Reactions of (η^5-C_5Me_5)ZrF_3, (η^5-C_5Me_4Et)ZrF_3, (η^5-C_5Me_5)$_2ZrF_2$, (η^5-C_5Me_5)HfF_3, and (η^5-C_5Me_5)TaF_4 with $AlMe_3$. Structure of the First Hafnium−Aluminum−Carbon Cluster

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The reaction of Cp*ZrF_3 (**1**) (Cp* = η^5-C_5Me_5) and $AlMe_3$ resulted in the formation of *cis*-{[Cp*ZrMe(μ_2-F)][(μ_2-F)$_2$$AlMe_2$]}$_2$ (**6**) and [(Cp*Zr)$_3$$Al_6Me_8$($\mu_3$-$CH_2$)$_2$($\mu_4$-CH)$_4$($\mu_3$-CH)] (**7**), respectively. Analogously, (η^5-C_5Me_4Et)ZrF_3 (**3**) reacts with $AlMe_3$ in a molar ratio of 1:5 with methane elimination to give the $Zr_3Al_6C_7$ cluster of composition {[(η^5-C_5Me_4Et)Zr]$_3$$Al_6Me_8$($\mu_3$-$CH_2$)$_2$($\mu_4$-CH)$_4$($\mu_3$-CH)} (**8**), which has been characterized by elemental analysis and ^{1}H NMR and mass spectrometry. Reaction of 2 equiv of $AlMe_3$ with Cp*$_2ZrF_2$ (**2**) leads quantitatively to Cp*$_2ZrMe_2$ (**12**). Reaction of Cp*HfF_3 (**4**) with $AlMe_3$ in an equimolar ratio gives {[Cp*HfMe (μ_2-F)][(μ_2-F)$_2$$AlMe_2$]}$_2$ (**9**) stereospecifically as its *cis* isomer in high yield. **9** crystallizes in the space group $P2_1/c$ with four molecules in the elemental cell ($Z = 16$). From the reaction of 1 equiv of Cp*HfF_3 (**4**) with 3 equiv of $AlMe_3$, Cp*$HfMe_3$ (**10**) can be obtained in a yield of 85%. As a byproduct of this reaction the $Hf_3Al_6C_7$ cluster [(Cp*Hf)$_3$-Al_6Me_8(μ_3-CH_2)$_2$(μ_4-CH)$_4$(μ_3-CH)] (**11**) can be isolated in a yield of 5%. The characterization of **11** by single-crystal X-ray diffraction and ^{1}H, ^{13}C NMR and mass spectroscopic data will be discussed. Cp*TaF_4 (**5**) reacts with a 5-fold excess of $AlMe_3$, leading quantitatively to Cp*$TaMe_4$ (**13**) without further decomposition via C−H activation processes.

Introduction

Reactions of transition metal(IV) organo halides with alkyls of group 13 elements, especially those of aluminum, are of particular interest with regard to the mechanisms of homogeneous catalysis for the polymerization of olefins. The methylation of a metallocene(IV) chloride is assumed to be the first step of activation of a polymerization catalyst when $AlMe_3$ containing methylalumoxane (MAO) is used.[1] Nevertheless, only a few examples of reactions of cyclopentadienyl-substituted titanium chlorides with $AlMe_3$, leading to well-defined products, are described in the literature: metathesis reaction with Cp*$TiCl_3$ (Cp* = η^5-C_5Me_5) yielding Cp*$TiCl_2Me$[2] and the reactions with titanocene dichlorides from which the Tebbe reagent, Cp_2Ti(μ_2-CH_2)(μ_2-Cl)$AlMe_2$,[3] and its analogues can be obtained. To the best of our knowledge, results of related investigations using zirconium chlorides have not been published. Presumably, this is due to the reversible equilibria in these systems, which prevent the isolation of defined products. It is striking that up to now organometallic fluorides were never used as starting materials for this type of reaction. Due to the strong Lewis acidity of $AlMe_3$, the equilibria of the reactions with these complexes should be shifted to the side of the products, so the study of the stepwise methylation should be facile.

Recently, we found that Me_3SnF and ^{n}Bu_3SnF are suitable fluorinating agents for high-yield syntheses of cyclopentadienyl-substituted fluorides of group 4 transition metals.[4] The solubility of the fluorides, Cp′MF_3 (M = Zr, Hf), in aromatic solvents is excellent when they are substituted with bulky ligands such as Cp*. Furthermore, we found that the complexes Cp*ZrF_3 (**1**) and Cp*$_2ZrF_2$ (**2**) are weakly active homogeneous catalysts for the polymerization of olefins when a 1000-fold excess of MAO is used as co-catalyst.[5] This activity is the presupposition for a mechanistic study of these systems, e.g., *via* ^{19}F NMR investigations.

With regard to this activity, we report herein the detailed reactions of $AlMe_3$ with the fluorides Cp*ZrF_3 (**1**), (η^5-C_5Me_4Et)ZrF_3 (**3**), Cp*$_2ZrF_2$ (**2**), Cp*HfF_3 (**4**), and Cp*TaF_4 (**5**), respectively.

Results and Discussion

Preparation of 6 and 7. In a recent communication[6] we reported the preliminary results of the methylation of **1** using $AlMe_3$. The reaction of **1** and $AlMe_3$ in an equimolar ratio in toluene as well as in *n*-hexane leads to a Me−F exchange, and the fluorine-bridged dimer *cis*-{[Cp*ZrMe(μ_2-F)][(μ_2-F)$_2$$AlMe_2$]}$_2$ (**6**) is formed stereoselectively. The X-ray structure of this complex has been determined. Four molecules of **6** as depicted in eq 1 occupy its unit cell. When an excess of $AlMe_3$ is

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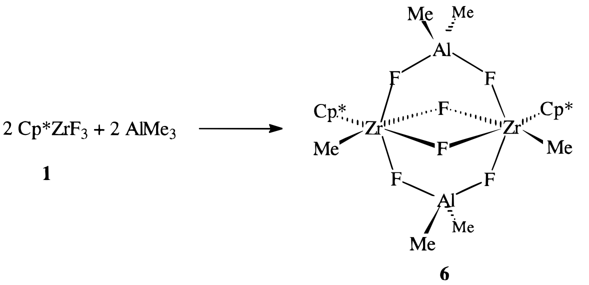
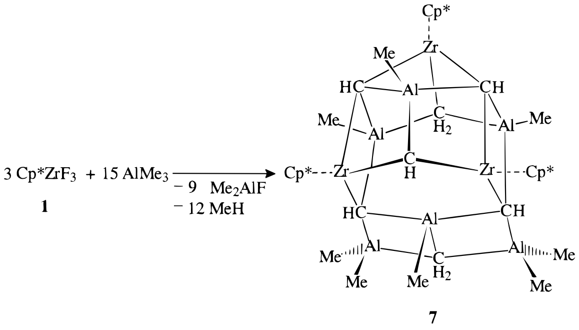


(1)

reacted with **1** in *n*-hexane, all the fluorines are displaced from the zirconium and methane evolution can be observed. The maximum amount of methane (3.5 equiv) can be achieved when 5 equiv of $AlMe_3$ is reacted with **1**. Finally, the $Zr_3Al_6C_7$ cluster $(Cp^*Zr)_3Al_6Me_8(CH_2)_2(CH)_5$ (**7**) can be isolated in yields of 30 (pure) and 70% (crude) as a yellow crystalline solid. From the relation of the evolved amount of methane to the theoretical required (eq 2) a maximum yield for **7** of 88% can be calculated. Single crystals of **7** could be obtained only from freshly prepared material by slowly reducing the volume of a solution of **7** in toluene. Its X-ray structure analysis has been reported. The hydrogen atoms on **7** were not set until now (eq 2) due to the spectroscopic information given herein. The freshly precipitated material of **7** is sparingly soluble in common organic solvents.



(2)

NMR Spectra of 6 and 7. Supplementary to the published spectroscopical data[6] of complex **6**, the signals of the ^{19}F NMR of **6** can be interpreted due to their coupling pattern. The fluorine atoms bridging the Zr atoms become chemically different due to the *trans* effect of either the Cp* ligands or the methyl groups. One of them exhibits a doublet from a quintet from a septet signal (δ −32.5 ppm) with $^{19}F-^{19}F$ and $^{1}H-^{19}F$ coupling constants ($^2J_{FF} = 33$ and 75 Hz, $^2J_{HF} = 9$ Hz). The other one gives a doublet of a quintet resonance (δ −69.5 ppm) with $^2J_{FF}$ coupling constants (20 and 75 Hz). The fluorine atoms linking the Zr and Al atoms resonate as a broad singlet (δ −108.2 ppm).

