

Formation of Cationic Monocyclopentadienyl Metal(IV) Compounds following Halide Abstraction from $[M(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ ($M = Zr$ or Hf): Crystal and Molecular Structure of $[Hf(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3 \cdot CH_2Cl_2$ †

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Treatment of $[M(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ ($M = Zr$ or Hf) with antimony(v) chloride in acetonitrile solution provides a convenient route to cationic monocyclopentadienyl metal(IV) species following halide abstraction. The hexachloroantimonate(v) salts $[M(\eta^5-C_5H_5)Cl_2(MeCN)_3][SbCl_6]$, $[M(\eta^5-C_5H_5)Cl(MeCN)_4][SbCl_6]_2$ and $[M(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3$ have been isolated and characterised by micro-analytical and spectroscopic (IR, ¹H NMR) data. The presence of geometrical isomers in solution is discussed. The structure of $[Hf(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3 \cdot CH_2Cl_2$ has been established by X-ray crystallographic studies: monoclinic, space group $P2_1/n$, $a = 22.627(7)$, $b = 18.956(8)$, $c = 22.699(7)$ Å, $\beta = 98.80(7)^\circ$. The structure shows two independent $[Hf(\eta^5-C_5H_5)(MeCN)_6]^{3+}$ cations, six $[SbCl_6]^-$ anions and two lattice solvent (CH_2Cl_2) molecules. The two cations show equivalent dimensions within experimental error and feature a seven-co-ordinate, pentagonal-bipyramidal metal geometry in which the cyclopentadienyl ligand occupies an axial position: Hf–C_{ring} 2.38(2)–2.53(2) (molecule 1) and 2.43(2)–2.51(2) Å (molecule 2).

Cationic bis(cyclopentadienyl) complexes based on $[M(\eta^5-C_5H_5)_2R]^+$ ($M = Ti, Zr$ or Hf ; $R =$ alkyl) continue to attract attention mainly due to their involvement as active catalytic sites for Ziegler–Natta olefin polymerisation.¹ Recent work by Pellecchia *et al.*² indicates that mono(cyclopentadienyl) derivatives of the type $[Zr(\eta^5-C_5R_5)(CH_2Ph)_2][B(CH_2Ph)(C_6F_5)_3]$ ($R = H$ or Me) can also be instrumental in promoting the polymerisation of certain olefins under suitable conditions. As part of our research interests in cationic Group 4 metal derivatives we recently reported the structure of the monocyclopentadienyltitanium(IV) compound $[Ti(\eta^5-C_5H_5)(MeCN)_5][SbCl_6]_3 \cdot 2MeCN$.³ The titanium 3+ cation is pseudo-octahedral and was obtained following treatment of $[TiCl_3(\eta^5-C_5H_5)]$ with $SbCl_5$ as chloride abstractor in acetonitrile solution. In the present paper we describe the results of further halide-abstraction studies using the related $[M(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ ($M = Zr$ or Hf) to complete the Group 4 series. Additionally we report the crystal structure of $[Hf(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3 \cdot CH_2Cl_2$ which provides the first example of a 3+ hafnium(IV) cation incorporating at least one cyclopentadienyl ligand.

Experimental

Manipulations of materials were carried out using a conventional Schlenk system in conjunction with a dinitrogen-filled glove-box. Solvents were stored over CaH_2 and subsequently P_4O_{10} and then freshly distilled under a dinitrogen atmosphere immediately prior to use. The compound $SbCl_5$ (Aldrich) was used as supplied commercially.

The IR spectra were recorded as mulls (Nujol) between CsI plates using a Perkin-Elmer 580B spectrometer, ¹H NMR spectra (220 MHz) on a Perkin-Elmer R34 spectrometer with samples in sealed tubes, and UV–VIS spectra on a Shimadzu UV35 spectrometer using MeCN solutions sealed in quartz

cells with a light path of 1 cm. Elemental analyses were performed by Medac, Brunel University, Uxbridge, Middlesex.

Preparation of Complexes.—(a) $[Zr(\eta^5-C_5H_5)Cl_3(MeCN)_2]$. Zirconium tetrachloride (11.65 g, 0.05 mol) and dichloromethane (100 cm³) were placed in a Schlenk tube equipped with a magnetic follower and dimethyl sulfide (6.20 g, 0.1 mol) was added dropwise at 0 °C. The resulting cloudy solution was stirred at room temperature for 10 h and then filtered to be rid of any insoluble hydrolytic species. The resulting clear yellow solution was then added dropwise to (tri-*n*-butylstannyl)cyclopentadiene (17.76 g, 0.05 mol) and the mixture stirred for 5 h at room temperature. Acetonitrile (50 cm³) was added with further stirring (5 h) at 50 °C. Slow removal of solvent *in vacuo* resulted in the deposition of a white microcrystalline solid. Recrystallisation from boiling acetonitrile–activated charcoal provided the product as colourless needle crystals. Yield 11.2 g (65%) (Found: C, 30.45; H, 3.25; Cl, 30.55; N, 8.20. C₉H₁₁Cl₃N₂Zr requires C, 31.35; H, 3.20; Cl, 30.85; N, 8.15%). $\delta_H(CD_3CN)$ 6.50 (5 H, s, C₅H₅). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2315, 2290 (C≡N), 3090, 1022, 811 ($\eta^5-C_5H_5$).

(b) $[Hf(\eta^5-C_5H_5)Cl_3(MeCN)_2]$. Similar procedures to those detailed in (a) above were followed using hafnium tetrachloride (16.02 g, 0.05 mol), (tri-*n*-butylstannyl)cyclopentadiene (17.76 g, 0.05 mol) and dimethyl sulfide (6.20 g, 0.1 mol). The product was obtained as colourless needle crystals. Yield 12.7 g (59%) (Found: C, 25.20; H, 2.70; Cl, 24.50; N, 6.40. C₉H₁₁Cl₃HfN₂ requires C, 25.00; H, 2.55; Cl, 24.60; N, 6.50%). $\delta_H(CD_3CN)$ 6.40 (5 H, s, C₅H₅). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2314, 2291 (C≡N), 3090, 1021, 815 ($\eta^5-C_5H_5$).

