å) differs little from that in **10** (1.98–2.02 Å). At the same time, the Al–H distances in **10** are nearly equal (1.52–1.53 Å)[5], while in **9** they are very different (1.39, 1.99 Å). The coordination polyhedron of the Al atom in **9** is a highly distorted octahedron, where the angle between the axial bonds is ca. 167°. The H^b_{endo} atom in **9**, unlike that in **10**, lies off the bisector plane of the metallocene fragment $\{Cp_2Zr\}$. The H^t–Zr–H^b_{exo} angle in **10** (93.7°)

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[3] It is likely that the AB_2 system is also formed in $[Cp'_2ZrH_2]^-$ anions, which are obtained by the reduction of $[Cp'_2ZrH(\mu\text{-}H)]_2$. The relatively high stability of these anions has been noted [4].

[4] Reaction (10) and the typical two-electron reduction reaction Zr(+4) → Zr(+2) are difficult to distinguish for dinuclear complexes. Gell et al. [22] reliably detected the collapse reduction Zr(+4) → Zr(+2) in mononuclear complexes. In dinuclear zirconium complexes, this reduction yields Zr(+3) [22]. This observation is explicable in terms of the veiled intramolecular reaction Zr(+4) + Zr(+2) → 2Zr(+3). In these terms, one can also explain the specific features of $[Cp'_2ZrH(\mu\text{-}H)]_2$ electroreduction. In dinuclear Zr(+3) compounds [22] and in $[Cp'ZrH_n(\mu\text{-}H)_{2-n}]_2^{2-}$ intermediate ions (whose formation is postulated in [4]), as in complex **8**, the two zirconium atoms may be somewhat non-equivalent.

[5] The accuracy of the determination of the structures of complexes **10** and **2** in their cocrystallization product is rather low ($R_1 = 0.1108$ [7]). Therefore, there may be large errors in the coordinates of the hydrido hydrogen atoms and, correspondingly, M–H distances and angles between metal–hydrogen bonds.

Table 3
Valence angles (°) and the environment of the Al atom in hydrido complexes of zirconocene(+4) and titanocene(+3)

Complex	H^{b}_{exo}–Zr–H^{t}	H^{b}–M–H^{b}	Environment of the Al atom	Reference
$[Cp'_2ZrH(\mu\text{-}H)_2]_3Al$ (**10**)	93.7	51.9	H_6 pseudooct.	[7]
$[Cp'_2ZrH(\mu\text{-}H)_2]_2AlH$ (**2**)	109.7	60.3	H_5 dist.sq.pyr.	[7]
$[Cp^*_2ZrH(\mu\text{-}H)_2AlH_2]_2$ (**11**)	108	63.3	H_5 dist.sq.pyr.	[6]
$[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$, R = Me	130	60		[2]
R = *t*-Bu	121	59		[3]
R = $SiMe_3$	[a]	62		[4]
$Cp_2ZrH(\mu\text{-}H)_2AlH_2{\cdot}L$, L = NMe_3	136	75	H_4N trig.bipyr.	[5]
L = qunuclidine	129	66	H_4N trig.bipyr.	[5]
$[Cp^*_2ZrH_3]Li$	132 [b]	66.3 [b]		[6]
$[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (**9**)	138	64.7	H_6 dist.oct.	this paper
$Cp_2Ti(\mu\text{-}H)_2AlH_2{\cdot}0.5TMEDA$		71.5	H_4N trig.bipyr.	[13]
$Cp_2Ti(\mu\text{-}H)_2AlCl_2{\cdot}OEt_2$		75	H_2Cl_2O dist.trig.bipyr.	[11]
$[Cp_2Ti(\mu\text{-}H)_2]_2AlX$ (**1**), X = Cl		63	H_4Cl trig.bipyr.	[14]
X = BH_4		73	H_6 pseudooct.	[10]
X = Me		60	H_4C sq.pyr.	[15]
$[Cp^*_2Ti(\mu\text{-}H)_2AlH_2]_2$		73	H_5 dist.trig.bipyr.	[16]
$[Cp_2Ti(\mu\text{-}H)_2AlHX]_2$, X = OEt		75.6	H_3O_2 trig.bipyr.	[17]
X = NEt_2		78	H_3N_2 trig.bipyr.	[17]
X = morpholinyl		72	H_3N_2 trig.bipyr.	[18]

[a] The H^{t} atom is not localized.

[b] Bond angles in the $[Cp^*_2ZrH_3]^-$ ion.