It is significant that bridging F atoms of transition metal fluoride complexes become electronically strong deshielded and are found in the high field of the corresponding ^{19}F NMR spectra. This is in contrast to the observations that can be made for fluorides of main group elements.[7]

The poor solubility of **7** prevents its characterization by ^{13}C NMR spectroscopy. Therefore, the interpretation of the ^1H NMR signals is difficult. However, the signals of the methylidene and methylidine protons can be detected at low field when it is dissolved in $CDCl_3$ (for assignment, see the Experimental Section). Surprisingly, no reaction of **7** with this solvent takes place. The results lead to the conclusion that the formula of **7** should be written correctly as $[(Cp^*Zr)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)]$.

Preparation of 8. A mixture of $(\eta^5\text{-}C_5Me_4Et)ZrF_3$ (**3**) and an excess of $AlMe_3$ in *n*-hexane reacts in the same manner as observed for **1** with 5 equiv $AlMe_3$ in *n*-hexane. Related to 1 mol of **3**, the evolution of 3.5 mol of methane was found and over a period of 6 days a yellow microcrystalline solid precipitates. Recrystallization from toluene gives the pure product, which was identified as $\{[(\eta^5\text{-}C_5Me_4Et)Zr]_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)\}$ (**8**).

$$\underset{\mathbf{3}}{3(\eta^5\text{-}C_5Me_4Et)ZrF_3} + 15AlMe_3 \rightarrow \underset{\mathbf{8}}{\{[(\eta^5\text{-}C_5Me_4Et)Zr]_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)\}} + 9Me_2AlF + 12MeH \quad (3)$$

Unfortunately, no suitable single crystals for X-ray diffraction measurement were available. Contrary to expectation, the solubility of **8** in common organic solvents is even worse than that in the case of **7**. In the EI mass spectrum of **8**, the basis peak was found at $m/z = 1008$ with composition of $[(C_5Me_4Et)Zr]_3Al_6Me_2(CH_2)_2(CH)_5$ where six methyl groups became abstracted from the molecular ion. The peak with the highest mass was found to be $[M^+ - 3Me]$ ($m/z = 1051$). This indicates a high thermal stability of **8** in the gaseous state as well as in the solid state which is discernable from its high decomposition point of 300 °C. In contrast, **8** decomposes to unidentified products already in solution when warmed to moderate temperatures, but without further methane elimination. This has also been observed for **7**.

^{1}H NMR Spectrum of 8. The ^1H NMR spectrum of **8** in C_6D_6 gives the signal pattern of the protons of the methyl groups at the Al atoms at high field and of the protons of the methylidine and methylidene moieties at low field. That is similar to that found for the corresponding protons of **7**. The protons of the methyl groups of the "face to face" bonded C_5Me_4Et groups in **8** were found to be magnetically not equivalent. They are split into three pairs of singlets (δ 1.91, 1.85, and 1.76 ppm) with integral ratios of 3:3, 3:3, and 6:6, respectively. This is possibly due to the steric hindrance of rotation of the C_5Me_4Et groups.

In order to increase the solubility of the cluster molecules, we have undertaken preliminary attempts to substitute the protons of the methylidine and methylidene moieties or the methyl groups at the Al atoms. But surprisingly no reaction takes place when, for example, **7** was stirred with $^tBuNH_2$ or $(Me_3Si)_2NH$. No definite product could be isolated from the reaction of **7** with ^tBuOH. Futhermore, it is impossible to insert 1-butene into the metal−carbon bonds, even under pressure. Therefore, it is not surprising that ethene does not polymerize when bubbled through a co-catalyst-free solution of **7** in toluene. No complex formation of **7** was observed with tertiary phosphines.

However, methylidene transfer reactions of **7** and carbonyl group-containing organics were successful. The results, including the reaction conditions, (not opti-

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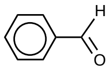
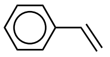
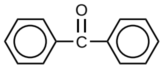
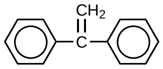
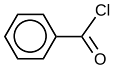
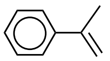
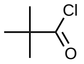
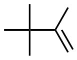
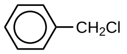
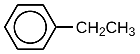
[7] Kräuter, T.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 597.

Table 1. Products and Yields in the Methylidene Transfer Reactions of 7[a]

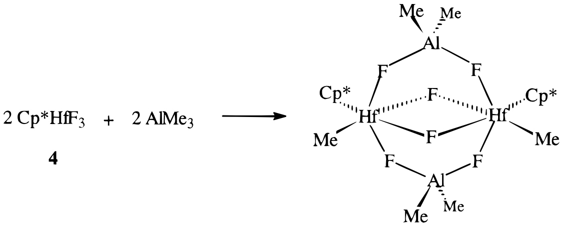
starting material	product	reaction conditions	yield (%)
		$CHCl_3$, room temp, 4 days	25
		toluene, 70 °C, 5 h	24
		$CHCl_3$, reflux, 4 h	7
		$CHCl_3$, reflux, 8 h	11
		toluene, reflux, 8 h	7

[a] Yields were determined by GC and are based on **7**.

mized) are summarized in Table 1. In all cases a 7-fold excess of the substrate was taken. Except for the reaction of $(Ph)_2CO$ with **7**, which was worked up with diluted HCl, the products were isolated directly from the reaction mixture by distillation. After chromatographic separation only the main product was characterized. The reactions in general do not occur when ether or pentane was used as a solvent. Surprisingly, esters do not react with **7** using boiling $CHCl_3$. The low yields of the products originating from chlorine-containing compounds could result from the additional methyl transfer reaction, which should be the rate-determining step of the reaction. Indeed, when benzyl chloride is reacted with **7**, only ethylbenzene can be identified in low yield.

Besides the Tebbe reagent as the classical representative of an active "Wittig-type" reagent of group 4 transition metals,[1,8] alkylidene transfer reactions using ketones are also well-known for the related Zr complex $Cp_2Zr[\mu_2\text{-}CH(Np)](\mu_2\text{-}Cl)Al^iBu_2$ (Np = *neo*pentyl)[9] when it is treated with HMPTA.[9c] In comparison, the Ti species is much more reactive than the Zr one.[9c] For both complexes, a free carbene intermediate is discussed to be necessary for a successful oxo methylidene conversion. A dissociative step cannot be assumed for complex **7**. However, $Et_2AlCH_2AlEt_2{\cdot}Et_2O$ gives $(Ph)_2C{=}CH_2$ from the reaction of $(Ph)_2CO$ without using final hydrolysis.[10]

Preparation of 9. A comparison of the metal−fluorine bond energies (Zr−F 661 kJ/mol, Hf−F 642 kJ/mol, Al−F 640 kJ/mol)[11] shows that treatment of Cp^*HfF_3 (**4**) with $AlMe_3$ should lead to the analogous hafnium complexes of **6**, **7**, and **8**. Indeed, when **4** and $AlMe_3$ were reacted in an equimolar ratio in toluene, the homologous hafnium complex of **6**, *cis*-$\{[Cp^*HfMe(\mu_2\text{-}F)][(\mu_2\text{-}F)_2AlMe_2]\}_2$ (**9**), could be isolated in quantitative yield. **9** is generated stereospecifically as its *cis* isomer, which is persistent in solution.



9

(4)

NMR Spectra of 9. The ^{19}F NMR spectrum of **9** reveals three magnetic nonequivalent types of fluorine atoms as observed for complex **6**. Both fluorine atoms bridging the Hf atoms become chemically different due to the *trans* effect of either the Cp* ligands or the methyl groups. One of them gives a doublet of a quintet resonance (δ −87.3 ppm) with $^2J_{FF}$ coupling constants (19 and 86 Hz). The second one exhibits a doublet from a quintet from a septet signal (δ −56.7 ppm) due to an additional $^1H-^{19}F$ coupling ($^2J_{HF}$ = 11 Hz). The intensity of these two signals compared to the intensity of a broad doublet (δ −109.8 ppm, $^2J_{FF}$ = 10 Hz) is 1:4. It originates from the four F atoms linking the Hf and Al atoms.