(c) $[Zr(\eta^5-C_5H_5)Cl_2(MeCN)_3][SbCl_6]$ 1. A solution of $SbCl_5$ (0.87 g, 2.9 mmol) in acetonitrile (20 cm³) was added dropwise to a chilled (0 °C) stirred solution of $[Zr(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ (1.00 g, 2.9 mmol) in acetonitrile (50 cm³) maintained under an atmosphere of dinitrogen. The resulting yellow solution was stirred at room temperature for 6 h to ensure completion of the reaction. Removal of solvent *in vacuo* gave a light yellow solid which was washed with dichloromethane (4 × 20 cm³) and hexane (4 × 20 cm³) and then

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

pumped dry *in vacuo* for several hours. Recrystallisation from acetonitrile-toluene (50:50) provided light yellow needle crystals. Yield 1.55 g (78%). These must be stored under an argon atmosphere preferably at low temperature to prevent discolouration which leads subsequently to substantial decomposition (Found: C, 18.60; H, 2.35; Cl, 41.20; N, 5.70. $C_{11}H_{14}Cl_8N_3SbZr$ requires C, 19.30; H, 2.05; Cl, 41.40; N, 6.15%). $\delta_H(CD_3CN$ with tetramethylsilane as internal reference) 6.64, 6.69, 6.73 (5 H, s, $\eta^5-C_5H_5$), and 2.53 (9 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2315, 2285 (C≡N), 346vs (Sb-Cl).

The following compounds were isolated using the same general procedures as detailed in (c) above.

(d) $[Zr(\eta^5-C_5H_5)Cl(MeCN)_4][SbCl_6]_2$ **2**. Reagents: $[Zr(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ (0.56 g, 1.6 mmol) and $SbCl_5$ (0.97 g, 3.2 mmol). Recrystallisation from acetonitrile-dichloromethane (50:50) provided small colourless diamond-shaped crystals. Yield 1.28 g (77%). These must be kept under an argon atmosphere preferably at low temperature to prevent discolouration which leads subsequently to substantial decomposition (Found: C, 15.35; H, 2.00; Cl, 44.60; N, 5.75. $C_{13}H_{17}Cl_{13}N_4Sb_3Zr$ requires C, 15.25; H, 1.65; Cl, 44.95; N, 5.45%). $\delta_H(CD_3CN)$ 6.86, 6.84 (5 H, s, $\eta^5-C_5H_5$) and 2.54 (12 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol), 2320, 2290 (C≡N), 345vs (Sb-Cl).

(e) $[Zr(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3$ **3**. Reagents: $[ZrCl_3(\eta^5-C_5H_5)(MeCN)_2]$ (0.50 g, 1.5 mmol) and $SbCl_5$ (2.60 g, 8.7 mmol). Recrystallisation from acetonitrile-dichloromethane (50:50) gave the product as a white semicrystalline solid. Yield 1.55 g (76%) (Found: C, 14.50; H, 1.60; Cl, 45.15; N, 5.80. $C_{17}H_{23}Cl_{18}N_6Sb_3Zr$ requires C, 14.50; H, 1.65; Cl, 45.40; N, 6.00%). $\delta_H(CD_3CN)$ 6.85 (5 H, s, $\eta^5-C_5H_5$) and 2.53 (18 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2320, 2290 (C≡N), 345vs (Sb-Cl).

(f) $[Hf(\eta^5-C_5H_5)Cl_2(MeCN)_3][SbCl_6]$ **4**. Reagents: $[Hf(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ (0.60 g, 1.4 mmol) and $SbCl_5$ (0.42 g, 1.4 mmol). Recrystallisation from acetonitrile-dichloromethane resulted in the deposition of the product as an off-white semicrystalline solid. Yield 0.80 g (75%) (Found: C, 16.90; H, 1.95; Cl, 36.50; N, 5.50. $C_{11}H_{14}Cl_8HfN_3Sb$ requires C, 17.10; H, 1.85; Cl, 36.75; N, 5.45%). $\delta_H(CD_3CN)$ 6.57, 6.52, 6.48 (5 H, s, $\eta^5-C_5H_5$) and 2.57 (9 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2315, 2290 (C≡N), 345vs (Sb-Cl).

(g) $[Hf(\eta^5-C_5H_5)Cl(MeCN)_4][SbCl_6]_2$ **5**. Reagents: $[Hf(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ (0.54 g, 1.2 mmol) and $SbCl_5$ (0.75 g, 2.5 mmol). Recrystallisation from acetonitrile-dichloromethane (75:25) provided colourless diamond-shaped crystals. Yield 1.04 g (72%) (Found: C, 13.85; H, 1.60; Cl, 41.00; N, 5.35. $C_{13}H_{17}Cl_{13}HfN_4Sb_2$ requires C, 14.05; H, 1.55; Cl, 41.45; N, 5.05%). $\delta_H(CD_3CN)$ 6.68, 6.66 (5 H, s, C_5H_5) and 2.57 (12 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2320, 2290 (C≡N), 344vs (Sb-Cl).

(h) $[Hf(\eta^5-C_5H_5)(MeCN)_6][SbCl_6]_3$ **6**. Reagents: $[Hf(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ (0.50 g, 1.2 mmol) and $SbCl_5$ (2.07 g, 6.9 mmol). This compound was obtained as the monosolvate (CH_2Cl_2) in the form of minute colourless cube-shaped crystals following recrystallisation of the crude product from acetonitrile-dichloromethane (25:75) in the presence of $SbCl_5$ (0.2 cm^3). Yield 1.23 g (71%) (Found: C, 13.55; H, 1.75; Cl, 44.40; N, 5.95. $C_{18}H_{25}Cl_{20}HfN_6Sb_3$ requires C, 13.70; H, 1.60; Cl, 44.95; N, 5.35%). $\delta_H(CD_3CN)$ 6.65 (5 H, s, C_5H_5) and 2.57

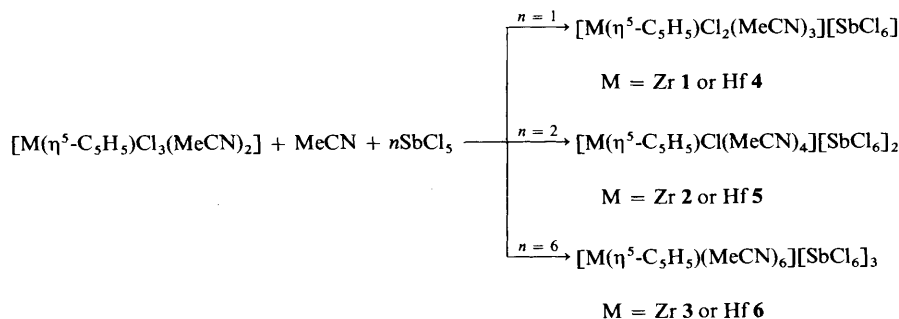
(18 H, s, MeCN). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2320, 2290 (C≡N), 345vs (Sb-Cl).

