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Hafnium halide compounds of methyl substituted allyl ligands. Synthesis, crystal structure and dynamics of $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1,2,3\text{-}Me_3allyl)HfBr_2$ and $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1,1,2\text{-}Me_3allyl)HfBr_2$

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Abstract

The reaction of Cp^*HfCl_3 with $(1,2,3\text{-}Me_3allyl)MgBr$ or $(1,1,2\text{-}Me_3allyl)MgBr$ and excess $MgBr_2$ yields $Cp^*(1,2,3\text{-}Me_3allyl)HfBr_2$ and $Cp^*(1,1,2\text{-}Me_3allyl)HfBr_2$. X-ray crystallography of these compounds shows a bent-metallocene-type geometry, with steric congestion in the asymmetrically methylated compound causing the greatest distortion yet observed of an η^3-allyl ligand towards an η^1-binding mode for an early-transition metal complex. For $Cp^*(1,2,3\text{-}Me_3allyl)HfBr_2$: cell constants $a=14.581(7)$, $b=14.725(8)$, $c=8.291(3)$ Å; space group *Pcmn*; $R=0.0425$, $R_w=0.0397$. For $Cp^*(1,1,2\text{-}Me_3allyl)HfBr_2$: cell constants $a=9.158(2)$, $b=13.141(4)$, $c=14.575(3)$ Å, $\beta=101.06(2)°$; space group $P2_1/n$; $R=0.0383$, $R_w=0.0401$. A variable temperature ^1H NMR study indicates that the allyl ligand in $(1,1,2\text{-}Me_3allyl)HfBr_2$ undergoes η^3–η^1 isomerization ($\Delta G^\ddagger(-53\ °C)=40.9\pm1$ kJ/mol).

Introduction

It has been shown that ligand methyl substituents and choice of metal can have a large effect on early-transition metal η^5-pentadienyl and η^5-cyclopentadienyl (Cp) complexes. For example, Ernst has shown that methyl substituents strongly influence the stability of early-transition metal η^5-pentadienyl complexes [1]. As for choice of metal, Negishi *et al.* have demonstrated that $Cp_2M(alkyl)_2$ compounds are unstable for M = Zr but stable for M = Hf [2]. Our research extends this investigation to early-transition metal η^3-allyl (C_3H_5) complexes by examining the effect of allyl methyl substituents and the choice of transition metal on their preparation, structure, dynamics and reactivity. Our previous work with $Cp^*(Me_nallyl)ZrX_2$ compounds (eqn. (1)) demonstrated that their yield, structure and dynamic properties are strongly influenced by both the number and pattern of allyl methyl substituents [3–5]. In addition, compounds **1**–**3** were isolated in relatively low yields due to unfavorable substitution kinetics which favored the formation of unstable tris-allyl complexes instead of the desired product. In this paper we explore the effect of the transition metal on the yield, structure and dynamics of $Cp^*(allyl)MX_2$ complexes by preparing and studying analogous hafnium compounds. We report here on the preparation, structure and dynamic behavior of $Cp^*(1,2,3\text{-}Me_3allyl)HfBr_2$ (**4**) and $Cp^*(1,1,2\text{-}Me_3allyl)HfBr_2$ (**5**).

$$Cp^*ZrCl_3 + BrMg(Me_3allyl) \longrightarrow Cp^*(Me_3allyl)ZrBr_2$$

1 1,2,3-Me$_3$allyl
2 1,1,2-Me$_3$allyl

$$Cp^*ZrCl_3 + Li(C_3H_5) \longrightarrow \underset{\mathbf{3}}{Cp^*(C_3H_5)ZrCl_2} \qquad (1)$$

Experimental

General comments

Ether, THF and hexane were distilled from sodium/benzophenone under argon. The allyl Grignards were prepared as described previously (the only modification was that both $(1,1,2\text{-}Me_3allyl)MgBr$ and $(1,2,3\text{-}Me_3allyl)MgBr$ were prepared in diethylether) [3].

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Cp*$HfCl_3$ was prepared as described elsewhere [6]. Hafnium tetrachloride was purchased from the Aldrich Chemical Co. and used without further purification. All syntheses and subsequent handling of compounds were conducted under anhydrous conditions in a dry argon atmosphere.

