X-Ray Crystal Structures of Two Monopentamethylcyclopentadienylhafnium(IV) Complexes

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Abstract—The crystal structures of two monopentamethylcyclopentadienylhafnium(IV) derivatives have been determined by X-ray diffraction analysis. The $[Hf(\eta^5\text{-}C_5Me_5)Cl_3]$ complex (**I**) crystallizes as a dimer in the monoclinic space group $C2/c$ with $Z = 8$. The structure of **I** is described as two $\{Hf(\eta^5\text{-}C_5Me_5)Cl_2\}$ units linked by two bridging chloride ligands. The $[\{Hf(\eta^5\text{-}C_5Me_5)Cl\}_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)]$ complex (**II**) crystallizes in the monoclinic space group Cc with $Z = 4$. The structure of **II** is described as three $\{Hf(\eta^5\text{-}C_5Me_5)Cl\}$ moieties connected by one or two bridging μ-chloride ligands and an additional μ_3-oxide group. The hitherto unknown compound **II** has also been characterized by spectroscopic and analytical methods. In the solid state, the molecules of both derivatives are linked by C–H···Cl hydrogen bonds and C–H···π interactions, providing an alternating layered pattern.

INTRODUCTION

The crystal structures of hafnium derivatives have been profusely determined in recent decades in the context on comprehending how molecular structure affects chemical properties. In particular, cyclopentadienyl hafnium complexes have been

investigated as catalysts or precatalysts in the polymerization of ethene [1,2], propene [3,4,5] or lactide [6]. Some of these compounds are also involved in studies on insertion reactions into metal–carbon bonds [7] or the preparation of frustrated Lewis pairs as potential initiators in polymerization processes [8]. Additionally, Chirik et al. have examined the dinitrogen cleavage and functionalization reactions using hafnocene complexes, providing a large family of cyclopentadienyl hafnium compounds [9,10,11]. Furthermore, Rosenthal et al. have synthesized numerous heterometallacyclic hafnocene derivatives, which have been analyzed by single-crystal X-ray diffraction methods [12,13], while several half-sandwich hafnium complexes have been also structurally characterized [14].

In recent years, we have reported on the synthesis, characterization and the X-ray studies of several half-sandwich pentamethylcyclopentadienyl derivatives of group 4 [15,16,17]. For example, we have optimized the conditions for the synthesis of $[Hf(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_3]$ through the metathesis reaction of $[Hf(\eta^5\text{-}C_5Me_5)Cl_3]$ (compound **I**) with $[LiCH_2SiMe_3]$ in hexane [18]. Compound **I** has been employed as starting material to achieve new hafnium derivatives with the η^5-pentamethylcyclopentadienyl ligand [14,19,20,21]. Herein we describe the X-ray diffraction analysis of the monopentamethylcyclopentadienylhafnium(IV) complexes $[Hf(\eta^5\text{-}C_5Me_5)Cl_3]$ (**I**) and $[\{Hf(\eta^5\text{-}C_5Me_5)Cl\}_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)]$ (**II**) (Fig. 1).
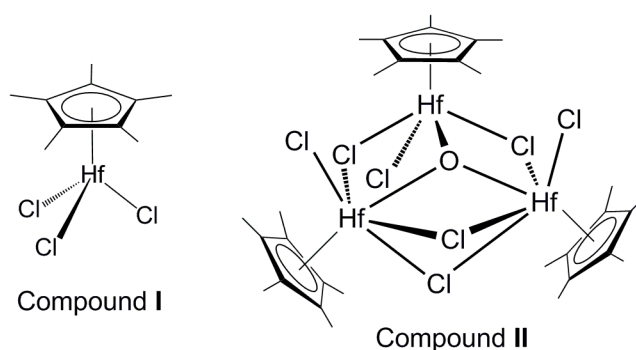

Fig. 1. Chemical diagrams of compounds **I** and **II**.

EXPERIMENTAL

Synthesis

All manipulations were carried out in an argon atmosphere using Schlenk line or glovebox techniques. Toluene and hexane were distilled from Na/K alloy just before use. The NMR solvent ($CDCl_3$) was dried with calcium hydride and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system ($\sim 10^{-3}$ Torr) and then filled with an inert gas. Anhydrous $HfCl_4$ (99.9%) was purchased from Aldrich and used as received. [$Si(C_5Me_5)Me_3$] was prepared according to the procedure [22].