The ^1H NMR spectrum of **9** shows a singlet resonance (δ 1.83 ppm) for the protons of the Cp* groups. The protons of the Hf-bonded methyl groups exhibit a doublet of a doublet (δ 0.24 ppm). One of the $^1H-^{19}F$ coupling constants can be determined (10 Hz). The protons of the Al-bonded methyl groups give, depending upon their *syn* or *anti* position in relation to the Cp* ligands, two multiplets (δ −0.37 and −0.46 ppm).

The resonances of the C atoms of the Cp* rings of **9** appear in the ^{13}C NMR spectrum as singlets (δ 122.4 and 10.6 ppm). However, the C atoms of the methyl groups at the Al atoms produce two multiplets (δ −11.1 and −12.2 ppm). Finally, for the C atoms of the Hf-connected methyl groups, a doublet of a doublet (δ 43.5 ppm) with $^2J_{CF}$ coupling constants of 15 and 30 Hz is found.

Crystal Structure of 9. Single crystals of **9** suitable for X-ray analysis at 153 K were obtained from a toluene solution of **9** by slowly reducing the volume under reduced pressure. Figure 1 shows the structure of **9** in the crystal. The relevant bond lengths and -angles of **9** are presented in Table 2. Four molecules of **9**, as depicted in Figure 1, occupy the elemental cell (Z = 16). **9** is isostructural to **6**.

The Hf−C(Me) bond distances amount to 224.4 pm. This value is in agreement with those found for Cp_2HfMe_2[12] (mean 223.7 pm) or $[(Cp_2HfMe)_2(\mu_2\text{-}O)]$ (mean 229.5(14) pm).[13] However, in another structure determination of Cp_2HfMe_2,[13] two different and much longer Hf−C(Me) bond lengths were reported (231.8(8) and 238.2(7) pm), which correspond to the Hf−C(Me) bond

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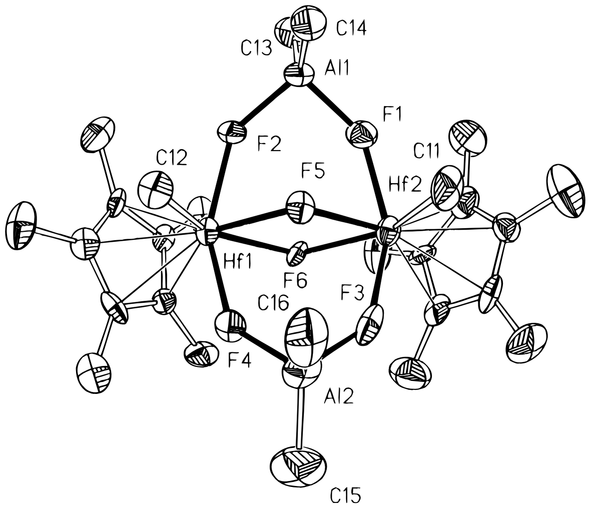


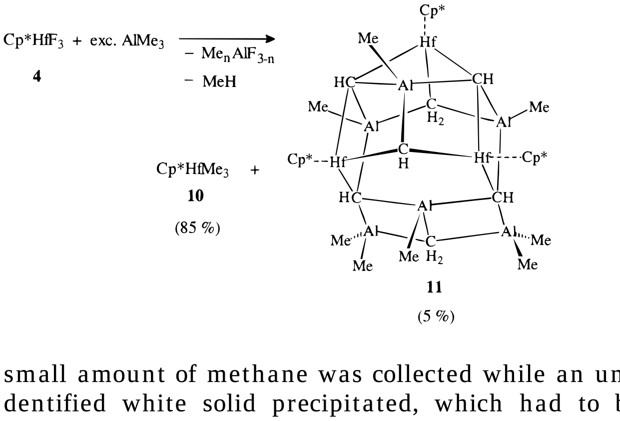
Figure 1. Crystal structure of *cis*-$\{[Cp^*HfMe(\mu_2\text{-}F)][(\mu_2\text{-}F)_2AlMe_2]\}_2$ (**9**), anisotropic displacement parameters depicting 50% probability. Only one of the four molecules of **9**, which occupy the elemental cell, is shown. The hydrogen atoms and the uncoordinated lattice toluene molecules have been omitted for clarity.

Table 2. Selected Bond Lengths (pm) and Angles (deg) of *cis*-$\{[Cp^*HfMe(\mu_2\text{-}F)][(\mu_2\text{-}F)_2AlMe_2]\}_2$ (9)

(a) Distances			
Hf(1)−C(1)	225.2(13)	Hf(1)−F(5)	217.2(6)
Hf(1)−F(2)	213.2(7)	Hf(2)−F(5)	214.5(6)
Hf(1)−F(4)	210.0(7)	Al(2)−F(4)	177.6(8)
(b) Angles			
F(2)−Hf(1)−C(12)	90.9(4)	F(4)−Hf(1)−F(2)	152.2(3)
F(4)−Hf(1)−C(12)	90.1(4)	F(1)−Hf(1)−F(2)	96.1(4)
Hf(2)−F(2)−Hf(1)	112.5(3)	Al(1)−F(2)−Hf(1)	139.9(4)

distances in $(\eta^5\text{-}C_9H_7)_2HfMe_2$ (mean 233.2(12) pm).[14] The bond distances of Hf and F are in the range of 210−217 pm and are comparable to the Zr−F bond lengths in complex **6**.[6]

Preparation of 10 and 11. When 1 equiv of Cp^*HfF_3 (**4**) with 3 equiv of $AlMe_3$ were reacted in *n*-hexane at room temperature for 16 h, different products were isolated in comparison to the analogous reaction using Cp^*ZrF_3 (**1**) or $(\eta^5\text{-}C_5Me_4Et)ZrF_3$ (**3**) and $AlMe_3$, according to eq 2 and eq 5, respectively. Only a small amount of methane was collected while an unidentified white solid precipitated, which had to be filtered off before removing all of the volatiles *in vacuo*. After repeated crystallization of the crude product, Cp^*HfMe_3 (**10**) can be obtained at −25 °C from *n*-hexane in a yield of 85% as colorless needles. The spectroscopical data found for **10** are in agreement with those given in literature.[15]



(5)

However, it was generally observed that the crystallization of **10** was accomplished with the formation of a yellow *n*-hexane-insoluble solid. Keeping the first filtrate of the reaction for several months, the byproduct of **10** accumulated, forming a yellow microcrystalline solid as well as yellow single crystals, which were suitable for an X-ray structure analysis. This revealed the formation of the $Hf_3Al_6C_7$ cluster $[(Cp^*Hf)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)]$ (**11**) as the byproduct of the metathesis reaction using Cp^*HfF_3 (**4**) and excess of $AlMe_3$. The maximum yield of **11** is 5%, corresponding to the small amount of methane generated from this reaction. The yield of **11** cannot be improved by using more than 3 equiv of $AlMe_3$. Furthermore, the reaction of Cp^*HfMe_3 and excess of $AlMe_3$ over a period of 3 weeks gives no significant amount of methane and **11**, respectively.

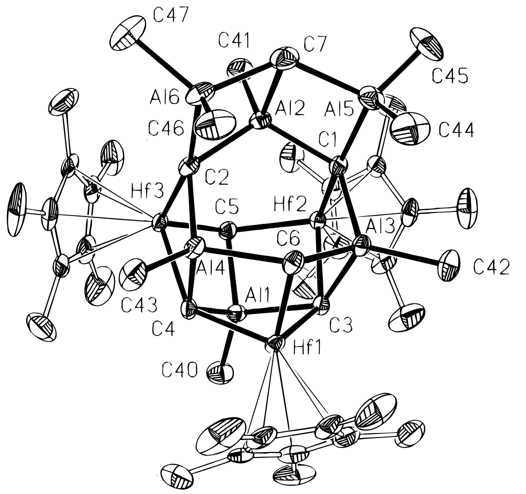


Figure 2. Crystal structure of $[(Cp^*Hf)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)]$ (**11**) and anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

Figure 2 shows the structure of **11** in the solid state while the relevant bond lengths and -angles of **11** are presented in Table 5.

Crystal Structure of 11. The solid state structure of **11** is comparable to that of complex **7** with the exception that **7** contains 2.5 molecules of toluene/molecule of **7**, localized on special crystallographic positions.

In **11**, three Hf, six Al, and seven C atoms are building an open core and all the metal atoms are tetragonally coordinated, but nearly all the C atoms are bond to the metal atoms hypervalently. The structure exhibits four μ_4 (C1, C2, C3, and C4) and one μ_3 (C5) bridging C atoms of methylidine units as well as two μ_3-bridging C atoms of methylidene groups between the metal centers.