Cp(1,2,3-Me$_3$allyl)HfBr$_2$ (4)*

An ether solution of (1,2,3-Me_3allyl)MgBr (0.0213 M, 300 ml, 6.4 mmol) was added dropwise over 2 h directly to 2.692 g (6.4 mmol) of Cp*$HfCl_3$ in a flask cooled to 0 °C. Excess $MgBr_2$ was also present in the Grignard [3]. The reaction solution was stirred throughout the Grignard addition during which it quickly turned yellow. The reaction remained yellow throughout the addition but darkened to an orange–yellow while stirring overnight at room temperature. The reaction solution was then reduced in volume to ~100 ml via trap to trap distillation and 100 ml of hexane was added. The reaction solution was further reduced in volume to ~60 ml and an additional 50 ml of hexane was added. The reaction solution was separated from the large amount of white magnesium salts via cannula. The salts were washed with an additional 50 ml of hexane and the wash was combined with the reaction solution via cannula. Successive concentrations and crystallizations at −40 °C yielded 1.327 g (37.2%) of orange crystals which were pure by ^{1}H NMR. Further recrystallization from ether at −40 °C yielded crystals suitable for X-ray analysis (m.p. 161.0–162.0 °C). *Anal.* Calc. for $C_{16}H_{26}HfBr_2$: C, 34.52; H, 4.71; Hf, 32.06; Br, 28.71. Found: C, 34.44; H, 4.81, Hf, 32.15; Br, 28.58%. ^{1}H NMR ($CDCl_3$/TMS 2%): δ 2.38 br (CH, allyl, 2H); 2.19 (CH_3, Cp* and allyl terminii, 21H); 1.72 (CH_3, allyl, 3H). ^{13}C NMR ($CDCl_3$/TMS 2%): δ 125.14 (interior C, allyl); 122.82 (C, Cp*); 88.23 (exterior C, allyl); 17.54 (CH_3, allyl); 13.05 (CH_3, Cp*); 12.47 (CH_3, allyl). IR (cm^{-1}, Nujol mull): 1244 m, 1154 vw, 1091 vw, 1023 m, 973 w, 892 vw, 845 s, 804 vw, 774 m, 723 s, 677 s, 623 vw, 594 m, 580 m, 549 w, 507 s, 470 s, 418 w, 412 m, 398 w, 350 vs.

Cp(1,1,2-Me$_3$allyl)HfBr$_2$ (5)*

An ether solution of (1,1,2-Me_3allyl)MgBr (0.0289 M, 260 ml, 7.5 mmol) was added dropwise over a 2 h period to a brown solution of Cp*$HfCl_3$ prepared *in situ* (LiCp*, 1.25 g, 8.8 mmol; $HfCl_4$, 2.64 g, 8.2 mmol; 75 ml of toluene). Excess $MgBr_2$ was also present in the Grignard [3]. The reaction solution lightened to yellow in color and then darkened to an orange–brown within 3 h after the Grignard addition was complete. The solvent was removed via trap to trap distillation. The remaining solid was extracted several times with a total of ~75 ml of hexane. Filtration of the extractions yielded a deep orange solution. Successive concentrations and crystallizations at −40 °C yielded 0.63 g (13.7%) of light brown solid which was pure by ^{1}H NMR. Subsequent recrystallization from ether at −40 °C yielded yellow crystals (m.p. 108.0–110.0 °C). *Anal.* Calc. for $C_{16}H_{26}HfBr_2$: C, 34.52; H, 4.71; Hf, 32.06; Br, 28.71. Found: C, 34.41; H, 4.60; Hf, 32.23; Br, 28.62%. ^{1}H NMR (toluene-d_8/TMS 2%): δ 2.12 (CH_3, allyl, 3H); 1.98 (CH_3, Cp*, 15H); 1.78 (CH_3, allyl, 3H); 1.18 (CH_2, allyl, 2H); 0.74 (CH_3, allyl 3H), the solvent $CDCl_3$ yielded poor resolution between the most downfield allyl methyl and Cp* signals. ^{13}C NMR ($CDCl_3$/TMS 2%): δ 133.01 (interior C, allyl); 124.16 (Me_2C, allyl); 123.58 (C, Cp*); 73.62 (CH_2, allyl); 24.56 (CH_3, allyl); 22.23 (CH_3, allyl); 21.26 (CH_3, allyl); 12.86 (CH_3, Cp*). IR (cm^{-1}, Nujol mull): 1285 w, 1187 m, 1122 sh, 1057 vw, 1019 s, 971 w, 959 vw, 891 w, 866 s, 807 s, 722 m, 596 w, 579 m, 511 w, 455 m, 418 m, 409 sh, 365 sh, 350 vs. IR (cm^{-1}, halocarbon grease): 2965 s, 2918 m, 2877 w.