Samples for infrared spectroscopy were prepared as KBr pellets and spectra were obtained using a Perkin-Elmer SPECTRUM 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C$\{^1$H$\}$ NMR spectra were recorded on a Varian Mercury-300 spectrometer. Chemical shifts (δ, ppm) in the ^{1}H and ^{13}C$\{^1$H$\}$ NMR spectra are given relative to residual protons or solvent carbon. Microanalysis (C, H, N) was performed in a Leco CHNS-932 microanalyzer.

[Hf(η^5-C$_5$Me$_5$)Cl$_3$] (I). The synthesis of compound **I** is a modification of the previously reported method [22]. A 100 mL ampule (Teflon stopcock) was charged with $HfCl_4$ (1.17 g, 3.65 mmol), [$Si(C_5Me_5)Me_3$] (1.00 mL, 4.05 mmol) and toluene (10 mL). The reaction mixture was stirred at 100°C for 20 h to give a pale yellow solid and a colorless solution. The volatiles were removed under reduced pressure and the resultant solid was washed with hexane (5 × 10 mL) to afford **I** (1.01 g, 66%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2984 (m), 2959 (s), 2918 (s), 1487 (s), 1447 (m), 1425 (s), 1382 (vs), 1069 (w), 1027 (vs), 881 (w), 825 (w), 807 (w), 596 (w), 426 (m). ^{1}H NMR (300 MHz, CDCl$_3$, 20°C): δ 2.28 (s). ^{13}C$\{^1$H$\}$ NMR (75 MHz, CDCl$_3$, 20°C): δ 126.7 (*C*$_5$Me$_5$), 12.1 (C$_5$*Me*$_5$).

[{Hf(η^5-C$_5$Me$_5$)Cl}$_3$(μ-Cl)$_4$(μ_3-O)] (II). Compound **II** was obtained as pale yellow crystals upon storage at room temperature of the hexane filtrates resulting from preparation of **I** (0.13 g). This complex is probably the product of the hydrolysis reaction of derivative **I** with adventitious water molecules in solvents. In fact, reaction of **I** with one equivalent of H_2O would result in the formation of two equivalents of hydrogen chloride and the dinuclear oxoderivative [{Hf(η^5-

C$_5$Me$_5$)Cl$_2$}$_2$(μ-O)], which can be stabilized with the mononuclear [Hf(η^5-C$_5$Me$_5$)Cl$_3$] moiety to yield **II**. IR (KBr, cm^{-1}): $\tilde{v}$ 2983 (m), 2957 (s), 2905 (s), 2855 (m), 2728 (w), 1490 (m), 1455 (s), 1431 (s), 1380 (vs), 1262 (w), 1100 (w), 1068 (m), 1026 (s), 806 (m), 623 (vs), 607 (vs), 594 (vs), 493 (vs), 420 (m). ^{1}H NMR (300 MHz, CDCl$_3$, 20°C): δ 2.20 (s). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20°C): δ 126.6 (*C*$_5$Me$_5$), 12.6 (C$_5$*Me*$_5$). Sharp NMR resonances at room temperature indicate that a low-energy dynamic process occurs in the solution. Elemental analysis: calculated for C$_{30}$H$_{45}$Cl$_7$Hf$_3$O (M_w = 1205.31): C 29.90, H 3.76 wt %. Found: C 30.03, H 3.87 wt %.

X-ray structure determination

Colorless crystals of **I** were grown by slow cooling the heated reaction mixture to room temperature. Pale yellow crystals of **II** were repeatedly obtained at room temperature as described above. The crystals were removed from the Schlenk tubes and covered with a viscous perfluoropolyether (Fomblin$^®$Y) layer. A suitable crystal was selected with a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. Intensity datasets were collected at 150 K on a Bruker-Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream 700.