The H atoms have not been localized in the structure refinement; they are however plausibly placed due to electronic and geometric reasons. This resulted in an electronic deficiency at the 12-electron Hf centers, and therefore, significant metal−metal interactions occur. The average value of the short Hf−Al distances amount to 285.2(2) pm. From the metal radii a Hf−Al distance of 302 pm can be derived.[16]

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[15] Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

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Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for 9[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Hf(1)	127(1)	2591(1)	1614(1)	24(1)	F(24)	2724(2)	−308(3)	−2675(3)	26(2)
Hf(2)	658(1)	2685(1)	3252(1)	29(1)	F(25)	2487(2)	148(3)	−3787(3)	24(2)
Al(1)	221(2)	3952(2)	2364(2)	36(1)	F(26)	2507(2)	−853(3)	−3800(3)	22(2)
Al(2)	68(2)	1387(2)	2554(2)	51(1)	C(41)	1365(5)	−1194(6)	−4300(6)	31(3)
F(1)	585(3)	3525(3)	2967(3)	40(2)	C(42)	1582(5)	−1274(6)	−4768(7)	37(4)
F(2)	178(3)	3467(3)	1771(3)	35(2)	C(43)	1364(5)	−888(6)	−5234(6)	34(4)
F(3)	476(3)	1838(2)	3116(3)	48(2)	C(44)	1002(5)	−568(6)	−5065(6)	39(4)
F(4)	79(3)	1766(3)	1896(3)	38(2)	C(45)	1008(5)	−768(6)	−4479(6)	32(3)
F(5)	−13(3)	2687(3)	2467(3)	32(2)	C(41*)	1473(6)	−1547(6)	−3734(7)	55(5)
F(6)	809(2)	2586(3)	2403(3)	24(2)	C(42*)	1972(5)	−1716(6)	−4776(8)	58(5)
C(1)	238(5)	2016(6)	757(6)	33(3)	C(43*)	1467(7)	−825(9)	−5835(7)	78(6)
C(2)	−40(5)	2494(6)	479(6)	34(4)	C(44*)	642(6)	−156(7)	−5455(8)	70(6)
C(3)	265(5)	2958(6)	674(5)	28(3)	C(45*)	685(6)	−568(7)	−4126(8)	57(5)
C(4)	741(5)	2785(5)	1084(5)	25(3)	C(46)	3992(5)	−744(7)	−3133(7)	42(4)
C(5)	727(5)	2200(6)	1144(6)	29(3)	C(47)	4018(5)	−531(5)	−2550(6)	31(3)
C(1*)	68(6)	1417(7)	657(7)	55(4)	C(48)	3679(5)	−853(6)	−2358(6)	33(3)
C(2*)	−546(5)	2498(7)	−14(7)	56(5)	C(49)	3442(5)	−1240(6)	−2801(7)	37(4)
C(3*)	126(6)	3535(7)	455(7)	55(4)	C(50)	3640(5)	−1174(6)	−3300(6)	39(4)
C(4*)	1182(5)	3151(6)	1377(6)	42(4)	C(46*)	4310(6)	−548(8)	−3504(8)	71(6)
C(5*)	1131(5)	1832(6)	1496(7)	42(4)	C(47*)	4386(6)	−122(7)	−2182(8)	58(5)
C(6)	1411(5)	3173(6)	3975(6)	42(4)	C(48*)	3600(6)	−788(8)	−1738(6)	63(5)
C(7)	1584(5)	2778(5)	3595(6)	31(3)	C(49*)	3057(6)	−1672(6)	−2776(8)	60(5)
C(8)	1486(5)	2236(7)	3750(6)	41(4)	C(50*)	3507(6)	−1531(7)	−3872(7)	69(6)
C(9)	1249(6)	2284(7)	4216(6)	45(4)	C(51)	1533(5)	511(6)	−4518(7)	43(4)
C(10)	1203(5)	2845(6)	4345(6)	36(3)	C(52)	3438(5)	520(5)	−3005(6)	33(3)
C(6*)	1473(7)	3791(6)	3991(8)	64(5)	C(53)	2827(6)	823(6)	−4901(7)	55(4)
C(7*)	1860(6)	2935(8)	3161(7)	59(5)	C(54)	3072(6)	−396(8)	−5500(7)	63(5)
C(8*)	1629(7)	1725(7)	3520(8)	70(5)	C(55)	2144(6)	722(7)	−2570(9)	66(5)
C(9*)	1070(8)	1801(7)	4525(8)	73(6)	C(56)	1930(6)	−604(9)	−2123(7)	72(6)
C(10*)	1034(6)	3066(8)	4844(8)	72(6)	Hf(7)	4347(1)	2508(1)	−627(1)	25(1)
C(11)	80(6)	2793(8)	3733(7)	58(5)	Hf(8)	4885(1)	2491(1)	1014(1)	20(1)
C(12)	−721(5)	2641(6)	1250(7)	40(4)	Al(7)	4875(2)	3794(2)	178(2)	40(1)
C(13)	639(7)	4556(7)	2255(8)	61(5)	Al(8)	4834(2)	1196(2)	147(2)	37(1)
C(14)	−433(6)	4052(7)	2471(2)	54(4)	F(31)	4901(3)	3347(3)	805(3)	33(2)
C(15)	423(8)	701(7)	2550(10)	92(7)	F(32)	4488(3)	3363(3)	−407(3)	37(2)
C(16)	−615(7)	1446(8)	2618(8)	77(6)	F(33)	4867(3)	1637(3)	783(3)	33(2)
Hf(3)	1845(1)	−344(1)	749(1)	22(1)	F(34)	4459(3)	1651(3)	−433(3)	34(2)
Hf(4)	3125(1)	−346(1)	1750(1)	22(1)	F(35)	5024(3)	2490(3)	160(3)	29(2)
Al(3)	2100(2)	−264(2)	2421(2)	42(1)	F(36)	4199(2)	2506(3)	228(3)	22(2)
Al(4)	2849(1)	77(2)	149(2)	30(1)	C(61)	3786(5)	2230(7)	−1664(6)	41(4)
F(11)	2721(3)	−361(3)	2369(3)	34(2)	C(62)	3535(6)	2057(7)	−1240(6)	48(4)
F(12)	1770(3)	−375(3)	1629(3)	33(2)	C(63)	3402(5)	2546(6)	−980(6)	38(4)
F(13)	3198(2)	−195(3)	883(3)	30(2)	C(64)	3563(6)	3013(7)	−1248(7)	46(4)
F(14)	2252(3)	−183(3)	141(3)	34(2)	C(65)	3802(5)	2797(6)	−1660(6)	36(3)
F(15)	2473(2)	141(3)	1289(3)	26(2)	C(61*)	3966(6)	1824(7)	−2059(7)	58(5)
F(16)	2500(2)	−856(3)	1204(3)	27(2)	C(62*)	3401(6)	1481(7)	−1138(9)	71(5)
C(21)	1326(5)	−799(6)	−244(6)	36(4)	C(63*)	3106(6)	2574(8)	−543(7)	66(6)
C(22)	1578(5)	−1215(5)	167(6)	33(3)	C(64*)	3467(7)	3617(7)	−1136(8)	72(6)
C(23)	1381(5)	−1231(6)	651(6)	35(4)	C(65*)	3999(6)	3170(7)	−2069(8)	63(5)
C(24)	1018(5)	−814(6)	564(6)	32(3)	C(66)	4751(5)	2011(5)	1909(5)	25(3)
C(25)	983(5)	−541(6)	−2(6)	33(3)	C(67)	5047(5)	2488(6)	2166(5)	28(3)
C(21*)	1387(7)	−659(8)	−846(7)	73(6)	C(68)	4761(5)	2967(5)	1924(6)	29(3)
C(22*)	1977(6)	−1599(7)	75(9)	77(6)	C(69)	4273(4)	2801(5)	1521(5)	22(3)
C(23*)	1531(7)	−1638(6)	1188(7)	62(5)	C(70)	4270(4)	2197(5)	1520(5)	25(3)
C(24*)	676(5)	−670(7)	946(7)	56(5)	C(66*)	4895(6)	1416(6)	2066(7)	50(4)
C(25*)	591(5)	−98(6)	−320(7)	52(4)	C(67*)	5557(5)	2478(7)	2654(6)	51(5)
C(26)	3676(5)	−899(6)	2661(6)	41(4)	C(68*)	4926(6)	3565(6)	2094(7)	45(4)
C(27)	3446(5)	−1268(6)	2167(7)	39(4)	C(69*)	3863(5)	3168(6)	1206(6)	42(4)
C(28)	3648(6)	−1152(6)	1692(6)	38(4)	C(70*)	3836(5)	1838(6)	1184(6)	33(3)
C(29)	3985(5)	−723(6)	1879(6)	37(4)	C(71)	4956(6)	2479(7)	−1087(7)	61(5)
C(30)	4005(5)	−556(6)	2475(6)	38(4)	C(72)	5724(5)	2481(5)	1383(6)	31(3)
C(26*)	3593(7)	−894(9)	3263(7)	82(7)	C(73)	4481(7)	4442(6)	246(8)	69(5)
C(27*)	3079(6)	−1734(7)	2180(9)	70(6)	C(74)	5532(6)	3830(8)	77(7)	64(5)
C(28*)	3533(6)	−1461(7)	1082(7)	64(5)	C(75)	4434(7)	563(6)	214(8)	66(5)
C(29*)	4294(6)	−463(8)	1535(8)	65(5)	C(76)	5492(6)	1145(7)	39(7)	56(4)
C(30*)	4361(6)	−138(7)	2870(8)	63(5)	C(81)	2525(7)	2233(14)	1759(11)	99(9)
C(31)	1494(5)	504(6)	617(7)	43(4)	C(82)	2442(6)	1968(8)	1235(9)	62(5)
C(32)	3417(5)	499(5)	2061(6)	34(3)	C(83)	2387(8)	2296(11)	710(16)	123(11)
C(33)	2023(7)	487(8)	2633(10)	91(7)	C(84)	2399(8)	2810(11)	669(13)	97(7)
C(34)	1963(7)	−903(9)	2855(8)	79(6)	C(85)	2521(8)	3098(12)	1315(15)	104(10)
C(35)	2844(6)	883(6)	187(7)	47(4)	C(86)	2570(7)	2830(9)	1819(17)	105(11)
C(36)	3051(6)	−327(7)	−460(7)	53(4)	C(87)	2587(7)	1982(13)	2318(12)	136(11)
Hf(5)	1860(1)	−348(1)	−4292(1)	22(1)	C(91)	2474(8)	−2434(11)	−1282(10)	88(7)
Hf(6)	3140(1)	−335(1)	−3286(1)	21(1)	C(92)	2673(10)	−2903(11)	−1006(12)	107(8)
Al(5)	2867(2)	20(2)	−4903(2)	31(1)	C(93)	3135(13)	−2905(11)	−523(12)	122(10)
Al(6)	2122(2)	−86(2)	−2652(2)	33(1)	C(94)	3389(9)	−2450(10)	−329(10)	83(6)
F(21)	2273(3)	−254(3)	−4902(3)	35(2)	C(95)	3205(9)	−1940(10)	−574(11)	90(7)
F(22)	3216(2)	−229(3)	−4167(3)	31(2)	C(96)	2749(8)	−1917(8)	−1056(10)	78(6)
F(23)	1781(2)	−286(3)	−3421(3)	30(2)	C(97)	1997(10)	−2396(12)	−1781(16)	164(14)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Crystal Data for 9 and 11