Nuclear magnetic resonance spectra

Proton chemical shifts were measured with a General Electric OMEGA GN-300 300 MHz spectrometer. Peak positions are reported as δ in parts per million relative to TMS at δ 0. Temperatures, determined by a copper/constantan thermocouple in the probe assembly, are estimated to be accurate to ±2.0 °C.

Infrared spectra

IR spectra were measured in the region 4000–300 cm^{-1} with a Nicolet 20-DX spectrophotometer equipped with a CsI beam splitter. The compounds were studied as mineral oil mulls between CsI plates. Compound **5** was also studied as a Halocarbon 25-5S grease mull (polychlorotrifluoroethylene oils thickened with silica gel, Halocarbon Products Corp., NJ, has no absorptions in the C–H stretching region). The estimated uncertainty in reported frequencies is ±2 cm^{-1}.

Melting points

Melting points were measured in sealed, evacuated capillaries using a calibrated thermometer.

X-ray structural determinations

Pertinent data for the structures of compounds **4** and **5** are in Table 1. The crystals were mounted on a Picker computer-controlled four-circle diffractometer equipped with a Furnas monochromator (HOG crystal) and cooled by a gaseous nitrogen cooling system. A systematic search of a limited

TABLE 1. Summary of crystal data and intensity collection for Cp*(1,2,3-Me_3allyl)$HfBr_2$ (**4**) and for Cp*(1,1,2-Me_3allyl)$HfBr_2$ (**5**)

	4	**5**
Formula	$C_{16}H_{26}HfBr_2$	$C_{16}H_{26}HfBr_2$
Formula weight	556.68	556.68
a (Å)	14.581(7)	9.158(2)
b (Å)	14.725(8)	13.141(4)
c (Å)	8.291(3)	14.575(3)
β (°)		101.06(2)
V ($Å^3$)	1780.18	1721.38
Z	4	4
D (g cm^{-3})	2.077	2.148
Space group	*Pcmn*	$P2_1/n$
Crystal dimensions (mm)	[100], 0.11 [010], 0.03 [001], 0.12	0.16×0.24×0.20
Transmission factors[a]	0.175–0.526	0.091–0.223
Temperature (°C)	−155	−155
Radiation	Mo Kα (λ=0.71069 Å)	Mo Kα (λ=0.71069 Å)
Linear absorption coefficient (cm^{-1})	102.445	105.944
Receiving aperature	3.0×4.0 mm; 22.5 cm from xtal	3.0×4.0 mm; 22.5 cm from xtal
Takeoff angle (°)	2.0	2.0
Scan speed	8.0° in 2θ/min	4.0° in 2θ/min
Background counts	4 s at each end	8 s at each end
2θ limits (°)	6–45	6–45
Data collected	$+h, +k, +l$	$+h, +k, \pm l$
Unique data	1219	2240
Unique data with $F_0^2 > 2.33\sigma(F_0^2)$	1028	1982
$R(F)$	0.0425	0.0383
$R_w(F)$	0.0397	0.0401

[a] The analytical method as employed in the absorption program AGNOST was used for the absorption correction [7].

hemisphere of reciprocal space for **4** located a set of diffraction maxima with symmetry and systematic absences consistent with the orthorhombic space groups *Pcmn* and $Pc2_1n$. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, *Pcmn* (note that *Pcmn* is a non-standard setting of *Pnma*)**. A similar search for **5** revealed symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Orientation matrices and accurate unit cell dimensions were determined at low temperature from least-squares fits of 32 reflections ($20 < 2\theta < 30°$) for both **4** and **5**. Intensity data were collected by using the $\theta/2\theta$ scan method; four standard reflections, monitored every 300 reflection measurements, showed only statistical fluctuations for both compounds. An absorption correction was performed for both compounds (see Table 1). The intensities were corrected for Lorentz and polarization factors and scaled to give the numbers of independent F_{hkl} values for $I > 2.33\sigma(I)$ indicated in Table 1.