Crystallographic data for complexes are presented in Table 1. The structures were solved using the WINGX package [23] by direct methods (**I**) (SHELXS-2013) [24] or by intrinsic phasing methods (**II**) (SHELXT) [25] and refined by the least-squares procedure using F^2 (SHELXL-2014/7) [24]. In both compounds, all atoms except hydrogen were refined in the anisotropic approximation of atomic displacement parameters, while hydrogen atoms were positioned geometrically and refined using the riding model. In the study of compound **I**, carbon atoms C(11)–C(20) of the pentamethylcyclopentadienyl ligand were treated according to RIGU instructions. The highest peak of 3.99 e·Å^{-3} found in the Fourier map is located near H(16*c*) (1.64 Å).

Table 1. Crystallographic characteristics, details of X-ray data collection and structure refinement parameters for compounds **I** and **II**

	I	II
Formula	$C_{10}H_{15}Cl_3Hf$	$C_{30}H_{45}Cl_7Hf_3O$
M_r	420.06	1205.28
T, K	150(2)	150(2)
Crystal system, space group, Z	Monoclinic, $C2/c$, 8	Monoclinic, Cc, 4
a, b, c, Å	14.880(3), 8.274(2), 21.460(3)	11.753(1), 20.595(1), 16.189(1)
β, deg	101.90(1)	109.39(1)
V, Å^3	2585.4(9)	3696.6(5)
ρ_{calc}, g cm^{-3}	2.158	2.166
μ, mm^{-1}	8.651	8.933
λ, Å	0.71073	0.71073
$F(000)$	1584	2272
Crystal size, mm	$0.19 \times 0.19 \times 0.14$	$0.30 \times 0.25 \times 0.22$
θ range, deg	3.06–25.02	3.32–27.50
hkl limits	$-17 \leq h \leq 17, -9 \leq k \leq 9, -25 \leq l \leq 25$	$-15 \leq h \leq 15, -26 \leq k \leq 26, -21 \leq l \leq 21$
Number of reflections: measured/unique (N_1), R_{int}/with $I > 2\sigma(I)$ (N_2)	24880/2274, 0.121/1846	36219/8448, 0.096/7956
R_1/wR_2 for N_1	0.059/0.111	0.047/ 0.116
$R_1{}^a$/wR_2 for N_2	0.042/0.098	0.042/0.108
S	1.158	0.835
$\Delta\rho_{min}$/$\Delta\rho_{max}$, e Å^{-3}	$-1.717/3.987$	$-2.573/3.517$

^{a} $R_1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$, $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

In the structure of compound **II**, RIGU restraints were also used for carbon atoms C(31)–C(40) of the pentamethylcyclopentadienyl group linked to Hf(3). Moreover, carbon atoms C(21)–C(30) of the C_5Me_5 ligand linked to Hf(2) were restrained with SIMU and DELU instructions. The highest peak of 3.52 e·Å^{-3} found in the Fourier map is located near Hf(2) (0.02 Å).

The crystallographic data have been deposited with the Cambridge Crystallographic Database under CCDC codes 2009151 and 2009152. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by email

RESULTS AND DISCUSSION

Compound **I** crystallizes in the monoclinic space group *C*2/*c* with *Z* = 8. X-ray structural analysis reveals the dimeric nature of **I** in the solid state with two {Hf(η^5-C$_5$Me$_5$)Cl$_2$} moieties, which are related by a centre of symmetry and held together by two bridging chloride ligands (Fig. 2).
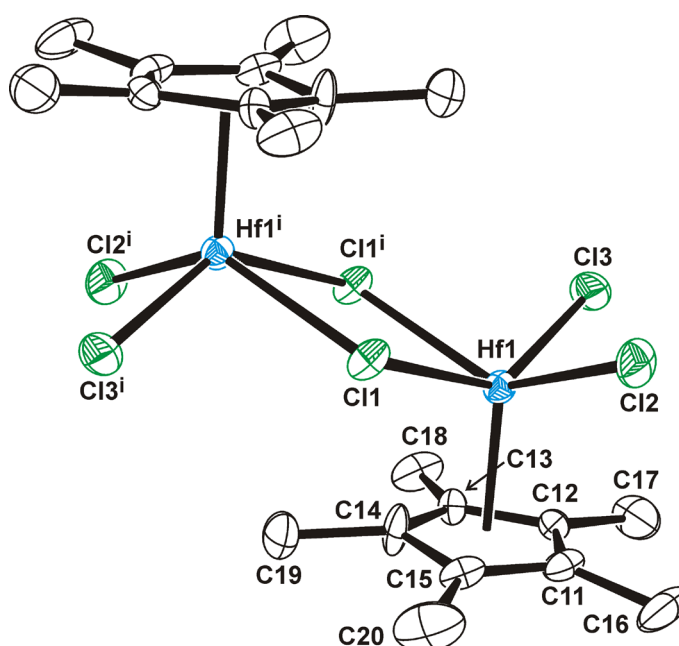

Fig. 2. Perspective view of compound **I** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) 3/2 − *x*, 3/2 − *y*, 1 − *z*.