	9	11
formula	$C_{29.50}H_{52}Al_2F_6Hf_2$	$C_{45}H_{78}Al_6Hf_3$
fw	931.65	1316.42
cryst size (mm)	0.6 × 0.4 × 0.4	0.3 × 0.4 × 0.4
space group	$P2_1/c$	$P2_1/c$
a (pm)	2804.7(6)	1218.1(3)
b (pm)	2398.9(6)	1991.7(6)
c (pm)	2304.0(6)	2486.6(9)
α (deg)	90	90
β (deg)	108.87	93.11(4)
γ (deg)	90	90
V ($nm^{3)}$	14.669(6)	6.024(3)
Z	16	4
temp (K)	153(2)	153(2)
ρc (Mg $m^{-3)}$	1.687	1.452
μ ($mm^{-1)}$	5.573	5.268
F(000)	7248	2568
2θ range (deg)	3.5–22.5	4–25
no. of reflns measd	19 355	15 224
no. of unique reflns	16 673	10 629
no. of restraints	1	0
refined param	1489	510
$R1$ [$I > 2\sigma(I)$]	0.0713	0.0439
w$R2$ (all data)	0.1468	0.1147
highest diff peak (10^{-6} e $pm^{-3)}$)	5.05	1.72

Table 5. Selected Bond Lengths (pm) and Angles (deg) of [$(Cp^*Hf)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)$] (11)

(a) Distances			
Hf1–C3	218.4(6)	Al3–C1	200.2(6)
Hf1–C4	217.9(6)	Al3–C3	218.2(7)
Hf1–C6	217.1(7)	Al2–Al5	268.9(3)
Hf2–C1	222.0(6)	Hf1–Al1	283.6(2)
Hf2–C3	225.7(6)	Hf1–Al3	283.8(2)
Hf2–C5	214.1(6)	Hf2–Al2	329.8(2)
Hf3–C2	221.9(6)	Al3–C6	212.4(7)
Hf3–C4	215.8(7)	Al4–C2	199.3(6)
Hf3–C5	213.1(6)	Al4–C4	215.8(7)
Al1–C3	212.8(6)	Al4–C6	211.4(7)
Al1–C4	212.6(7)	Al5–C1	211.0(7)
Al1–C5	202.9(6)	Al5–C7	206.3(8)
Al2–C1	202.0(7)	Al6–C2	212.3(7)
Al2–C2	202.2(7)	Al6–C7	204.7(8)
Al2–C7	207.1(8)		

(b) Angles			
C1–Al2–C2	115.5(3)	Al2–C7–Al6	81.1(3)
C4–Hf1–C3	90.5(2)	Al3–C6–Al4	124.7(3)
C6–Hf1–C3	94.2(2)	Al3–C6–Hf1	82.9(2)
C6–Hf1–C4	93.9(2)	Al4–C6–Hf1	83.0(2)
C4–Al1–C3	93.5(3)	Al4–C4–Hf1	81.8(2)
Hf3–C5–Hf2	124.5(3)	Al4–C2–Al6	104.1(3)
Al1–C5–Hf3	86.7(2)	Al5–C14–Hf3	82.2(2)
Al1–C5–Hf2	86.8(2)	Al5–C7–Al6	132.8(4)
Al1–C1–Hf2	102.0(3)	Al6–C2–Hf3	166.0(3)
Al2–C2–Al6	80.5(2)		

The Al2–Al5 (268.9(3) pm) and Al2–Al6 (267.8(3) pm) distances are also close to those found in [$(Me_3Si)_2CH]_2AlAl[CH(SiMe_3)_2]_2$ (266.0 pm)[17] and $[Cp^*Al]_4$ (276.9 pm),[18] respectively, and are much shorter than calculated once from the metal radii (286 pm).[16]

The Hf-μ-C bond lengths of **11** are in a wide range (213.1(6)–227.0(6) pm) and are comparable to the Zr-μ-C bond lengths in **7**. This fact is supported by *ab initio* studies of the theoretical molecules $H_2Zr{=}CH_2$ (199 pm) and $H_2Hf{=}CH_2$ (198 pm), which reveal no significant differences in the bond strengths between Zr and Hf carbenes.[19] However, the Hf-μ-C bond lengths in **11** are all shorter than the Hf–C′ (243.2(6) pm) and the Hf–C″ (231.0(6) pm) distances in the only known heterobimetallic Hf–C–Al complex {$Cp_2Hf[\mu\text{-}\eta^1{:}\eta^2\text{-}MeCC'(c\text{-}C_6H_{11})][\mu\text{-}C''C(c\text{-}C_6H_{11})]AlMe_2$}.[20] In comparison to the Hf-μ-C bonds, the very long distances Hf2–C3 (225.7(6) pm) and Hf3–C2 (227.0(6) pm) deviate significantly to four proportional short Al2-μ-C bonds (202.2(7), 202.2(7), 207.1(8), and 196.2(7) pm). Therefore, an intramolecular polarization in **11** could be postulated. This finding, likewise observed for complex **7**, could serve as an explanation for their poor solubility in common organic solvents.