Both structures were solved by a combination of direct methods (MULTAN78) and Fourier techniques. All atoms, including hydrogens, were located for both compounds. For both compounds, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were refined isotropically; refinements converged to values for the conventional **R** indices shown in Table 1. The maximum residual in the final difference Fourier synthesis for **4** and **5** was 1.13 (at the Hf site) and 0.45 e/$Å^3$, respectively. The weighting scheme used in the final calculations was of the form $w = 1/\sigma F^2$. Scattering factors were taken from ref. 8. The scattering factor for the Hf and Br atoms were corrected for the real and imaginary parts of anomalous dispersion by using values from ref. 8. All computations were carried out on a 386 PC using programs described elsewhere [9]. The positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 2, the atom numbering schemes being

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**The equivalent positions for *Pcmn* are: x, y, z; $\frac{1}{2}-x, y, \frac{1}{2}+z$; $x, \frac{1}{2}-y, z$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, -z$; $-x, \frac{1}{2}+y, -z$; $\frac{1}{2}-x, -y, \frac{1}{2}+z$; $-x, -y, -z$.

TABLE 2. Coordinates ($\times 10^4$) and equivalent isotropic temperature factors for Cp*(1,2,3-Me_3allyl)$HfBr_2$ [a] (4) and Cp*(1,1,2-Me_3allyl)$HfBr_2$ [a] (5)

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
4				
Hf	234.2(5)	2500*	3531(1)	1.3
Br	493(1)	1239(1)	5578(2)	2.3
C1	1330(9)	1680(11)	1856(17)	2.4
C2	1766(13)	2500*	2182(23)	2.2
C3	1714(11)	762(12)	2149(22)	3.2
C4	2581(15)	2500*	3311(25)	3.1
C5	−796(11)	2500*	1108(20)	1.8
C6	−1007(7)	1729(9)	2035(15)	1.4
C7	−1385(7)	2012(9)	3514(16)	1.9
C8	−540(17)	2500*	−654(27)	2.9
C9	−936(11)	731(10)	1525(20)	2.6
C10	−1799(11)	1393(13)	4770(24)	3.4
5				
Hf	5918.7(5)	2536.4(3)	3586.4(3)	1.5
Br1	7842(1)	1059(1)	3893(1)	2.2
Br2	5930(1)	2842(1)	5304(1)	2.5
C1	3389(15)	2645(11)	3133(11)	2.8
C2	3423(11)	1615(8)	3529(8)	2.1
C3	4254(12)	887(8)	3165(8)	2.4
C4	2724(14)	1458(10)	4372(9)	2.8
C5	4447(15)	−191(9)	3552(10)	3.1
C6	4727(14)	1073(10)	2266(8)	2.6
C7	6122(12)	3643(7)	2236(7)	1.6
C8	7552(13)	3236(8)	2572(8)	2.4
C9	8090(11)	3636(7)	3478(7)	1.7
C10	6986(12)	4313(8)	3705(8)	2.0
C11	5763(11)	4294(8)	2931(7)	1.8
C12	5216(17)	3526(11)	1259(10)	3.4
C13	8387(18)	2559(12)	2037(12)	3.9
C14	9598(16)	3487(12)	4064(11)	3.5
C15	7199(16)	4997(9)	4526(9)	2.5
C16	4427(15)	4976(10)	2851(11)	3.1

[a] Parameters marked by an asterisk were not varied. e.s.d.s. are given in parentheses. Equivalent isotropic thermal parameters are calculated by using the formula given in ref. 10.

shown in Fig. 1 for compounds **4** and **5**. See also 'Supplementary material'.