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data were collected with Mo-K α radiation using the MAR research image plate system. The crystal was positioned 75 mm from the image plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.⁴ The reflections were initially indexed in an orthorhombic unit cell ($R_{int} = 0.095$). However, the structure could not be solved successfully. We then considered the possibility of a twinned monoclinic unit cell (with very similar a and c lengths) in space group $P2_1/n$ ($R_{int} = 0.053$). The second twin had c^* and a^* axes overlapping a^* and c^* axes in the first twin thus giving an orthorhombic appearance to the reciprocal lattice. The structure was determined in this space group from the Patterson-difference maps and the structure successfully refined using the TWIN option in the SHELXL program.⁵ The twin ratio refined to 0.63(2):0.37(2). The structure consisted of two $[Hf(\eta^5-C_5H_5)(MeCN)_6]^{3+}$ cations, six $SbCl_6^-$ anions and two CH_2Cl_2 solvent molecules, each with half occupancy and with two alternative positions for the central carbon atoms. One of the anions was disordered and two alternative positions were included for four equatorial atoms. One of the cyclopentadienyl rings appeared disordered but we were unable to find a satisfactory model and the ring was refined as a rigid group. Apart from those disordered atoms, all non-hydrogen atoms were refined anisotropically and hydrogen atoms, which were included in geometric positions, isotropically. Methyl groups were refined as rigid groups. The structure was refined on F^2 by full-matrix least squares using the SHELXL program.⁵ The C-Cl distances were constrained at expected values as were Sb-Cl and Cl...Cl distances in the disordered anion. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. The final coordinates are given in Table 2 and important dimensions in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Lund and Livinghouse⁶ have recently shown that $[MCl_4(Me_2S)_2]$ (formed directly *in situ* from MCl_4 and 2 equivalents of Me_2S) react with $C_5H_5(SiMe_3)$ (for $M = Zr$) and $C_5H_5-(SnBu^a_3)$ (for $M = Hf$) with 1,2-dimethoxyethane (dme) as solvent to give the corresponding $[M(\eta^5-C_5H_5)Cl_3(dme)]$ in good yield. By the simple expedient of using acetonitrile rather than dme as solvent in these reactions we find that the bis adducts $[M(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ can equally be isolated in good yield, *viz.* $M = Zr$ (65%) or Hf (59%). In this study we have established that chloride ions can be removed from these monocyclopentadienylmetal(IV) compounds to give singly, doubly and triply charged cationic species following direct treatment with antimony(V) chloride in acetonitrile solution (Scheme 1).

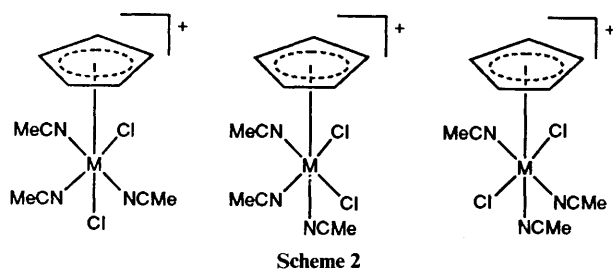


Scheme 1

As noted previously in the $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]\text{-SbCl}_5\text{-MeCN}$ system³ the control of stoichiometry is critical. Thus whilst single and double halide abstraction to give the relevant mono- (**1** and **4**) and di-cations (**2** and **5**) can be achieved under facile stoichiometric conditions, the removal of the third and final chlorine atom requires a healthy excess of SbCl_5 (1:6). Even then the solvated $[\text{M}(\eta^5\text{-C}_5\text{H}_5)]^{3+}$ species (**3** and **6**) can only be isolated *via* recrystallisation in the presence of an excess of SbCl_5 . Compounds **1–6** have been isolated and characterised as the hexachloroantimonate(v) salts by analytical and spectroscopic (IR, ¹H NMR, UV/VIS) measurements and, in the case of **6**, by a crystal-structure determination. These salts exhibit similar properties, both physical and spectroscopic; solubility is restricted to polar solvents most notably acetonitrile in which they form yellow solutions. All are sensitive to air, moisture and heat especially in solution when decomposition (hydrolysis) occurs to give deposition of unidentified oxo and/or hydroxo species. Even in the solid state the hafnium(IV) compounds in particular slowly discolour at room temperature over a period of weeks and are best stored sealed under an atmosphere of argon in a refrigerator.

The close similarity of the IR spectra of compounds **1–6** is striking: a sharp doublet profile at *ca.* 2315–2320, 2285–2290 cm^{-1} is indicative of co-ordinated acetonitrile. Interestingly this high-energy shift [free MeCN, $\nu(\text{CN})$ 2295 and 2270 cm^{-1}] associated with strong ligand binding to such cationic species⁷ appears to be insensitive to increasing cationic charge. Equally the characteristic cyclopentadienyl ring vibrations, *e.g.* 3080, 1020 and 820 cm^{-1} ,⁸ show little change through the series $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3(\text{MeCN})_2]$ to $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6]^{3+}$. In all cases the low-energy region is dominated by an intense broad band at *ca.* 344–346 cm^{-1} due to the SbCl_6^- ion $\{\text{K}[\text{SbCl}_6], \nu(\text{SbCl}) (\nu_3) 346 \text{ cm}^{-1}\}$ ⁹ which almost certainly obscures any $\nu(\text{M-Cl})$ and/or $\nu[\text{M}(\eta^5\text{-C}_5\text{H}_5)]$ components that may be present. The room-temperature ¹H NMR (CD_3CN) spectrum of complex **1** shows three sharp singlets at δ 6.64, 6.69, and 6.73 (relative intensity 5) due to the cyclopentadienyl ring protons and a broader signal at δ 2.53, integrating at 9 H, corresponding to three co-ordinated acetonitrile molecules; the latter signal relocates to δ 1.95 over a period of 24 h (or as a result of warming the solution) as the co-ordinated acetonitrile is slowly 'washed' into bulk solvent. The downfield shift of the cyclopentadienyl resonance by *ca.* 0.20 ppm relative to that of the starting material is consistent with monocation formation. On warming the solution to 76 °C the three-singlet pattern changes to two singlets and then coalesces to a single broad resonance δ 6.70 as the system becomes extremely labile. The reappearance of the initial three singlets on gradual cooling to room temperature is taken as evidence for the presence of all three possible isomers in solution at room temperature (Scheme 2).

In somewhat similar fashion the room-temperature ¹H NMR spectrum of compound **2** features a two-signal pattern δ 6.84 and 6.86 (relative intensity 5) for the cyclopentadienyl ring protons and a signal at δ 2.54 for co-ordinated solvent molecules (integrating for 12 H) which shifts to δ 1.95 over a period of 24 h. On warming the solution to 76 °C the two cyclopentadienyl resonances coalesce, δ 6.85, only to re-emerge on gradual cooling of the solution to room temperature. The



position of the cyclopentadienyl resonance *ca.* 0.15 ppm downfield from that of **1** and *ca.* 0.35 ppm downfield from that of the starting material is in accord with dication formation; the doublet pattern points to the presence of the two possible isomers (Scheme 3).