The η^5-C$_5$Me$_5$ ligands are arranged in a transoid fashion around the planar Hf$_2$(µ-Cl)$_2$ core. Hafnium atoms have the geometry of a four-legged piano-stool with two terminal chloride and two bridging chloride groups on the legs. The most important lengths and angles are listed in Table 2. The hafnium–chlorine bond lengths of the terminal ligands (2.376(3) and 2.386(3) Å) are similar to those found in the cyclopentadienyl complexes [Hf(η^5-C$_5$Me$_4$H)Cl$_3$] (2.357(2) and 2.385(2) Å) [26], [Hf(η^5-C$_9$H$_7$)Cl$_3$] (2.374(3) and 2.389(3) Å) [27] and [Hf(η^5-C$_8$Me$_6$H)Cl$_3$]

(2.376(4) and 2.384(3) Å) [6]. The Hf–Cl (terminal) distances are clearly shorter than those related with the bridging ligands (2.565(2) and 2.574(2) Å), although these values are similar in the mentioned hafnium complexes (range 2.555(3)–2.580(3) Å). The angles inside the $Hf_2(\mu\text{-}Cl)_2$ core on compound **I** (74.5(1)° and 105.5(1)° for the angles chlorine–hafnium–chlorine and hafnium–chlorine–hafnium, respectively) are also comparable with those found earlier in the hafnium cyclopentadienyl derivatives (average values of 75.0(6)° and 105.0(6)°). The overall dimeric structure of **I** is similar to that determined for the analogous zirconium complex $[Zr(\eta^5\text{-}C_5Me_5)Cl_3]$ [28].

Table 2. Selected lengths (Å) and angles (deg) for complex **I**

Hf(1)–Cl(1)	2.574(2)	Hf(1)–Cl(2)	2.376(3)
Hf(1)–Cl(3)	2.386(3)	Hf(1)–Cl(1)^i	2.565(2)
Hf(1)–Cm^a	2.128	Hf(1)···Hf(1)^i	4.092(1)
Cl(1)–Hf(1)−Cl(2)	83.2(1)	Cl(1)–Hf(1)−Cl(3)	139.2(1)
Cl(1)–Hf(1)−Cl(1)^i	74.5(1)	Cl(2)–Hf(1)−Cl(3)	91.6(1)
Cl(2)–Hf(1)−Cl(1)^i	136.4(1)	Cl(3)–Hf(1)−Cl(1)^i	82.3(1)
Cl(1)–Hf(1)−Cm^a	107.9	Cl(2)–Hf(1)−Cm^a	113.3
Cl(3)–Hf(1)−Cm^a	111.2	Hf(1)–Cl(1)–Hf(1)^i	105.5(1)

^{a} Cm is the centroid of the C(11)–C(15) cyclopentadienyl carbon atoms. Symmetry code: (i) $3/2 - x$, $3/2 - y$, $1 - z$.