Results and discussion

Synthesis and reactivity of methylated allyl hafnium compounds

The hafnium compounds **4** and **5** were prepared by slow dropwise addition of a dilute ether solution of the appropriate allyl Grignard to Cp*$HfCl_3$. The solutions of allyl Grignard provided excess amounts of $MgBr_2$ due to preactivation of the magnesium with dibromoethane.

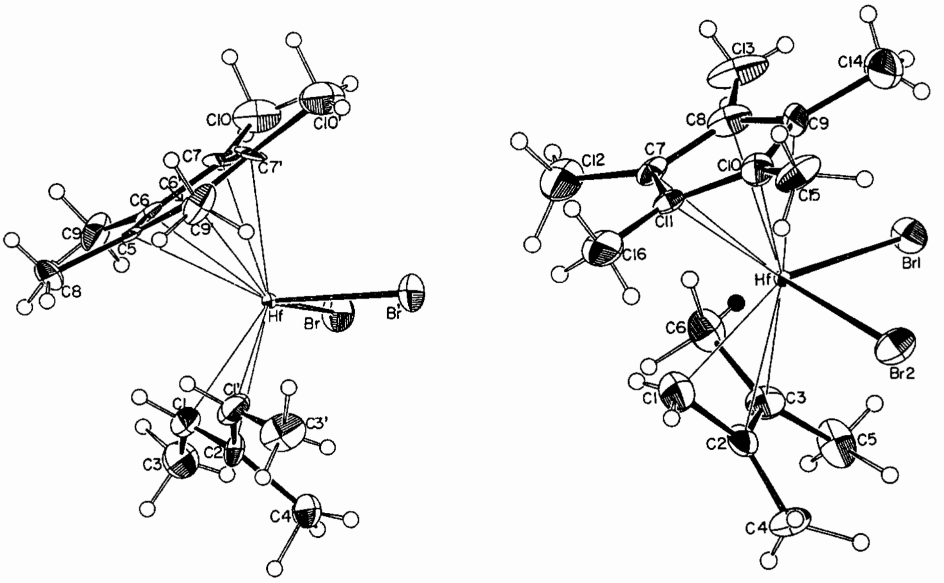
$$\text{Cp*HfCl}_3 + \text{(allyl)MgBr} + x\text{sMgBr}_2 \longrightarrow \underset{\mathbf{4,\ 5}}{\text{Cp*(allyl)HfBr}_2} \qquad (2)$$

allyl = 1,2,3-trimethylallyl (**4**)
= 1,1,2-trimethylallyl (**5**)

Compounds **4** and **5**, both yellow crystals, are air sensitive and quickly decompose on exposure to the atmosphere. Both compounds **4** and **5** melt without decomposition (see 'Experimental') and their solutions in common deuterated solvents ($CDCl_3$, d_8-toluene, d_8-THF) are stable if protected from the atmosphere. As mentioned in the 'Introduction', the analogous Zr compounds **1** and **2** are isolated in relatively low yields (<34%; eqn. (1)). This is due to the substitution kinetics which favor initial formation of Cp*Zr(Me_3allyl)$_3$ complexes. These intermediate tris-allyl compounds quickly decompose to give Cp*Zr(Me_3allyl)(Me_2butadiene) complexes which then ligand exchange with unreacted Cp*$ZrCl_3$ to yield **1** and **2** [5, 11]. Such a route would yield a maximum yield of 33%. Given that the yields for the hafnium compounds **4** and **5** were 37.2% and 13.7%, respectively (similar to the zirconium analogs), it would appear that switching from zirconium to hafnium has little effect on the route to final product. Evidently, early-transition metal halides will incur maximum allyl substitution regardless of the reaction stoichiometry of allyl Grignard to metal halide employed.