In contrast the room-temperature ¹H NMR spectrum of compound **3** shows just one signal for cyclopentadienyl ring protons at δ 6.85 (relative intensity 5) and a singlet at δ 2.53 (relative intensity 18) due to co-ordinated acetonitrile. This cyclopentadienyl signal, which is almost identical to that of **2**, remains unchanged following warming the solution to 76 °C. Moreover, even with the addition of an excess of SbCl_5 there is no indication of the expected downfield shift commensurate with complete halide removal and trication formation. In our view strong ion pairing of the type shown in Scheme 4 could well be responsible for the apparent absence of a M^{3+} species in solution.¹⁰ An alternative rationale might suggest that the

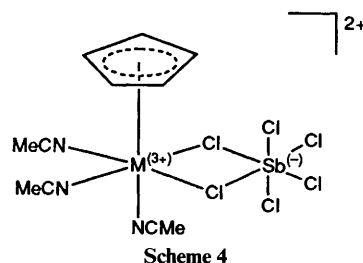
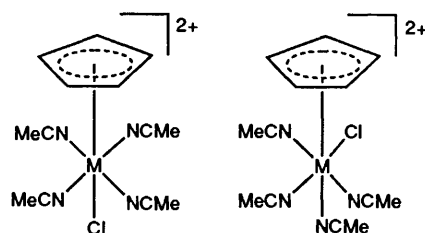


Table 1 Crystal data and structure refinement for compound **6**

Empirical formula	$\text{C}_{36}\text{H}_{50}\text{Cl}_{40}\text{Hf}_2\text{N}_{12}\text{Sb}_6$
<i>M</i>	3156.36
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> /Å	22.627(7)
<i>b</i> /Å	18.956(8)
<i>c</i> /Å	22.699(7)
β /°	98.80(7)
<i>U</i> /Å ³	9621(8)
<i>Z</i>	4
<i>D_c</i> /Mg m ⁻³	2.179
μ/mm^{-1}	4.952
<i>F</i> (000)	5920
Crystal size/mm	0.03 × 0.04 × 0.02
<i>T</i> /K	293(2)
$\lambda(\text{Mo-K}\alpha)/\text{Å}$	0.710 70
θ range for data collection/°	1.75–25.07
<i>hkl</i> ranges	–26 to 26, 0–22, –25 to 23
Reflections collected	29 691
Independent reflections	15 803 ($R_{\text{int}} = 0.061$ 9)
% of independent reflections	83.3
Data/parameters	15 803/844
Goodness-of-fit on F^2	1.020
Final <i>R</i> 1 [$I > 3\sigma(I)$]	0.0723 (10 374 data)
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1067, 0.2610
Weighting scheme, <i>w</i>	$1/[\sigma^2(F_o^2) + (0.14P)^2 + 68.3P]$ $P = [\max(F_o^2, 0) + 2F_c^2]/3$
Largest difference peak and hole/eÅ ⁻³	1.709, –2.322

Table 2 Atomic coordinates ($\times 10^4$) for compound **6**

Atom	x	y	z	Atom	x	y	z
Hf(1)	1 110(1)	2 702(1)	871(1)	Cl(34)	4 620(4)	6 880(4)	1 248(4)
N(11)	1 502(8)	2 656(8)	1 848(7)	Cl(35)	5 512(3)	5 668(5)	1 964(4)
C(111)	1 664(9)	2 626(15)	2 326(13)	Cl(36)	4 749(6)	5 296(6)	654(4)
C(112)	1 810(15)	2 591(20)	2 965(15)	Sb(4)	8 501(1)	4 316(1)	565(1)
N(12)	907(6)	3 809(7)	1 167(7)	Cl(41)	8 807(3)	3 161(3)	469(4)
C(121)	800(9)	4 339(11)	1 290(10)	Cl(42)	8 073(5)	4 336(6)	-446(4)
C(122)	677(18)	5 048(11)	1 484(14)	Cl(43)	7 628(4)	3 887(4)	832(6)
N(13)	316(9)	2 634(8)	1 373(10)	Cl(44)	9 374(3)	4 733(4)	256(4)
C(131)	-24(10)	2 649(11)	1 687(14)	Cl(45)	8 949(5)	4 324(5)	1 567(4)
C(132)	-467(11)	2 586(17)	2 068(13)	Cl(46)	8 166(4)	5 460(3)	696(4)
N(14)	921(7)	1 583(7)	1 056(8)	Sb(5)	513(1)	4 515(1)	3 576(1)
C(141)	775(11)	1 009(13)	1 147(13)	Cl(51)	638(5)	3 831(5)	2 750(4)
C(142)	718(15)	282(11)	1 235(17)	Cl(52)	389(6)	5 248(6)	4 361(5)
N(15)	1 935(8)	2 045(9)	839(9)	Cl(53) ^a	1 282(7)	5 162(9)	3 245(9)
C(151)	2 370(14)	1 774(12)	857(12)	Cl(54) ^a	-231(7)	3 790(9)	3 817(8)
C(152)	2 925(13)	1 436(18)	873(16)	Cl(55) ^a	-203(7)	5 163(9)	2 967(8)
N(16)	1 940(7)	3 398(10)	859(9)	Cl(56) ^a	1 222(8)	3 817(9)	4 166(8)
C(161)	2 337(12)	3 713(12)	891(10)	Cl(57) ^a	-488(7)	4 673(10)	3 165(8)
C(162)	2 926(13)	4 089(16)	929(16)	Cl(58) ^a	312(8)	3 539(8)	4 085(8)
C(100)	355(12)	2 357(16)	38(12)	Cl(59) ^a	1 535(7)	4 456(10)	3 995(8)
C(101)	894(14)	2 217(12)	-177(10)	Cl(60) ^a	745(9)	5 572(8)	3 078(8)
C(102)	1 159(16)	2 821(16)	-211(11)	Sb(6)	7 003(1)	7 707(1)	1 089(1)
C(103)	867(12)	3 364(10)	-24(10)	Cl(61)	6 341(6)	7 109(8)	1 501(7)
C(104)	336(12)	3 137(13)	91(10)	Cl(62)	7 030(9)	6 876(8)	349(8)
Hf(2)	5 827(1)	2 663(1)	1 133(1)	Cl(63)	7 743(5)	8 349(7)	646(6)
N(21)	6 808(9)	2 629(9)	1 553(8)	Cl(64)	7 760(9)	7 161(13)	1 686(10)
C(211)	7 281(11)	2 539(18)	1 688(10)	Cl(65)	6 307(5)	8 361(8)	444(5)
C(212)	7 927(13)	2 466(26)	1 931(20)	Cl(66)	6 983(7)	8 595(7)	1 769(5)
N(22)	6 109(8)	3 771(7)	915(8)	Sb(7)	8 537(1)	10 574(1)	530(1)
C(221)	6 227(11)	4 325(13)	801(9)	Cl(71)	7 986(5)	10 161(8)	-346(5)
C(222)	6 395(14)	5 037(10)	685(11)	Cl(72)	9 118(6)	10 961(7)	1 401(4)
N(23)	5 830(9)	3 351(10)	1 929(10)	Cl(73)	9 165(4)	9 596(4)	566(4)
C(231)	5 801(11)	3 664(13)	2 364(12)	Cl(74)	7 885(7)	11 516(7)	537(6)
C(232)	5 904(17)	4 055(21)	2 956(17)	Cl(75)	9 124(7)	11 194(7)	-5(7)
N(24)	5 787(9)	2 008(11)	1 960(12)	Cl(76)	7 978(6)	9 982(8)	1 138(8)
C(241)	5 810(10)	1 691(14)	2 381(13)	Sb(8)	3 803(1)	2 493(1)	3 075(1)
C(242)	5 779(17)	1 345(23)	2 951(16)	Cl(81)	4 469(9)	3 385(10)	3 190(15)
N(25)	6 060(8)	1 546(8)	930(10)	Cl(82)	3 187(6)	2 962(9)	2 242(7)
C(251)	6 192(13)	987(13)	838(12)	Cl(83)	4 429(6)	1 922(7)	3 819(5)
C(252)	6 362(14)	272(13)	690(13)	Cl(84)	3 134(7)	1 567(6)	3 003(9)
N(26)	6 362(13)	2 649(8)	318(10)	Cl(85)	4 296(7)	1 824(15)	2 437(7)
C(261)	6 659(13)	2 582(12)	6(11)	Cl(86)	3 257(6)	3 048(10)	3 701(7)
C(262)	6 966(22)	2 591(18)	-452(16)	C(91) ^b	7 754(17)	5 090(30)	2 164(22)
C(200)	4 747(10)	2 808(11)	1 241(8)	C(92) ^b	7 393(39)	5 658(38)	2 167(37)
C(201)	4 890(10)	3 315(8)	825(10)	Cl(91) ^a	7 994(7)	5 664(10)	2 762(6)
C(202)	5 036(10)	2 948(11)	321(8)	Cl(92) ^a	7 018(8)	4 847(15)	2 203(8)
C(203)	4 983(10)	2 214(10)	425(9)	C(93) ^b	2 495(67)	-277(46)	2 071(19)
C(204)	4 805(11)	2 127(9)	994(10)	C(94) ^b	2 221(40)	-253(27)	2 403(35)
Sb(3)	4 499(1)	5 732(1)	1 556(1)	Cl(93) ^a	2 142(7)	548(11)	1 995(8)
Cl(31)	3 515(4)	5 776(4)	1 145(6)	Cl(94) ^a	2 791(7)	-431(11)	2 823(8)
Cl(32)	4 343(4)	4 601(4)	1 893(4)				
Cl(33)	4 316(5)	6 192(5)	2 472(4)				