Analysis of intermolecular interactions for compound **I** reveals crystal packing in alternating layers. Each dimer is bonded with other four molecules through C–H···Cl hydrogen bonds (C(18)–H(18b)···Cl(2)^{iii} and C(19)–H(19a)···Cl(3)^{iv} interactions in Fig. 3 and Table 3), displaying a layer with molecules in the same orientation. The second layer with a different orientation is connected to the former one by C–H···Cl hydrogen bonds and C–H···π interactions (C(16)–H(16c)···Cl(3)^{ii} and C(17)–H(17a)···C_5Me_5 ring in Fig. 3).
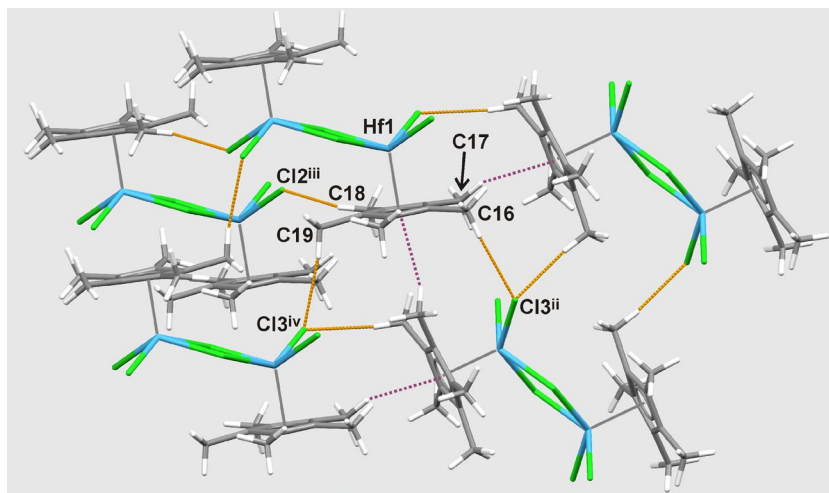
Fig. 3. Perspective view of the most relevant intermolecular contacts for compound **I**. C–H···Cl hydrogen bonds and C–H···π interactions are drawn by dashed lines. Symmetry codes: (ii) $3/2 - x$, $-1/2 + y$, $3/2 - z$; (iii) $1/2 + x$, $-1/2 + y$, z; (iv) x, $-1 + y$, z.

Table 3. Relevant C–H···Cl hydrogen bonds[a] for complex **I**

	$D···A$, Å
C(16)–H(16c)···Cl(3)[ii]	3.77(1)
C(18)–H(18b)···Cl(2)[iii]	3.68(1)
C(19)–H(19a)···Cl(3)[iv]	3.73(1)

[a]A is an acceptor, D is a donor. Symmetry codes: (ii) $3/2 - x$, $-1/2 + y$, $3/2 - z$; (iii) $1/2 + x$, $-1/2 + y$, z; (iv) x, $-1 + y$, z.

Compound **II** crystallizes in the monoclinic space group Cc with $Z = 4$. The crystal structure (Fig. 4 and Table 4) consists of three {Hf(η^5-C$_5$Me$_5$)Cl} moieties with three metallic centers at the vertices of an isosceles triangle (Hf(1)···Hf(2), Hf(1)···Hf(3) and Hf(2)···Hf(3) are separated by 3.532(1), 3.544(1) and 3.452(1) Å, respectively). The two longest edges of the triangle are bridged by a chlorine atom, and two chloride ligands bridge the shortest one. Additionally, an oxygen atom caps the hafnium triangle. The O(1), Cl(22), Cl(33), Cl(23) atoms, and the pentamethylcyclopentadienyl ring linked to Hf(1) are positioned on the same face of the isosceles triangle, while the Cl(11), Cl(12), Cl(13), Cl(32) atoms and the C$_5$Me$_5$ ligands bound to Hf(2) and Hf(3) are on the opposite face. This arrangement is similar to that found for a similar zirconium complex [29] and trinuclear derivatives

$[\{Mo(\eta^5\text{-}C_5H_5)Cl\}_3(\mu\text{-Cl})_4(\mu_3\text{-O})]$ [30] and $[\{M(\eta^5\text{-}C_5Me_5)Cl\}_3(\mu\text{-Cl})(\mu\text{-O})_3(\mu_3\text{-O})]$ (M = Nb [31,32], Ta [33]).