The classification of C5 as methylidenic and C6 as methylidinic carbon is supported by the structural data of **11**. As expected, all metal-μ-C5 bonds are significantly shorter than the related metal-μ-C6 bonds. Furthermore, the angles between Hf1–C6–Al4 (83.0(2)°) and Hf1–C6–Al3 (82.9(2)°) are on average 3.8° more acute than the angles between Hf2–C5–Al6 (86.8(2)°) and Hf3–C5–Al1 (86.7(2)°). This is obviously due to the requirement of more space for the two H atoms at C6. Similar observations can also been made for complex **7**.

^{1}H NMR Spectrum of 11. In the ^{1}H NMR spectrum of **11**, measured in toluene-d_8, the protons of the Cp* groups at Hf2 and Hf3 are found to be magnetically equivalent. They give a singlet (δ 1.98 ppm) which has a 2:1 ratio compared to the proton signal of the third Cp* group (δ 1.92 ppm). The resonances for the protons of the methyl groups at the Al atoms (C40–C47) are found in the high-field region and can be assigned on the basis of their integral intensities. The most shielded protons are those at the methylidene bridge of Al5, Al6, and Al2. They are diastereotopic and generate a doublet (δ −1.63 ppm) with a coupling constant of 11 Hz, while the protons of the second methylidene bridge are assigned to a much more low-field-shifted doublet (δ 6.57 ppm, $^2J_{HH} = 11$ Hz). The most deshielded proton is that of the methylidine bridge of Hf2, Hf3, and Al1. It shows a doublet of a doublet (δ 7.48 ppm, $^2J_{HH} = 1.7$ Hz), however, the Hf_2Al_2CH and the $HfAl_3CH$ protons give just singlets (δ 5.16 and 2.82 ppm).

In comparison to **7** or **8**, the chemical shift of the latter indicates a much more deshielding influence of Zr than Hf on the protons of alkylidene bridges. This has also been observed for other bimetallic M–Al alkylidene complexes (M = Zr, Hf).[21]

Preparation of 12 and 13. It can be seen that eq 2 has a certain resemblance to that for the formation of the Tebbe reagent.[3] In this context, we were primarily interested in whether it is possible to generate a Zr–F analogous complex. To our knowledge, the reaction of zirconocene difluorides and $AlMe_3$ has not been studied before.

During the reaction of 2 equiv of $AlMe_3$ with $Cp^*_2ZrF_2$ (**2**) in toluene, no gas evolution was observed, and as expected, $Cp^*_2ZrMe_2$[22] (**12**) can be isolated quantitatively. Interestingly, from the analogous reaction of

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Cp*$_2$HfF$_2$ with 2 equiv of AlMe$_3$, only ∼50% of Cp*$_2$HfMe$_2$ is formed after 6 days stirring the reaction mixture at ambient temperature. A metathesis reaction occurs when Cp*TaF$_4$[23] (**5**) is reacted with an excess of AlMe$_3$. Cp*TaMe$_4$[24] (**13**) can be obtained in high yield.

Conclusion

As expected, in contrast to transition metal organo chlorides, reversible reactions of the corresponding fluorides with an excess of AlMe$_3$ are suppressed due to the generation of (Me$_2$AlF)$_4$. This is one reason as well as the elimination of methane from the involved CH activation processes, which finally result in the facile formation of Zr−C−Al and Hf−C−Al clusters, respectively.

In summary, from the results and discussion here presented, one can draw conclusions concerning different aspects of the problem in study. First, one can comment on the ability of the fluoride complexes to function as single-source Ziegler−Natta catalysts. Then one can argue the possibility of hypervalent CH units in complex species involved in catalytic cycles. Such species are thought to persist in MAO-activated zirconocene catalyst solutions from which a permanent methane evolution can be observed, and it is presumed that they inhibit the polymerization catalysis.[25] This suggestion corresponds with the result of the catalytical inactivity of the described Zr clusters, when no cocatalyst is added.

EPR spectroscopic investigations of the reactions of monocyclopentadienyl titanium and zirconium trichlorides and MAO have shown that reduction of the transition metals occurs in this case, forming radical species.[26] Our future studies will be directed at reacting organometal fluorides using MAO as well as co-catalyst and investigating such systems by applying the herein collected ^{19}F NMR spectroscopical data.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen with Schlenk techniques or in a nitrogen glovebox. Solvents were dried over Na/K alloy and distilled prior to use.

NMR spectra were obtained with a Bruker AM 250 and were recorded in benzene-d_6, toluene-d_8, and CDCl$_3$ with SiMe$_4$ or CFCl$_3$ as external standard. EI mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH 5 instruments. Infrared spectra were acquired on a Bio-Rad FTS-7. Elemental analyses were obtained from the Mikroanalytisches Labor Beller, Göttingen, Germany.[27]

Cp*ZrF$_3$[4] (**1**), (η^5-C$_5$Me$_4$Et)ZrF$_3$[4] (**3**), Cp*$_2$ZrF$_2$[4] (**2**), Cp*HfF$_3$[4] (**4**), and Cp*TaF$_4$[23] (**5**) were synthesized according to literature methods. AlMe$_3$ solutions (Aldrich) were used as purchased.

6. To a suspension of Cp*ZrF$_3$ (2.00 g, 7.1 mmol) in *n*-hexane (50 mL) was added an equimolar amount of AlMe$_3$ (3.53 mL of a 2 M solution in *n*-hexane, 7.1 mmol) *via* syringe at once, at room temperature. After a short time (10−15 min), the reaction suspension abruptly turned into a yellow solution. The reaction mixture was stirred for an additional 1 h. Then the volume of the solution was reduced slowly under vacuum (20 mL), and the product began to crystallize. Precipitation of colorless crystals of **6** was completed by keeping the reaction mixture at −25 °C. They were filtered and dried in vacuum. The reaction yielded 1.92 g (2.7 mmol, 76%) of pure product. Mp: 208 °C. ^{1}H NMR (250 MHz C$_6$D$_6$): δ 1.76 (s, 30 H, C$_5$(CH$_3$)$_5$), 0.54 and 0.50 (2 m, $^2J_{FF} = 10$ Hz, 6 H, ZrCH$_3$), −0.35 (m, 6 H, AlCH$_3$), −0.46 (m, 6 H, AlCH$_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 124.9 (s, *C*$_5$Me$_5$), 45.2 (dd, $^2J_{CF} = 11$ Hz, $^2J_{CF} = 30$ Hz, ZrCH$_3$), 10.8 (s, C$_5$(*C*H$_3$)$_5$), −11.1 (m, AlCH$_3$), −12.0 (m, AlCH$_3$). ^{19}F NMR (235 MHz, C$_6$D$_6$): δ −32.5 (d quint sept, $^2J_{FF} = 33$ Hz, $^2J_{FF} = 75$ Hz, $^2J_{HF} = 9$ Hz, 1 F, ZrFZr), −69.5 (d quint, $^2J_{FF} = 20$ Hz, $^2J_{FF} = 75$ Hz, 1 F, ZrFZr), −108.2 (s, 4 F, ZrFAl). IR (Nujol, CsI): ν 1194 s, 1133 s, 1027 s, 804 s, 699 vs, 595 vs, 570 vs, 542 vs, 474 s, 400 vs, 348 vs, 312 vs. MS (70 eV): *m*/*z* (%) 696 (100) (M$^+$ − Me), 620 (50) (M$^+$ − Me − Me$_2$AlF), 544 (50) (M$^+$ − Me − 2Me$_2$AlF). Anal. Calcd (Found): C, 43.92 (43.7); H, 6.80 (6.8); F, 16.03 (16.1).