^a Population parameter 0.5. ^b Population parameter 0.25.

'extra' electron density afforded by the seven-co-ordinate metal centre in compound **3** (as opposed to the six-coordinate arrangement in compound **2**) precludes a characteristic down-field shift on going from solvated $[M(\eta^5-C_5H_5)Cl]^{2+}$ to $[M(\eta^5-C_5H_5)]^{3+}$. A similar pattern (and analysis) is evident in the 1H NMR data for the analogous hafnium(IV) series **4** \rightarrow **5** \rightarrow **6**.

By comparison with the 1H NMR spectroscopic details of $[Ti(\eta^5-C_5H_5)Cl_a(MeCN)_{5-a}]^{(3-a)+}$ ($a = 2, 1$ or 0) discussed previously,³ two main points emerge. (i) Whereas exchange between free and co-ordinated acetonitrile is rapid on the NMR time-scale for the cationic titanium(IV) species¹¹ it is much less so for the cationic zirconium(IV) and hafnium(IV) counterparts as witnessed by the broad resonances at δ 2.5 observed at the outset for all six compounds under discussion here. In turn this

has allowed the recognition of geometrical isomers in solution for **1**, **2**, **4** and **5**, with seemingly no one isomer highly favoured over the others. For the starting materials $[M(\eta^5-C_5H_5)Cl_3(MeCN)_2]$ ($M = Zr$ or Hf) only one signal is observed for the cyclopentadienyl ring protons, δ 6.50 ($M = Zr$) and 6.40 (Hf). Presumably the three geometrical isomers possible for these neutral species interconvert rapidly on the NMR time-scale. For $[Zr(\eta^5-C_5H_5)Cl_3(thf)_2]$ ($thf =$ tetrahydrofuran) where rapid exchange behaviour has been noted, *i.e.* the room-temperature 1H NMR spectrum shows only one $\eta^5-C_5H_5$ signal at δ 6.54, the pseudo-octahedral structure features two mutually *cis* tetrahydrofuran molecules with one located *trans* to the cyclopentadienyl ring and the other in the equatorial plane.¹² The same isomeric form has been noted for $[Zr(\eta^5-C_5H_4Me)Cl_3(thf)_2]$,¹² $[Zr(\eta^5-C_5H_5)Cl_3(dme)]$ ¹³ and $[Ti(\eta^5-$