Molecular structures for 4 and 5

Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **4** and **5** are presented in Table 2; see also 'Supplementary material'. Perspective views showing the molecular geometry and the atom numbering schemes are presented in Fig. 1. In the orthorhombic unit cell for **4** each molecule lies on a crystallographic mirror plane passing through atoms C(2), C(4), C(5), C(8) and Hf, whereas in the monoclinic cell for **5**, each molecule occupies a general position. The molecular structures of **4** and **5** are similar to that of a bent metallocene, with the Cp*(centroid)–Hf–allyl(centroid) angles being 119.7 and 135.4°, respectively. These are both approximately one degree larger than the similar angles measured in the analogous Zr compounds [3]. Crystallographic studies have established that the corresponding Cp(centroid)–M–Cp(centroid) angle in a bent metallocene can vary from 148° in Cp_2MoH_2 to 126° in Cp_2ZrI_2 [12]. The larger angle in **5** (relative to **4**) is likely due to an attempt to minimize the crowding between allyl methyl C(6) and Cp* methyl



4 **5**

Fig. 1. ORTEP diagrams of Cp*(1,2,3-Me$_3$allyl)HfBr$_2$ (**4**) and Cp*(1,2,3-Me$_3$allyl)HfBr$_2$ (**5**). The darkened methyl hydrogen on C(6) for **5** is 2.124(16) Å from the Hf atom.

C(12) (the non-bonded contact is 0.39 Å less than the sum of the van der Waals radii [13]**, no such repulsive contact exists in **4**). The same situation was found in the analogous Zr compounds [3].

As observed elsewhere [3, 14], all of the Cp* methyl groups are bent out of the Cp* plane away from the Hf atom for **4** and **5**, and the normal to the Cp plane is essentially colinear with the Hf–Cp* (centroid) vector (angles of 1.4° for both **4** and **5**). The unique aspects of these structures involve the metal–allyl bonding. For compound **4** the allyl ligand assumes a supine orientation with respect to Cp* (the central carbon of the allyl ligand points down, away from Cp*). In compound **5** the allyl ligand is rotated about its Hf–centroid vector from the supine orientation by 32.9° such that allyl methyl C(6) is rotated away from the Cp* methyl C(12). A similar rotation was noted in the analogous Zr complex **2** [3]. In addition, the allyl ligand planes of **4** and **5** are tilted, the angle between the normal to the allyl plane and the Hf–(allyl)centroid vector being 31.3 and 32.9°, respectively. For compound **4** the tilt of the allyl ligand is towards the Cp*, resulting in a longer Hf–C distance to the central allyl carbon atom (2.498 Å) than to the terminal allyl carbon atoms (2.437 Å) for the 1,2,3-Me$_3$allyl ligand. The 1,1,2-Me$_3$allyl ligand in **5** displays the same tilt, with a longer Hf–C(2) distance to the central allyl carbon atom (2.574 Å) than to the unsubstituted terminal allyl C(1) atom (2.228 Å). However, as in **2**, there is an elongation of the Hf–C bond to the dimethylated allyl carbon atom C(3) (2.653 Å). Both the elongated Hf–C(3) bond length and the rotation of the ligand about its centroid in **5** are due to the increased bulk at the dimethylated end of the 1,1,2-Me$_3$allyl ligand and an attempt to minimize the methyl(Cp*)–methyl(allyl) repulsive contact mentioned previously. As a consequence, **5** may be thought of as possessing an η^3-allyl ligand that has been significantly distorted toward an η^1-binding mode in which the dimethylated end is no longer bound to the metal. This distortion is also apparent in the allyl C–C bond distances in **5** (C1–C2, 1.471(17) Å; C2–C3, 1.389(16) Å). The distortion towards η^1 is 28% greater for **5** than it is for **2**, representing the greatest distortion of this type yet observed for an early-transition metal η^3-allyl complex (percentage calculated as $[\Delta(\text{Hf–C})-\Delta(\text{Zr–C})]/\Delta(\text{Zr–C})$; $\Delta = (\text{M–C})_{\text{max}}-(\text{M–C})_{\text{min}}$). Correspondingly, the results of a variable-temperature ^{1}H NMR study indicate that the allyl ligand in **5** undergoes rapid η^3–η^1 isomerization via bond rupture only at the dimethylated end of the ligand with a barrier $\Delta G^{\ddagger}$ considerably lower than for **2** (*vide infra*).