7. Cp*ZrF$_3$ (5.00 g, 17.5 mmol) was suspended in *n*-hexane (40 mL), and AlMe$_3$ in *n*-hexane (44.25 mL of an 2 M solution, 88.5 mmol) was added. After the reaction mixture has been stirred for 18 h, no further gas evolution was observed. The yellow solution was concentrated to a quarter of the original volume. **7** precipitated as a yellow microcrystalline solid. The solution was decanted from the product. The recrystallization from toluene (50 mL) afforded yellow **7**. Yield: 4.00 g (3.79 mmol, 70%). Range of decomposition: 305−333 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ 9.94 (dd, $^4J_{HH} = 1.7$ Hz, $^4J_{HH} = 0.8$ Hz, 1 H, Zr$_2$AlCH), 7.07 (s, 2 H, Zr$_2$Al$_2$CH), 4.26 (d, $^2J_{HH} = 11$ Hz, 2 H, ZrAl$_2$CH$_2$), 2.74 (m, 2 H, ZrAl$_3$CH), 2.22 (s, 30 H, C$_5$(CH$_3$)$_5$), 2.09 (s, 15 H, C$_5$(CH$_3$)$_5$), −0.62 (s, 12 H, Al(CH$_3$)$_2$), −0.71 (s, 6 H, AlCH$_3$), −0.76 (s, 3 H, AlCH$_3$), −0.97 (s, 3 H, AlCH$_3$), −1.74 (d, $^2J_{HH} = 11$ Hz, 2 H, Al$_3$CH$_2$). IR (Nujol, KBr): ν 1187 s, 1024 s, 832 s, 787 s, 693 vs, 679 vs, 662 vs, 607 s, 501 s, 365 vs. MS (70 eV): *m*/*z* (%) 1040 (4) (M$^+$ − Me), 965 (100) (M$^+$ − 6Me), 951 (20) (M$^+$ − 7Me), 483 (20) (M^{2+} − 6Me). Anal.[27]

8. (η^5-C$_5$Me$_4$Et)ZrF$_3$ (1.50 g, 5.0 mmol) was suspended in *n*-hexane (50 mL), and AlMe$_3$ in *n*-hexane (12.50 mL of a 2 M solution, 25.0 mmol) was added. After the reaction mixture has been stirred for 18 h, no further gas evolution was observed. The yellow solution was concentrated to a third of the original volume. **8** precipitated over a period of 6 days as a grayish yellow microcrystalline solid. The solution was decanted from the product. The recrystallization from toluene afforded yellow **8**. Yield: 1.29 g (1.2 mmol, 70%). Range of decomposition: 292−300 °C. ^{1}H NMR (250 MHz, C$_6$D$_6$): δ 9.14 (dd, $^4J_{HH} = 2.4$ Hz, $^4J_{HH} = 2.4$ Hz, 1 H, Zr$_2$AlCH), 4.01 (s, 1 H, Zr$_2$Al$_2$CH), 4.00 (s, 1 H, Zr$_2$Al$_2$CH), 2.43 (d, $^2J_{HH} = 11$ Hz, 2 H, ZrAl$_2$CH$_2$), 2.27 (q, $^3J_{HH} = 7.5$ Hz, 6 H, C$_5$Me$_4$C*H*$_2$CH$_3$), 1.92 (s, 3 H, C$_5$(C*H*$_3$)$_4$Et), 1.90 (s, 3 H, C$_5$(C*H*$_3$)$_4$Et), 1.86 (s, 3 H, C$_5$(C*H*$_3$)$_4$Et), 1.84 (s, 3 H, C$_5$(C*H*$_3$)$_4$Et), 1.81 (s, 12 H, C$_5$(C*H*$_3$)$_4$Et), 1.77 (s, 6 H, C$_5$(C*H*$_3$)$_4$Et), 1.76 (s, 6 H, C$_5$(C*H*$_3$)$_4$Et), 0.88 (2t, $^3J_{HH} = 7.5$ Hz, 9 H, C$_5$Me$_4$CH$_2$C*H*$_3$), −0.02 (s, 3 H, AlCH$_3$), −0.08 (s, 3 H, AlCH$_3$), −0.11 (s, 3 H, AlCH$_3$), −0.31 (s, 6 H, Al(CH$_3$)$_2$), −0.36 (s, 3 H, AlCH$_3$), −0.37 (s, 3 H, AlCH$_3$), −0.67 (s, 3 H, AlCH$_3$), −1.68 (dd, $^2J_{HH} = 5.5$ Hz, 2 H, Al$_3$CH$_2$). IR (Nujol, KBr): ν 1187 s, 1097 s, 1024 s, 832 s, 787 s, 693 vs, 679 vs, 662 vs, 607 s, 501 s, 365 vs. MS (70 eV): *m*/*z* (%) 1051 (5) (M$^+$ − 3Me), 1008 (100) (M$^+$ − 6Me), 993 (20) (M$^+$ − 7Me), 504 (20) (M^{2+} − 6Me). Anal. Calcd (Found): C, 52.57 (51.6); H, 7.72 (7.8).

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Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for 11

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Hf(1)	1839(1)	3227(1)	4589(1)	18(1)	C(21)	5900(5)	2883(3)	3040(3)	25(1)
Hf(2)	4204(1)	3259(1)	3476(1)	16(1)	C(22)	5934(5)	3593(4)	3054(3)	26(2)
Hf(3)	1599(1)	2293(1)	3110(1)	18(1)	C(23)	6044(5)	3784(4)	3612(3)	30(2)
Al(1)	3062(2)	2249(1)	4048(1)	20(1)	C(24)	6084(5)	3203(4)	3932(3)	35(2)
Al(2)	2183(2)	3809(1)	2656(1)	21(1)	C(25)	6119(7)	1924(5)	3741(5)	57(3)
Al(3)	2959(2)	4237(1)	4029(1)	20(1)	C(26)	5856(7)	2477(5)	2542(3)	44(2)
Al(4)	380(2)	3282(1)	3660(1)	21(1)	C(27)	5950(7)	4044(5)	2580(3)	46(2)
Al(5)	2628(2)	5089(1)	2933(1)	31(1)	C(28)	6191(7)	4491(5)	3821(4)	57(3)
Al(6)	46(2)	4125(1)	2545(1)	29(1)	C(29)	6289(7)	3170(6)	4521(4)	61(3)
C(1)	3232(5)	4167(3)	3245(3)	20(1)	C(30)	1762(6)	1356(3)	2451(3)	30(2)
C(2)	880(5)	3292(3)	2910(3)	20(1)	C(31)	763(6)	1681(4)	2316(3)	30(2)
C(3)	3497(5)	3241(3)	4297(3)	19(1)	C(32)	66(6)	1572(4)	2749(3)	39(2)
C(4)	1349(5)	2461(3)	3998(3)	21(1)	C(33)	647(8)	1185(4)	3144(3)	42(2)
C(5)	3336(5)	2358(3)	3254(2)	20(1)	C(34)	1690(7)	1034(4)	2960(3)	38(2)
C(6)	1259(5)	4053(3)	4079(3)	22(1)	C(35)	2703(7)	1292(5)	2099(4)	54(3)
C(7)	1406(6)	4694(4)	2420(3)	34(2)	C(36)	487(9)	2020(5)	1794(3)	54(2)
C(10)	653(6)	3257(5)	5367(3)	40(2)	C(37)	−1107(7)	1810(6)	2768(5)	74(4)
C(11)	1228(7)	2626(5)	5398(3)	41(2)	C(38)	182(11)	893(5)	3640(4)	76(4)
C(12)	2353(7)	2770(4)	5512(3)	36(2)	C(39)	2532(11)	599(5)	3224(5)	79(4)
C(13)	2495(6)	3464(4)	5548(3)	33(2)	C(40)	3625(7)	1470(4)	4442(3)	36(2)
C(14)	1454(6)	3763(4)	5467(3)	34(2)	C(41)	2845(6)	3461(4)	2010(3)	33(2)
C(15)	−545(7)	3361(8)	5296(4)	85(5)	C(42)	3602(6)	4957(4)	4476(3)	36(2)
C(16)	727(12)	1944(6)	5371(4)	80(4)	C(43)	−1165(6)	3184(4)	3824(3)	37(2)
C(17)	3253(10)	2267(5)	5640(4)	60(3)	C(44)	1903(9)	5676(5)	3452(4)	55(2)
C(18)	3552(7)	3821(5)	5689(3)	50(2)	C(45)	3809(8)	5527(4)	2569(4)	57(3)
C(19)	1190(9)	4495(5)	5519(4)	60(3)	C(46)	−889(7)	4627(5)	3028(3)	44(2)
C(20)	6008(5)	2641(4)	3578(3)	34(2)	C(47)	−736(8)	3825(5)	1877(3)	53(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