Table 3 Bond lengths (Å) and angles (°) for complex **6**

Hf(1)–N(14)	2.22(2)	Hf(1)–C(103)	2.38(2)	Hf(2)–N(23)	2.23(2)	Hf(2)–C(202)	2.43(2)
Hf(1)–N(15)	2.25(2)	Hf(1)–C(100)	2.44(2)	Hf(2)–N(25)	2.25(2)	Hf(2)–C(203)	2.45(2)
Hf(1)–N(11)	2.26(2)	Hf(1)–C(104)	2.44(2)	Hf(2)–N(24)	2.27(2)	Hf(2)–C(201)	2.46(2)
Hf(1)–N(13)	2.27(2)	Hf(1)–C(102)	2.48(3)	Hf(2)–N(22)	2.27(2)	Hf(2)–C(204)	2.50(2)
Hf(1)–N(12)	2.27(2)	Hf(1)–C(101)	2.53(2)	Hf(2)–N(21)	2.28(2)	Hf(2)–C(200)	2.51(2)
Hf(1)–N(16)	2.30(2)			Hf(2)–N(26)	2.36(3)		
N(14)–Hf(1)–N(15)	70.3(6)	N(11)–Hf(1)–C(100)	150.9(8)	N(23)–Hf(2)–N(25)	138.2(7)	N(24)–Hf(2)–C(203)	103.2(7)
N(14)–Hf(1)–N(11)	80.5(6)	N(13)–Hf(1)–C(100)	81.9(8)	N(23)–Hf(2)–N(24)	69.1(8)	N(22)–Hf(2)–C(203)	113.3(7)
N(15)–Hf(1)–N(11)	78.9(7)	N(12)–Hf(1)–C(100)	109.2(9)	N(25)–Hf(2)–N(24)	72.2(9)	N(21)–Hf(2)–C(203)	151.1(6)
N(14)–Hf(1)–N(13)	70.1(6)	N(16)–Hf(1)–C(100)	128.6(8)	N(23)–Hf(2)–N(22)	70.7(6)	N(26)–Hf(2)–C(203)	85.7(7)
N(15)–Hf(1)–N(13)	134.9(7)	N(14)–Hf(1)–C(104)	108.9(8)	N(25)–Hf(2)–N(22)	138.1(8)	N(23)–Hf(2)–C(201)	80.4(7)
N(11)–Hf(1)–N(13)	74.1(7)	N(15)–Hf(1)–C(104)	132.1(8)	N(24)–Hf(2)–N(22)	137.3(7)	N(25)–Hf(2)–C(201)	129.4(6)
N(14)–Hf(1)–N(12)	140.7(5)	N(11)–Hf(1)–C(104)	148.9(7)	N(23)–Hf(2)–N(21)	78.1(7)	N(24)–Hf(2)–C(201)	111.7(8)
N(15)–Hf(1)–N(12)	136.5(6)	N(13)–Hf(1)–C(104)	81.3(9)	N(25)–Hf(2)–N(21)	79.3(6)	N(22)–Hf(2)–C(201)	74.4(6)
N(11)–Hf(1)–N(12)	79.1(6)	N(12)–Hf(1)–C(104)	75.3(7)	N(24)–Hf(2)–N(21)	78.3(7)	N(21)–Hf(2)–C(201)	151.0(6)
N(13)–Hf(1)–N(12)	72.1(5)	N(16)–Hf(1)–C(104)	107.2(9)	N(22)–Hf(2)–N(21)	80.2(6)	N(26)–Hf(2)–C(201)	107.8(8)
N(14)–Hf(1)–N(16)	137.2(7)	N(14)–Hf(1)–C(102)	108.3(8)	N(23)–Hf(2)–N(26)	134.7(6)	N(23)–Hf(2)–C(204)	103.2(7)
N(15)–Hf(1)–N(16)	68.6(7)	N(15)–Hf(1)–C(102)	81.8(9)	N(25)–Hf(2)–N(26)	70.4(7)	N(25)–Hf(2)–C(204)	80.4(7)
N(11)–Hf(1)–N(16)	80.5(7)	N(11)–Hf(1)–C(102)	154.6(9)	N(24)–Hf(2)–N(26)	137.2(8)	N(24)–Hf(2)–C(204)	74.3(7)
N(13)–Hf(1)–N(16)	138.4(7)	N(13)–Hf(1)–C(102)	131.2(10)	N(22)–Hf(2)–N(26)	69.2(6)	N(22)–Hf(2)–C(204)	129.3(6)
N(12)–Hf(1)–N(16)	71.1(6)	N(12)–Hf(1)–C(102)	104.5(8)	N(21)–Hf(2)–N(26)	75.2(7)	N(21)–Hf(2)–C(204)	149.7(6)
N(14)–Hf(1)–C(103)	129.8(7)	N(16)–Hf(1)–C(102)	77.1(9)	N(23)–Hf(2)–C(202)	113.4(7)	N(26)–Hf(2)–C(204)	118.2(7)
N(15)–Hf(1)–C(103)	110.4(8)	N(14)–Hf(1)–C(101)	79.4(7)	N(25)–Hf(2)–C(202)	103.0(7)	N(23)–Hf(2)–C(200)	74.9(7)
N(11)–Hf(1)–C(103)	149.6(6)	N(15)–Hf(1)–C(101)	79.1(8)	N(24)–Hf(2)–C(202)	129.4(7)	N(25)–Hf(2)–C(200)	112.8(7)
N(13)–Hf(1)–C(103)	111.1(8)	N(11)–Hf(1)–C(101)	154.1(7)	N(22)–Hf(2)–C(202)	80.1(7)	N(24)–Hf(2)–C(200)	79.4(7)
N(12)–Hf(1)–C(103)	74.6(6)	N(13)–Hf(1)–C(101)	113.4(9)	N(21)–Hf(2)–C(202)	151.9(6)	N(22)–Hf(2)–C(200)	103.3(7)
N(16)–Hf(1)–C(103)	76.7(8)	N(12)–Hf(1)–C(101)	126.6(7)	N(26)–Hf(2)–C(202)	79.3(7)	N(21)–Hf(2)–C(200)	149.7(6)
N(14)–Hf(1)–C(100)	75.9(9)	N(16)–Hf(1)–C(101)	103.8(9)	N(23)–Hf(2)–C(203)	129.8(7)	N(26)–Hf(2)–C(200)	134.6(7)
N(15)–Hf(1)–C(100)	108.3(10)			N(25)–Hf(2)–C(203)	73.9(6)		
Sb(3)–Cl(31)	2.281(8)	Cl(31)–Sb(3)–Cl(34)	89.7(3)	Cl(32)–Sb(3)–Cl(35)	90.6(3)	Cl(31)–Sb(3)–Cl(36)	90.4(5)
Sb(3)–Cl(34)	2.315(7)	Cl(31)–Sb(3)–Cl(32)	88.9(3)	Cl(31)–Sb(3)–Cl(33)	93.1(4)	Cl(34)–Sb(3)–Cl(36)	90.7(4)
Sb(3)–Cl(32)	2.321(6)	Cl(34)–Sb(3)–Cl(32)	177.2(3)	Cl(34)–Sb(3)–Cl(33)	87.9(3)	Cl(32)–Sb(3)–Cl(36)	91.8(4)
Sb(3)–Cl(35)	2.338(8)	Cl(31)–Sb(3)–Cl(35)	178.8(4)	Cl(32)–Sb(3)–Cl(33)	89.8(3)	Cl(35)–Sb(3)–Cl(36)	88.6(4)
