APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 259–266 (1995)

# A New Family of Heavy Transition Metal Coordination Compounds and its Application, I. Design, Synthesis and Characterization of Volatile Organohafnium Precursors

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**The first three representatives of a new family of volatile organohafnium compounds suitable as metallo-organic chemical vapour deposition precursors were synthesized. A combination of cyclopentadienyl- and alkoxo-ligands with a bicyclo[2.2.1]heptane framework was used. Volatility at relatively low temperatures for hafnium compounds was found and the precursors were characterized by elemental analysis and spectroscopic methods (IR, $^1$H and $^{13}$C NMR, mass spectrometry and mass-analysed ion kinetic energy spectroscopy). The outlook for use in hafnium functional materials synthesis was derived from the fragmentation data.**

**Keywords: volatile precursors; hafnium; hafnocene; bicyclo[2.2.1]heptane; alcoholates; NMR spectra; fragmentation patterns**

## INTRODUCTION

Advancement of future technology depends to a great extent on the development of new materials. For instance materials based on zirconium, hafnium and tantalum can be utilized both as protective coatings (those based on hafnium and tantalum) under extremely severe conditions such as thermal load, coupled with aggressive and/or oxidative media, and as Kaminsky-type[1] olefin polymerization catalysts of the highest efficiency (those based on zirconium and hafnium).

In forthcoming papers in this series, we intend to draw attention to both the chemical and materials science aspects, starting from the design and synthesis of the organometallic precursors and progressing via their characterization to their application, either for vapour-phase synthesis of functional materials or as polymerization catalysts.

At present, only carbides, oxycarbides and oxides of hafnium are known amongst materials resistant beyond 2000 °C which are attracting particular attention in the aerospace industry and for vacuum electronics. Among a large number of deposition methods, metallo-organic chemical vapour deposition (MOCVD) is one of the most promising. This technique may be controlled by a wide set of parameters, but it is the precursor's nature that predetermines chemical processes. The organometallic or coordination compounds to be used as precursors should possess some specific properties, such as:

(a) molecular transition to a vapour phase;
(b) thermal stability in a vapour phase in a broad temperature range;
(c) controllable thermal decomposition, leading to formation of a proper solid phase.[2]

Property (c) is mainly dependent on the atoms bonded to the metal, and to a lesser extent on the chemical structural peculiarities, while (a) and (b) are determined by the structural aspects. The molecule must possess a periphery that consists of the atom end-groups (the substituents in the ligand) which must interact weakly with each other and with other parts of the neighbouring molecules. In fact such interaction is favoured by coordinative unsaturation of the central metal atom (as occurs in many traditional hafnium pre-

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CCC 0268–2605/95/030259–08

*Received 25 February 1994*
*Accepted 24 October 1994*

cursors: hafnium tetrachloride, isopropoxide etc.). Compounds of this type have a pronounced tendency to oligomerization or polymerization, or they may coordinate with other donor ligands (e.g. solvent molecules); hence their volatility and/or thermal stability are significantly reduced.

Previously Bower and Tennent[3] reported the synthesis and characterization of hafnium and zirconium tetra-bicyclo[2.2.1]hept-1-yls but these compounds are relatively unstable (they undergo decomposition at room temperature within one week or on contact with air), and the ligand is not commercially available.

Taking the above into consideration, we have synthesized as a first step some new organohafnium compounds of the type $Cp_2HfX_2$, where X represents various alkoxide groups with a voluminous and delicate carbon framework of bicyclo-[2.2.1]heptane. In these compounds, the well-known volatility and thermal stability of metallocenes[4] is combined with the shielding properties of the lateral ligands. Moreover, some of the principal needs of technology are satisfied: all compounds used for the synthesis are industrial products or by-products; in addition, they are not expensive.

## EXPERIMENTAL

All syntheses were carried out in nitrogen-filled dry boxes (Braun).