Table 4. Selected lengths (Å) and angles (deg) for complex **II**

Hf(1)–Cl(11)	2.410(4)	Hf(1)–Cl(12)	2.529(4)
Hf(1)–Cl(13)	2.551(4)	Hf(1)–O(1)	1.998(10)
Hf(2)–Cl(22)	2.416(3)	Hf(2)–Cl(12)	2.571(3)
Hf(2)–Cl(23)	2.557(3)	Hf(2)–Cl(32)	2.644(3)
Hf(2)–O(1)	2.132(10)	Hf(3)–Cl(33)	2.407(4)
Hf(3)–Cl(13)	2.555(3)	Hf(3)–Cl(23)	2.578(3)
Hf(3)–Cl(32)	2.650(3)	Hf(3)—O(1)	2.131(11)
Hf(1)–Cm(1)[a]	2.175	Hf(2)–Cm(2)[a]	2.221
Hf(3)–Cm(3)[a]	2.226	Hf(1)⋯Hf(2)	3.532(1)
Hf(1)⋯Hf(3)	3.544(1)	Hf(2)⋯Hf(3)	3.452(1)
Cl(11)–Hf(1)–Cl(12)	84.4(1)	Cl(11)–Hf(1)–Cl(13)	84.6(1)
Cl(11)–Hf(1)–O(1)	128.5(3)	Cl(12)–Hf(1)–Cl(13)	139.0(1)
Cl(12)–Hf(1)–O(1)	78.5(3)	Cl(13)–Hf(1)–O(1)	78.0(3)
Cl(22)–Hf(2)–Cl(12)	90.9(1)	Cl(22)–Hf(2)–Cl(23)	86.9(1)
Cl(22)–Hf(2)–Cl(32)	151.6(1)	Cl(22)–Hf(2)–O(1)	84.1(3)
Cl(12)–Hf(2)–Cl(23)	151.6(1)	Cl(12)–Hf(2)–Cl(32)	92.2(1)
Cl(12)–Hf(2)–O(1)	75.3(3)	Cl(23)–Hf(2)–Cl(32)	77.1(1)
Cl(23)–Hf(2)–O(1)	76.3(3)	Cl(32)–Hf(2)–O(1)	69.5(3)
Cl(33)–Hf(3)–Cl(13)	93.0(1)	Cl(33)–Hf(3)–Cl(23)	89.7(1)
Cl(33)–Hf(3)–Cl(32)	151.9(1)	Cl(33)–Hf(3)–O(1)	83.6(3)
Cl(13)–Hf(3)–Cl(23)	150.9(1)	Cl(13)–Hf(3)–Cl(32)	87.9(1)
Cl(13)–Hf(3)–O(1)	75.7(3)	Cl(23)–Hf(3)–Cl(32)	76.6(1)
Cl(23)–Hf(3)–O(1)	75.9(3)	Cl(32)–Hf(3)–O(1)	69.4(3)
Hf(1)–Cl(12)–Hf(2)	87.6(1)	Hf(1)–Cl(13)–Hf(3)	87.9(1)
Hf(2)–Cl(23)–Hf(3)	84.5(1)	Hf(2)–Cl(32)–Hf(3)	81.4(1)
Hf(1)–O(1)–Hf(2)	117.5(5)	Hf(1)–O(1)–Hf(3)	118.2(5)
Hf(2)–O(1)–Hf(3)	108.1(4)		