Sb(3)–Cl(33)	2.349(8)	Cl(34)–Sb(3)–Cl(35)	90.8(3)	Cl(35)–Sb(3)–Cl(33)	88.0(4)	Cl(33)–Sb(3)–Cl(36)	176.2(4)
Sb(3)–Cl(36)	2.356(10)						
Sb(4)–Cl(43)	2.301(7)	Cl(43)–Sb(4)–Cl(41)	88.4(3)	Cl(46)–Sb(4)–Cl(44)	91.7(3)	Cl(43)–Sb(4)–Cl(42)	91.2(4)
Sb(4)–Cl(41)	2.317(6)	Cl(43)–Sb(4)–Cl(46)	89.2(3)	Cl(43)–Sb(4)–Cl(45)	90.4(5)	Cl(41)–Sb(4)–Cl(42)	90.5(4)
Sb(4)–Cl(46)	2.332(7)	Cl(41)–Sb(4)–Cl(46)	177.2(3)	Cl(41)–Sb(4)–Cl(45)	90.3(3)	Cl(46)–Sb(4)–Cl(42)	90.9(4)
Sb(4)–Cl(44)	2.334(7)	Cl(43)–Sb(4)–Cl(44)	177.7(4)	Cl(46)–Sb(4)–Cl(45)	88.4(3)	Cl(44)–Sb(4)–Cl(42)	86.7(4)
Sb(4)–Cl(45)	2.343(8)	Cl(41)–Sb(4)–Cl(44)	90.7(3)	Cl(44)–Sb(4)–Cl(45)	91.6(4)	Cl(45)–Sb(4)–Cl(42)	178.2(4)
Sb(4)–Cl(42)	2.351(9)						
Sb(5)–Cl(51)	2.332(9)	Cl(52)–Sb(5)–Cl(51)	176.8(4)	Cl(54)–Sb(5)–Cl(53)	173.6(7)	Cl(58)–Sb(5)–Cl(60)	177.4(6)
Sb(5)–Cl(52)	2.312(10)	Cl(54)–Sb(5)–Cl(52)	89.7(5)	Cl(52)–Sb(5)–Cl(53)	96.7(6)	Cl(51)–Sb(5)–Cl(60)	91.4(5)
Sb(5)–Cl(53)	2.345(14)	Cl(54)–Sb(5)–Cl(55)	89.3(6)	Cl(55)–Sb(5)–Cl(53)	91.0(6)	Cl(57)–Sb(5)–Cl(60)	88.5(6)
Sb(5)–Cl(54)	2.303(14)	Cl(52)–Sb(5)–Cl(55)	89.1(5)	Cl(51)–Sb(5)–Cl(53)	81.2(5)	Cl(59)–Sb(5)–Cl(60)	87.6(6)
Sb(5)–Cl(55)	2.315(13)	Cl(54)–Sb(5)–Cl(51)	92.4(5)	Cl(56)–Sb(5)–Cl(53)	90.1(6)	Cl(51)–Sb(5)–Cl(58)	90.8(5)
Sb(5)–Cl(56)	2.337(13)	Cl(55)–Sb(5)–Cl(51)	88.6(5)	Cl(58)–Sb(5)–Cl(57)	92.8(6)	Cl(52)–Sb(5)–Cl(57)	90.3(5)
Sb(5)–Cl(57)	2.334(14)	Cl(54)–Sb(5)–Cl(56)	89.4(6)	Cl(51)–Sb(5)–Cl(57)	88.8(5)	Cl(52)–Sb(5)–Cl(58)	92.3(5)
Sb(5)–Cl(58)	2.264(14)	Cl(52)–Sb(5)–Cl(56)	92.9(5)	Cl(58)–Sb(5)–Cl(59)	91.0(6)	Cl(52)–Sb(5)–Cl(59)	86.8(5)
Sb(5)–Cl(59)	2.364(14)	Cl(55)–Sb(5)–Cl(56)	177.5(7)	Cl(51)–Sb(5)–Cl(59)	93.8(5)	Cl(52)–Sb(5)–Cl(60)	85.5(5)
Sb(5)–Cl(60)	2.40(2)	Cl(51)–Sb(5)–Cl(56)	89.4(5)	Cl(57)–Sb(5)–Cl(59)	175.3(7)		
Sb(6)–Cl(61)	2.198(11)	Cl(61)–Sb(6)–Cl(64)	90.7(8)	Cl(66)–Sb(6)–Cl(62)	175.6(6)	Cl(61)–Sb(6)–Cl(63)	178.9(6)
Sb(6)–Cl(64)	2.265(14)	Cl(61)–Sb(6)–Cl(66)	90.4(6)	Cl(61)–Sb(6)–Cl(65)	95.9(6)	Cl(64)–Sb(6)–Cl(63)	88.3(8)
Sb(6)–Cl(66)	2.290(10)	Cl(64)–Sb(6)–Cl(66)	91.4(8)	Cl(64)–Sb(6)–Cl(65)	173.3(8)	Cl(66)–Sb(6)–Cl(63)	89.8(5)
Sb(6)–Cl(62)	2.312(11)	Cl(61)–Sb(6)–Cl(62)	93.1(6)	Cl(66)–Sb(6)–Cl(65)	87.3(5)	Cl(62)–Sb(6)–Cl(63)	86.7(5)
Sb(6)–Cl(65)	2.336(10)	Cl(64)–Sb(6)–Cl(62)	91.2(9)	Cl(62)–Sb(6)–Cl(65)	89.8(7)	Cl(65)–Sb(6)–Cl(63)	85.2(5)
Sb(6)–Cl(63)	2.411(9)						
Sb(7)–Cl(75)	2.262(10)	Cl(75)–Sb(7)–Cl(76)	175.7(7)	Cl(71)–Sb(7)–Cl(74)	90.4(5)	Cl(75)–Sb(7)–Cl(73)	91.6(5)
Sb(7)–Cl(76)	2.301(11)	Cl(75)–Sb(7)–Cl(71)	89.9(5)	Cl(75)–Sb(7)–Cl(72)	89.5(5)	Cl(76)–Sb(7)–Cl(73)	88.8(4)
Sb(7)–Cl(71)	2.314(9)	Cl(76)–Sb(7)–Cl(71)	94.4(6)	Cl(76)–Sb(7)–Cl(72)	86.2(6)	Cl(71)–Sb(7)–Cl(73)	90.4(4)
Sb(7)–Cl(74)	2.318(11)	Cl(75)–Sb(7)–Cl(74)	91.7(6)	Cl(71)–Sb(7)–Cl(72)	177.9(4)	Cl(74)–Sb(7)–Cl(73)	176.6(5)
Sb(7)–Cl(72)	2.321(9)	Cl(76)–Sb(7)–Cl(74)	87.9(5)	Cl(74)–Sb(7)–Cl(72)	91.6(5)	Cl(72)–Sb(7)–Cl(73)	87.6(4)
Sb(7)–Cl(73)	2.330(8)						
Sb(8)–Cl(81)	2.25(2)	Cl(81)–Sb(8)–Cl(86)	89.8(9)	Cl(83)–Sb(8)–Cl(84)	91.0(5)	Cl(81)–Sb(8)–Cl(85)	96.0(10)
Sb(8)–Cl(86)	2.278(12)	Cl(81)–Sb(8)–Cl(83)	86.6(7)	Cl(81)–Sb(8)–Cl(82)	96.6(8)	Cl(86)–Sb(8)–Cl(85)	174.1(9)
Sb(8)–Cl(83)	2.302(9)	Cl(86)–Sb(8)–Cl(83)	95.2(7)	Cl(86)–Sb(8)–Cl(82)	90.9(6)	Cl(83)–Sb(8)–Cl(85)	84.3(6)
Sb(8)–Cl(84)	2.308(12)	Cl(81)–Sb(8)–Cl(84)	177.3(10)	Cl(83)–Sb(8)–Cl(82)	173.1(7)	Cl(84)–Sb(8)–Cl(85)	85.1(8)
Sb(8)–Cl(82)	2.344(11)	Cl(86)–Sb(8)–Cl(84)	89.0(7)	Cl(84)–Sb(8)–Cl(82)	86.0(6)	Cl(82)–Sb(8)–Cl(85)	89.3(6)
Sb(8)–Cl(85)	2.33(2)						