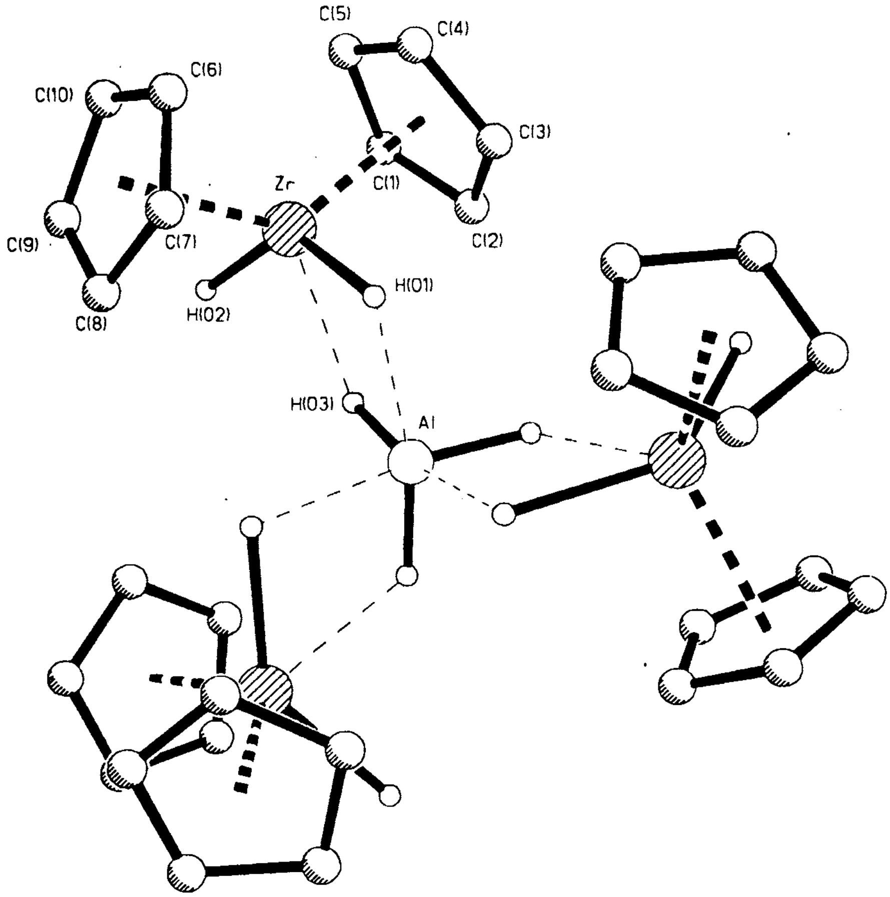

Fig. 2. The structure of $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (**9**).

Table 4
Main bond lengths (Å) and angles (°) for $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (**9**)

Zr–Al	2.997(1)	H(1)–Zr–H(2)	138.2
Zr–H(1)	2.00(1)	H(1)–Zr–H(3)	64.7
Zr–H(2)	1.93(1)	H(1)–Al–H(1a)	89.3
Zr–H(3)	2.06(1)	H(3)–Al–H(3a)	99.5
Al–H(1)	1.99(1)	H(3)–Al–H(1b)	93.8
Al–H(3)	1.39(1)	H(1)–Al–H(3)	166.8
$Zr–C_{av}$	2.49(1)	H(3)–Al–H(1a)	77.9
$Zr–Cp_{av}$	2.20(1)	Cp(1)–Zr–Cp(2)	132.6

differs greatly from that in **9** (138°). The Zr···Al distance in **9** (2.997 Å) is somewhat shorter than those in **10** (3.020, 3.033 Å). The marked difference between the actual and expected structures of **9** is likely due to the tendency of the Al atom to be octahedrally coordinated by hydrogen atoms. The steric effect observed in **9** is even stronger than that in **10** [7].

Note that the hydrido complexes of titanocene(+3) and aluminium with Ti:Al = 3:1 have so far been obtained only in solutions [23]. At the same time, there exists the fluoro complex $[Cp'_2Ti(\mu\text{-}F)_2]_3Al$ ($Cp' = C_5H_4Me$) [24], whose $\{[Ti(\mu\text{-}F)_2]_3Al\}$ fragment is isostructural to the fragment $[Zr(\mu\text{-}H)_2]_3Al$ in **9**. On the one hand, this fact once again points to the structural similarity between titanocene(+3) and zirconocene (+4) complexes. On the other hand, it is evidence of the structural similarity between hydrido and fluoro complexes. Therefore, it seems possible to obtain hydrido complexes of the type $[Cp'_2Ti(\mu\text{-}H)_2]_3Al$ not only in solution but also as crystals.