9. To a solution of Cp^*HfF_3 (2.10 g, 5.0 mmol), dissolved in toluene (50 mL), was added an equimolar amount of $AlMe_3$ (2.50 mL of a 2 M solution in *n*-hexane, 5.0 mmol) *via* syringe within 30 s, at room temperature. To complete the reaction, the solution was stirred for 1 h. The volume of the solution was reduced slowly under vacuum (20 mL), and the product already began to crystallize. Precipitation of colorless crystals of **9** was completed by keeping the reaction mixture at −20 °C. They were filtered and dried under vacuum for 3 h. The reaction yielded 1.95 g (2.2 mmol, 88%) of pure product. Mp: 217 °C. ^1H NMR (250 MHz C_6D_6): δ 1.83 (s, 30 H, $C_5(CH_3)_5$), 0.26 and 0.22 (2 m, $^2J_{FF} = 10$ Hz, 6 H, $HfCH_3$), −0.37 (m, 6 H, $AlCH_3$), −0.46 (m, 6 H, $AlCH_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 122.4 (s, C_5Me_5), 43.5 (dd, $^2J_{CF} = 15$ Hz, $^2J_{CF} = 30$ Hz, $HfCH_3$), 10.6 (s, $C_5(CH_3)_5$), −11.1 (m, $AlCH_3$), −12.2 (m, $AlCH_3$). ^{19}F NMR (235 MHz, C_6D_6): δ −56.7 (d quint sept, $^2J_{FF} = 19$ Hz, $^2J_{FF} = 86$ Hz, $^2J_{HF} = 11$ Hz, 1 F, HfFHf), −87.3 (d quint, $^2J_{FF} = 19$ Hz, $^2J_{FF} = 86$ Hz, 1 F, HfFHf), −109.8 (s, 4 F, HfFAl). IR (Nujol, CsI): ν 1195 s, 1156 s, 1026 s, 804 s, 706 vs, 600 vs, 573 vs, 547 vs, 475 s, 408 vs, 362 vs, 280 vs. MS (70 eV): *m*/*z* (%) 871 (100) ($M^+ - Me$), 795 (40) ($M^+ - Me - Me_2AlF$), 719 (40) ($M^+ - Me - 2Me_2AlF$). Anal. Calcd (Found): C, 35.26 (35.9); H, 5.46 (5.6); F, 12.87 (12.5).

10. A 9.5 mL aliquot of a 2 M solution (19.0 mmol) of $AlMe_3$ in *n*-hexane was added to a suspension of Cp^*HfF_3 (2.22 g, 6.0 mmol) in *n*-hexane (70 mL). After a short time, the reaction suspension abruptly turned into a yellow solution. This was stirred for 3 days at ambient temperature. During this time methane (30 mL) was evolved and an off-white solid precipitated. After filtration, all volatiles were evaporated under vacuum and the residue was redissolved in *n*-hexane (20 mL). At −40 °C, **10** was obtained as colorless crystals. Yield: 1.83 g (5.1 mmol, 85%). Spectroscopically pure product was obtained after repeated recrystallization from *n*-hexane. Mp: 83 °C. ^1H NMR (250 MHz, C_6D_6): δ 1.81 (s, 15 H, $C_5(CH_3)_5$), 0.05 (s, 9 H, $HfCH_3$). ^{13}C NMR (63 MHz, C_6D_6): δ 122.4 (s, C_5Me_5), 58.0 (s, $HfCH_3$), 10.9 (s, $C_5(CH_3)_5$). MS (70 eV): *m*/*z* (%) 360 (40) (M^+), 135 (100) (Cp^{*+}). Anal. Calcd (Found): C, 43.52 (43.2); H, 6.74 (6.6).

11. Analogous to the preparation of **10**, Cp^*HfF_3 (2.22 g, 6.0 mmol) and $AlMe_3$ in *n*-hexane (9.5 mL of a 2 M solution, 19.0 mmol) were reacted in *n*-hexane (50 mL) for 3 days. The reaction mixture was filtered, and the resulting yellow solution was stored for 3 months. During this time, complex **11** precipitates as microcrystalline yellow solid as well as yellow single crystals, suitable for X-ray structure analysis. Yield: 132 mg (0.1 mmol), 5%. Mp: 310 °C dec. ^1H NMR (250 MHz, toluene-d_8): δ 7.48 (dd, $^4J_{HH} = 1.7$ Hz, $^4J_{HH} = 0.8$ Hz, 1 H, Hf_2AlCH), 6.52 (d, $^2J_{HH} = 11$ Hz, 2 H, $HfAl_2CH_2$), 5.16 (s, 2 H, Hf_2Al_2CH), 2.82 (m, 2 H, $HfAl_3CH$), 1.98 (s, 30 H, $C_5(CH_3)_5$), 1.92 (s, 15 H, $C_5(CH_3)_5$), −0.17 (s, 6 H, $Al(CH_3)_2$), −0.18 (s, 6 H, $Al(CH_3)_2$), −0.51 (s, 6 H, $AlCH_3$), −0.57 (s, 3 H, $AlCH_3$), −0.86 (s, 3 H, $AlCH_3$), −1.63 (d, $^2J_{HH} = 11$ Hz, 2 H, Al_3CH_2). ^{13}C NMR (100 MHz, toluene-d_8): δ 189.0 (s, Hf_2CHAl), 121.2 (s, C_5Me_5), 119.1 (s, C_5Me_5), 84.9 (s, Hf_2Al_2CH), 76.3 (s, $HfAl_3CH$), 24.9 (s, $HfAl_2CH_2$), 12.0 (s, $C_5(CH_3)_5$), 10.6 (s, $C_5(CH_3)_5$), 1.1 (s, $AlCH_3$), −2.1 (s, $AlCH_3$), −2.7 (m, $AlCH_3$), −19.6 (s, Al_3CH_2). IR (Nujol, KBr): ν 1187 s, 1097 s, 1024 s, 832 s, 787 s, 693 vs, 679 vs, 662 vs, 607 s, 501 s, 365 vs. MS (70 eV): *m*/*z* 1301 (6) ($M^+ - Me$), 1226 (100) ($M^+ - 6Me$), 1211 (20) ($M^+ - 7Me$), 613 (20) ($M^{2+} - 6Me$). Anal. Calcd (Found): C, 41.05 (39.5); H, 5.97 (6.0).

12. $AlMe_3$ in toluene (3.1 mL of a 2 M solution, 6.2 mmol) was reacted with $Cp^*_2ZrF_2$ (1.30 g, 3.0 mmol), dissolved in toluene (15 mL) for 5 h at room temperature. After evaporation of all volatiles *in vacuo*, the off-white residue was redissolved in *n*-hexane (15 mL). **12** precipitated at −25 °C as colorless crystals. They were filtered and dried *in vacuo*. Yield: 1.10 g (2.8 mmol, 93%). Mp: 168 °C. ^1H NMR (250 MHz, C_6D_6): δ 1.76 (s, 30 H, $C_5(CH_3)_5$), −0.57 (s, 6 H, $ZrCH_3$). Anal. Calcd (Found): C, 55.16 (55.1); H, 7.57 (7.4).

13. To a solution of Cp^*TaF_4 (3.00 g, 7.6 mmol) in toluene (30 mL) was added 4-fold excess of $AlMe_3$ in toluene (15.3 mL of a 2 M solution, 30.6 mmol). The reaction mixture was stirred for 5 h at room temperature. After evaporation of all volatiles *in vacuo*, the off-white residue was redissolved in *n*-hexane (20 mL). **13** precipitated at −25 °C as colorless crystals. They were filtered and dried *in vacuo*. Yield: 2.72 g (7.2 mmol, 95%). Mp: 160 °C dec. ^1H NMR (250 MHz, C_6D_6): δ 1.67 (s, 15 H, $C_5(CH_3)_5$), 0.68 (s, 12 H, $TaCH_3$). MS (70 eV): *m*/*z* (%) 361 (100) ($M^+ - Me$), 345 (30) ($M^+ - 2Me$), 329 (60) ($M^+ - 3Me$). Anal. Calcd (Found): C, 44.68 (44.4); H, 7.23 (7.2).

X-ray Measurements of 9 and 11. Crystal data for the two structures are presented in Table 4. All data were collected at low temperatures using an oil-coated shock-cooled crystal[28] on a Stoe-Siemens AED with Mo Kα ($\lambda = 71.073$ pm) radiation. The structures were solved by direct methods using SHELXS-90[29] and refined with all data on F^2 with a weighting scheme of $\omega^{-3} = \sigma^2(F_o^2) + (g1P)^2 + g2P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[30] In **9** and **11**, the positions of the hydrogen atoms were geometrically idealized and refined using a riding model. Selected bond lengths and angles of **9** and **11** can be found in Tables 2 and 5, relevant crystallographic data for **9** and **11** are in Table 4, and fractional coordinates of **9** and **11** are presented in Table 3 and Table 6.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, and coordinates and fully labeled figures of 50% anisotropic displacement parameters for **9** and **11** (35 pages). Ordering information is given on any current masthead page.

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