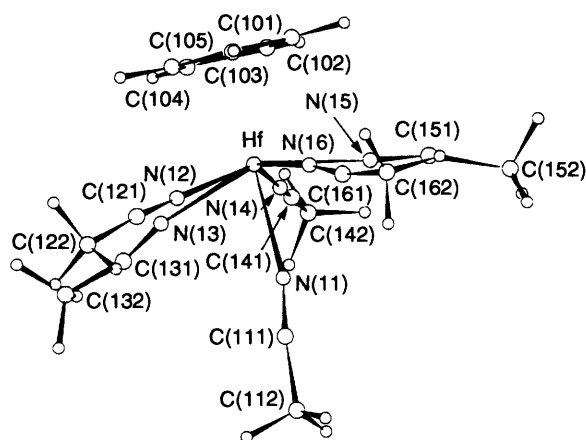


Fig. 1 Structure of the $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6]^{3+}$ cation showing the atomic numbering scheme

$\text{C}_5\text{H}_5\text{Cl}_3(\text{dmpe})$] ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$).¹⁴ (ii) Although ion pairing is evidently prevalent in the titanium(IV) species, the presence of a discrete $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_5]^{3+}$ cation can be observed in solution;³ no such equivalent solvated M^{3+} cation is seen in the present instance of $\text{M} = \text{Zr}$ or Hf .

Structural Considerations.—A search of the Cambridge Data Base files revealed that there are few cationic monocyclopentadienyl Group 4 metal complexes that have been structurally characterised, *viz.* $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2(\text{thf})_2][\text{BPh}_4]^{15}$ $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2(\text{dmpe})(\text{thf})][\text{BPh}_4]^{15}$ $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}(\text{acac})_2]^+[\text{O}_3\text{SCF}_3]^{16}$ ($\text{acac} = \text{acetylacetonate}$) and $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_5][\text{SbCl}_6]_3 \cdot 2\text{MeCN}$.³ The only structural data available for cationic hafnium(IV) compounds incorporating at least one cyclopentadienyl ring are provided by $[\text{Hf}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}(\text{thf})][\text{BPh}_4]^{17}$ and $[\text{Hf}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CH}_2\text{CHMe}_2)(\text{thf})][\text{BPh}_4] \cdot 2\text{thf}$.¹⁸

The solid-state structure of compound 6 shows two independent $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6]^{3+}$ cations, six $[\text{SbCl}_6]^-$ anions and two solvent (CH_2Cl_2) molecules. The structure of one of the individual cations is shown in Fig. 1, together with the atom numbering scheme. The dimensions of the two cations are shown in Table 3 and are equivalent within experimental error. In both cases the metal atom environment is best considered as a seven-co-ordinate pentagonal bipyramid with the cyclopentadienyl ligand (regarded as unidentate) and an acetonitrile molecule occupying the axial positions and five acetonitrile molecules in the equatorial plane. For the latter the nitrogen donor atoms are approximately coplanar (maximum deviation of a nitrogen from the N_5 plane being 0.10 Å for molecule 1 and 0.09 Å for molecule 2). The $\text{Hf}-\text{C}_{\text{ring}}$ distances 2.38(2)–2.53(2) Å [2.43(2)–2.51(2) Å for molecule 2] are significantly shorter than those observed for neutral hafnocene(IV) complexes, *e.g.* $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2\text{Me}_2]$ shows¹⁹ $\text{Hf}-\text{C}_{\text{ring}}$ 2.479(12)–2.534(14) Å and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}_2]$ shows²⁰ $\text{Hf}-\text{C}_{\text{ring}}$ 2.437(8)–2.497(7) Å as a direct reflection of the formal 3+ charge on the metal. The cyclopentadienyl ring plane and the equatorial N_5 plane intersect at angles of 4.2 [0.7°] in the two molecules. There is evidently no significant distortion within the equatorial girdle of solvent molecules with $\text{N}_{\text{eq}}\text{-Hf-N}_{\text{eq}}$ angles 68.6(7)–72.1(5) [69.1(8)–72.2(9)°] close to the ideal 72°. However, with the metal atoms displaced 0.45 [0.47 Å] above this plane, the $\text{N}_{\text{ax}}\text{-Hf-N}_{\text{eq}}$ angles 74.1(7)–80.5(7) [75.2(7)–80.2(7)°] have been squeezed considerably from the ideal 90°. To an approximation the cyclopentadienyl ring has a staggered conformation with respect to the five equatorial nitrogen atoms in the two molecules. In the pseudo-octahedral $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_5]^{3+}$ cation the bond length to the axial nitrogen atom *trans* to the cyclopentadienyl ring is significantly longer than the equatorial Ti-N bond distances consistent with the expected stronger *trans* influence of $\eta^5\text{-C}_5\text{H}_5$ versus

MeCN .³ Interestingly in the present structure the axial Hf-N bond lengths $\text{Hf}(1)\text{-N}(11)$ 2.26(2) [$\text{Hf}(2)\text{-N}(21)$ 2.28(2) Å] fall in the middle of the range of the equatorial Hf-N bond distances. Although direct comparisons are not available, the Hf-N bond distance 2.027(8) Å observed for $[\text{Hf}(\eta^5\text{-C}_5\text{Me}_5)_2\text{H}(\text{NHMe})]^{21}$ is believed to represent a reasonable value for a formal $\text{Hf}=\text{N}(\text{sp}^2)$ double-bond length. One final point concerns the change in co-ordination number from six to seven on going from the 2+ to the 3+ cations. This expansion from the 16-electron $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{MeCN})_4]^{2+}$ to the 18-electron $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_6]^{3+}$ can be regarded as a direct result of the increased Lewis acidity of the metal, coincident with the removal of all the chlorine atoms with their attendant (and substantial) π -bond components.

The SbCl_6^- anions are unexceptional, except for one instance where some disorder is evident, with essentially octahedral co-ordination around Sb atoms [Sb-Cl 2.198(11)–2.411(9), mean 2.315 Å; Cl-Sb-Cl mean 89.9 and 177.8°].

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