3. Conclusion

Previous studies have already demonstrated that zirconium aluminium and titanium aluminium hydrido complexes, though representing very similar classes of compound, differ in reactivity and stability. Our results point to these differences once again. This brings up the question: what are the contributions to these differences from electronic factors and from purely structural factors, primarily the atomic (ionic) radius of the transition metal? In the great majority of cases, the electronic structure models of the Cp_2M fragment [19–21] are consistent with the observed geometries. Note, however, some exceptions. For example, the samarium atoms in $[Cp_2SmAlH_4{\cdot}NEt_3]_2$ [25], the hafnium atom in $Cp_2Hf(BH_4)_2$ [26], and the uranium atoms in $[Cp'_2UF(BF_4)]_2$ [27] each are coordinated to four hydrogen or fluorine atoms, while the cerium atoms in $[Cp'_2Ce(BH_4)]_2$ [28] are each coordinated to six hydrogens. These examples demonstrate that, as the atomic number of the central atom increases and its electronic structure becomes more complicated, cyclopentadienyl ligands may lose, to a considerable extent, their crucial role in defining the composition and structure of metallocene complexes. Apparently, one has to take this possibility into account when considering the properties of heterometallic hydrido complexes of zirconium and comparing them with the properties of titanium analogs.

4. Experimental

All manipulations were performed in argon or vacuo. Solvents were boiled over an appropriate drying agent and then distilled.

4.1. $[Cp_2Zr(\mu\text{-}H)]_2(\mu\text{-}H)AlCl_2$ (*8*)

Method 1. $LiAlH_4$ (1.45 mmol) dissolved in toluene (5 ml) was added, in drops to a stirred and cooled (0°C) solution of Cp_2TiBH_4 [29] (0.27 g, 1.4 mmol) and Cp_2ZrCl_2 (0.41 g, 1.4 mmol) in 50 ml of toluene. The reaction mixture was stirred for 20 min at 0°C, filtered, held at 40°C for 3 h, reduced by half in vacuo, and left to stand overnight at room temperature. The resulting red crystals (0.07 g, 20%) were separated from the mother liquor, rinsed, and dried in vacuo. Anal. Found: Al, 4.6; Zr, 33.5; Cl, 12.9. Calc. for $C_{20}H_{23}AlZr_2Cl_2$: Al, 4.97; Zr, 33.57; Cl, 13.05%. One crystal was selected for X-ray structure determination.

Method 2. $Cp_2Zr(Cl)BH_4$ [30] (0.34 g, 1.6 mmol) in toluene (25 ml) was added to a filtered solution of Cp_2TiAlH_4 (1.6 mmol) stirred at 0°C (the latter was prepared [13] from $(Cp_2TiCl)_2$ (0.34 g, 0.8 mmol) and $LiAlH_4$ (1.65 mmol) in a mixture of toluene (30 ml) and ether (5 ml)). The reaction mixture was stirred at 0°C for 20 min and then treated as in method 1. Yield: 0.08 g (18%). Anal. Found: Al, 4.5; Zr, 33.5; Cl, 13.0. Calc. for $C_{20}H_{23}Zr_2Cl_2$: Al, 4.97; Zr, 33.57; Cl, 13.05%.

Method 3. To a mixture of $(Cp_2TiCl)_2$ (0.37 g, 0.85 mmol) and Cp_2ZrCl_2 (0.50 g, 1.7 mmol) in toluene (60 ml), stirred at 0°C, was added first $LiBH_4$ (1.7 mmol in 5 ml Et_2O) and then $LiAlH_4$ (1.7 mmol in 10 ml Et_2O). The reaction mixture was stirred at 0°C for 20 min. The LiCl precipitate was filtered off, and the filtrate was treated as in method 1. Yield: 0.1 g (22%). Anal. Found: Al, 4.5; Zr, 33.5; Cl, 13.0. Calc. for $C_{20}H_{23}AlZr_2Cl_2$: Al, 4.97; Zr, 33.57; Cl, 13.05%.

4.2. $[Cp_2ZrH(\mu\text{-}H)_2]_3Al$ (*9*)

To a cooled (0°C) solution of Cp_2ZrCl_2 (0.93 g, 3.2 mmol) and Cp_2TiCl_2 (0.04 g, 0.16 mmol) in THF (60 ml) were added $LiBH_4$ (7 mmol in10 ml Et_2O), and $LiAlH_4$ (3.5 mmol in 15 ml Et_2O). The reaction mixture was held at 40°C for 4 h, reduced in vacuo to 1/3 of the initial volume, and left to stand overnight at room temperature. The resulting white crystals (0.01 g) were separated from the dark purple mother liquor, washed, and dried in vacuo. One crystal was selected for X-ray structure determination.

4.3. X-ray crystallography

The structures of complexes **8** and **9** were determined on single crystals sealed in glass capillaries. The data-collection conditions and basic crystallographic parameters of the complexes are presented in Table 1. The structures were solved by heavy-atom methods and refined by anisotropic full-matrix least-squares with the use of the SHELXTL-PLUS and SHELXL software packages. Hydride hydrogen atoms were located from difference syntheses, and their coordinates and isotropic thermal parameters were not refined. The other hydrogen atoms were placed geometrically, and their coordinates were introduced in the refinement with fixed displacement and thermal parameters.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 144039 for compound **8** and no. 144040 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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