**Pauling gives the van der Waals radius of a methyl group, an aromatic CH and a hydrogen atom to be 2.0, 1.7 and 1.2 Å, respectively. A lower limit of 1.44 Å, the covalent radius of Hf, is taken for the van der Waals radius, which is unknown.

A final point of interest is the relatively short distance (2.124(16) Å) between the Hf atom and the methyl hydrogen atom H(18) (shown in Fig. 1 as the blackened hydrogen atom on methyl carbon C(6)). This distance is shorter than was observed in **2** (2.34(9) Å) [3] and is well within the sum of the van der Waals' radii of the Hf and H atoms [13]. However, as in **2**, we do not consider this to be an agostic interaction [15]. This is supported by a lack of any significant deviations from the expected C–H bond lengths or C–C–H bond angles involving methyl group C(6). Also, there is no evidence in the IR spectrum of **5** of a weakened C–H stretch (2700–2350 cm^{-1}) sometimes observed for agostic hydrogens [15, 16] (C–H stretching for **5** occurs from 2965–2877 cm^{-1}). The short Hf–H distance in **5** is simply a consequence of steric crowding as it was in **2**.

Dynamic behavior of 5

The ^1H NMR spectrum of **5** consists of five singlets (see 'Experimental'). The occurrence of an allyl methyl resonance at δ 0.74, far upfield of the other methyl peaks, is unique to **5** and is assigned to the unique anti methyl group C(6). A similar upfield shift for the anti methyl group was noted for **2** [3]. The spectrum of **5** is consistent with the observed static structure found in the crystalline state with the exception that the terminal allylic CH_2 group should appear as an AX pair of doublets. The inferred conclusion, that the 1,1,2-Me_3allyl ligand exhibits dynamic behavior, was confirmed by variable temperature ^1H NMR spectroscopy. Spectra were measured in d_8-toluene from −85 °C (CH, allyl, b, δ 0.20; CH, allyl, b, δ 1.52) to +22 °C (CH_2, allyl, sharpened singlet at δ 1.18 (this peak experiences an upfield temperature dependent shift upon cooling to approx. δ 0.9 at 5 °C above the coalescence temperature)), yielding $\Delta G^{\ddagger}(-53\ °C) = 40.9 \pm 1.0$ kJ/mol, as estimated from the coalescence of the methylene protons using the slow-exchange approximation [17]**. A mechanism for **5**, whereby the η^3-1,1,2-Me_3allyl ligand becomes η^1 via rupture of the Hf–C bonds to the substituted carbon atoms, followed by rotation about the remaining Hf–C bond and the C–C single bond and return to the η^3-bonding mode is consistent with this. Such η^3–η^1 isomerization for allyl complexes is well known [3, 18]. Interestingly, this barrier is 10.6 kJ/mol lower than for the identical process in **2** complex ($\Delta G^{\ddagger} = 51.5$ kJ/mol) [3]. This is no doubt partially due to the fact that the η^3-1,1,2-trimethylallyl ligand in **5** is 28% more distorted towards an η^1-mode than in the Zr compound. It should also be pointed out the rearrangement barriers for fluxional butadiene compounds are consistently lower for Hf compounds than for analagous Zr complexes [19–22]. Finally, **4** differs from the analogous Zr compound **1** in that only the latter exhibits two isomeric forms in solution (*anti–anti* and *anti–syn* with respect to the terminal allyl methyls) [3]. ^1H NMR spectra of **4** measured from −60 to 60 °C in $CDCl_3$ exhibit only the *anti–anti* form.

Conclusions

While the compounds Cp*(1,2,3-Me_3allyl)MBr_2 and Cp*(1,1,2-Me_3allyl)MBr_2 for M = Zr and Hf are quite similar with regard to yield, structure and dynamics, there are some interesting differences involving the finer points of allyl bonding, barriers to allyl rearrangement and isomeric forms. Since Zr and Hf are essentially the same size, these differences must be due to the different electronic natures of the metals.

Supplementary material

The following data are available from author M.S. on request: anisotropic thermal parameters for non-hydrogen atoms (Table 3); hydrogen atom coordinates and isotropic thermal parameters (Table 4); structure factors for compounds **4** (Table 5) and **5** (Table 6); bond distances and angles for both compounds (Table 7).

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