[a] Cm(1) is the centroid of C(11)–C(15) cyclopentadienyl carbon atoms; Cm(2) is the centroid of C(21)–C(25) cyclopentadienyl carbon atoms; Cm(3) is the centroid of C(31)–C(35) cyclopentadienyl carbon atoms.
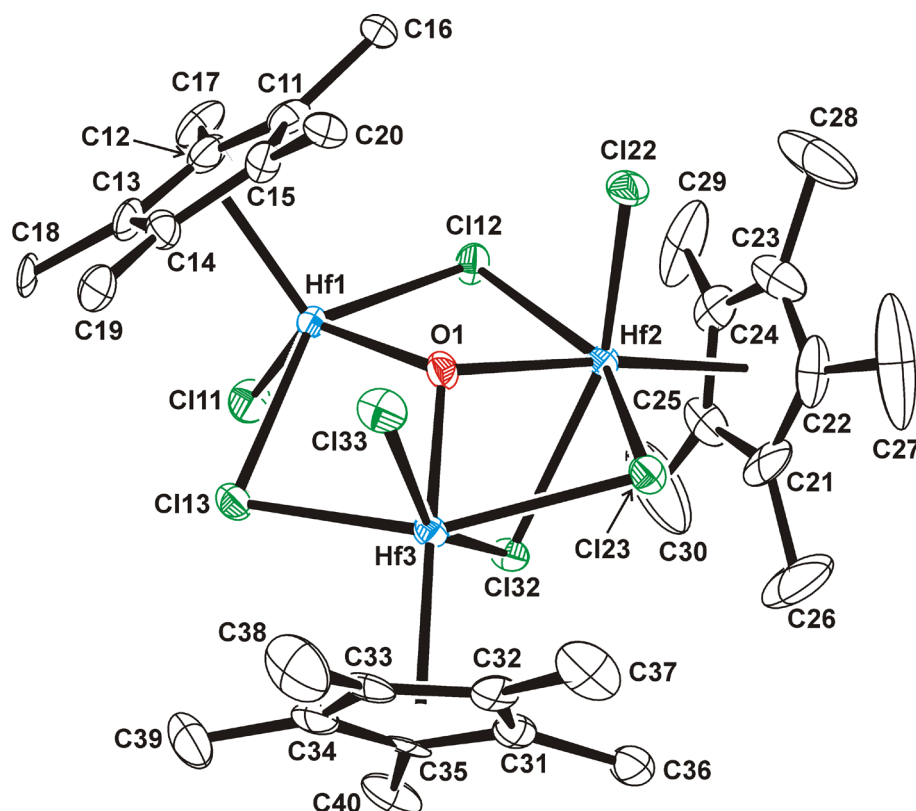
Fig. 4. Perspective view of compound **II** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

While the Hf(1) atom shows a four-legged piano-stool disposition, the geometry around the Hf(2) and Hf(3) atoms is better described as a distorted octahedron when considering the centroids of the pentamethylcyclopentadienyl ligands. Most of the hafnium–chlorine (bridging) bond lengths (range from 2.529(4) to 2.578(3) Å) are comparable to those determined for **I**. However, the Hf(2)–Cl(32) and Hf(3)–Cl(32) hafnium–chlorine (bridging) distances of 2.644(3) and 2.650(3) Å are clearly longer, although these values are similar to the Hf–Cl (bridging) bond lengths in other hafnium complexes [19, 34]. The hafnium–chlorine (terminal) distances (average 2.411(4) Å) are slightly longer than those found in compound **I**. On the other hand, the Hf(1)–O(1) distance of 1.998(10) Å is shorter than the other two hafnium–oxygen lengths (2.131(11) and 2.132(10) Å), probably due to the lower coordination environment of Hf(1). Furthermore, the shorter Hf(1)–Cm(1) distance (2.175 Å, Cm is the centroid of the cyclopentadienyl ligand) compared to the other hafnium–centroid bond lengths in the molecule (Hf(2)–Cm(2) 2.221 Å,

and Hf(3)–Cm(3) 2.226 Å) can also be related with the electronic unsaturation of Hf(1) relative to Hf(2) and Hf(3).

The analysis of the crystal packing shows that each molecule of compound **II** is linked with other three molecules through C–H⋯π interactions, forming a two-dimensional array (Fig. 5). Additionally, molecules of different 2D arrangements are connected by weak C–H⋯Cl hydrogen bonds (C(18)–H(18a)⋯Cl(22)[i] and C(37)–H(37a)⋯Cl(32)[ii] interactions in Fig. 6), providing an alternating layered pattern.
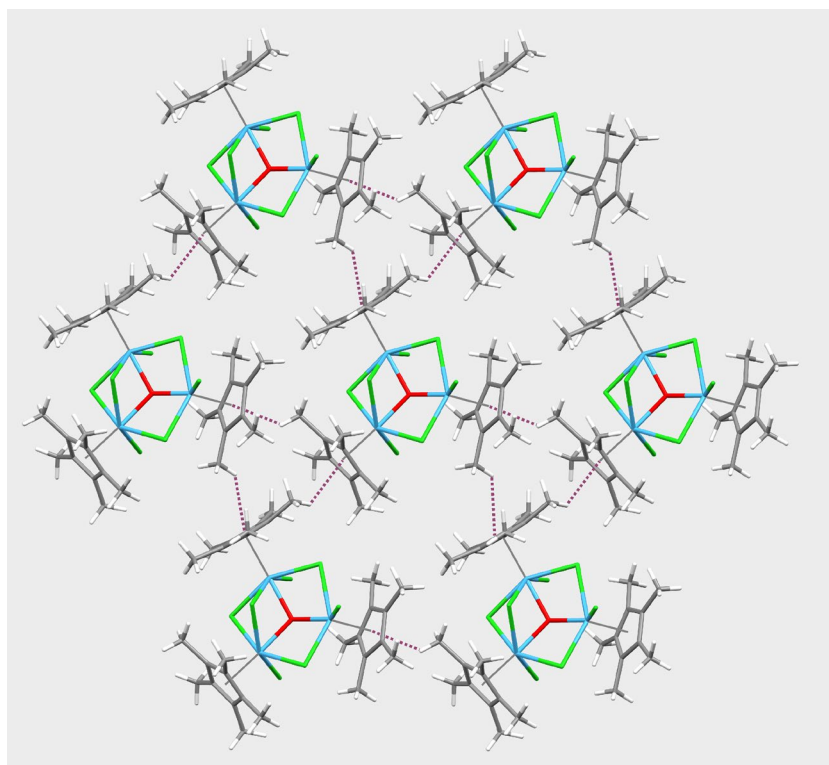

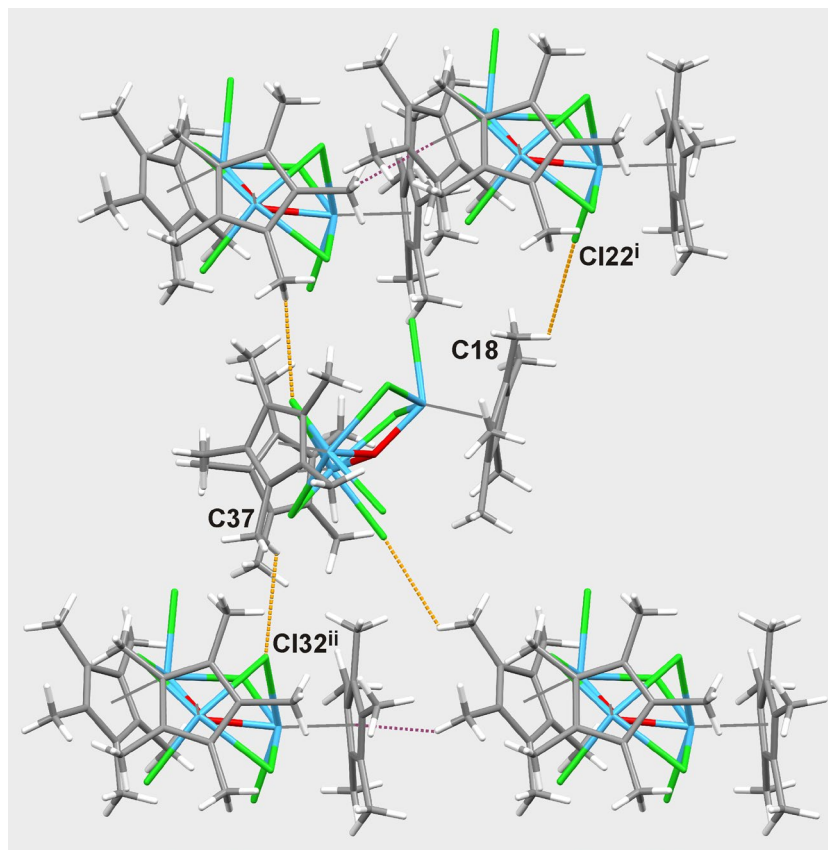**Fig. 5.** Perspective view of a layer in compound **II** with C–H⋯π interactions drawn by dashed lines.

Fig. 6. Perspective view of interactions between layers in compound **II**. C–H⋯Cl hydrogen bonds and C–H⋯π interactions are drawn by dashed lines. Donor–acceptor distances in C–H⋯Cl hydrogen bonds are: $C(18) \cdots Cl(22)^i$ 3.52(2) Å, $C(37) \cdots Cl(32)^{ii}$ 3.46(2) Å. Symmetry codes: (i) $1/2 + x$, $3/2 - y$, $1/2 + z$, (ii) x, $1 - y$, $-1/2 + z$.

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DECLARATIONS

The authors declare no conflicts of interest related to the content of this article.

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