### Reagents

Hafnium tetrachloride (Experimental plant of the Physico-Chemical Institute of the National Academy of Sciences of Ukraine, Odessa, Ukraine), a 2.0 M solution of sodium cyclopentadienylide (NaCp) in tetrahydrofuran (THF) (Aldrich, Milwaukee, WI, USA), (+)-*endo*-norborneol (*endo*-HONBL) (Aldrich), (+)-*exo*-norborneol (*exo*-HONBL) (Aldrich), [(1*S*)-*endol*-(−)-borneol (HOBL) (Aldrich), and a solution of buthyl-lithium (1.6 M) in hexanes (Aldrich) were used as supplied. Trichloroethylene (Prodotti chimici Riuniti, Padova, PD, Italy) was purified by reflux (with subsequent distillation) over fused calcium chloride ($CaCl_2$). All other solvents were purified by reflux over K benzophenone followed by distillation.

### Syntheses

#### [$Cp_2HfCl_2$]

This was synthesized by a method similar to that described by Druce *et al.*[5] The dried solid residue was extracted in a Soxhlet apparatus with trichloroethylene and was then repeatedly recrystallized with activated carbon, to give white crystals. The product was identified by IR and $^1H$ and $^{13}C$ NMR.

#### [$Cp_2Hf(OBL)_2$] (1)

For this complex a two-step synthesis was performed. The lithium derivative of HOBL was obtained in a 100 ml Erlenmeyer flask: 6.25 ml of 1.6 M buthyl-lithium solution (10 mmol of BuLi) was diluted with 15 ml of toluene. A solution of 1.543 g (10 mmol) of HOBL in a mixture of 10 ml of THF and 30 ml of toluene was added dropwise with stirring at ambient temperature during 1 h. The transparant reaction mixture was stirred for another hour. Afterwards, a solution of 1.9 (5 mmol) of $Cp_2HfCl_2$ in the same mixture of solvents was added dropwise at room temperature during 2 h and then refluxed for a further 2 h with continuous stirring. The solvents were removed *in vacuo* and the solid obtained was suspended in 70 ml of hexane. The fine undissolved LiCl was separated by filtration, while the liquid phase was purified by treating with activated carbon (Aldrich). After the removal of hexane the resulting solid was allowed to dry *in vacuo* for several hours. Yield: 2.24 g of **1** (82.4%).

#### [$Cp_2Hf$(*endo*-ONBL)$_2$] (2) and [$Cp_2Hf$(*exo*-ONBL)$_2$] (3)

These complexes were synthesized by the method described above. The only difference was noted for the *exo*-ONBL derivative: after the addition of nearly one-half of the $Cp_2HfCl_2$, the reaction mixture became turbid, and up to the end of the reaction a fine precipitate appeared. Yields: for **2**, 87.3%; for **3**, 85.8%.

The composition was confirmed by chemical elemental analysis performed by Dornis und Kolbe Mikroanalytisches Laboratorium (Müllheim a. d. Ruhr, Germany). The data are presented in Table 1.

### Equipment

Infrared spectra were recorded on a Mattson 3000 Galaxy FTIR spectrometer (USA) in KBr pellets.

$^1H$ and $^{13}C$ spectra were obtained in benzene-$d_6$

**Table 1** Hafnium complexes with mono- and bi-cyclic ligands

| Compound | Appearance | Yield (%) | MW[a] | Analytical data (%) (Found/Calcd) Hf | C | H | Sublimation point (°C) |
|---|---|---|---|---|---|---|---|
| $[Cp_2Hf(\textit{endo}\text{-}ONBL)_2]$ | Yellowish powder | 87.3 | 529 | 33.48/33.81 | 54.17/54.12 | 6.08/6.06 | 118–120 |
| $[Cp_2Hf(\textit{exo}\text{-}ONBL)_2]$ | Yellowish powder | 85.8 | 529 | 33.62/33.81 | 54.08/54.12 | 6.03/6.06 | 118–120 |
| $[Cp_2Hf(OBL)_2]$ | Yellowish powder | 82.4 | 613 | 28.82/29.01 | 58.36/58.57 | 7.17/7.21 | 95–96 |

[a] Values determined by MS for the $^{176}$Hf isotope.

(Aldrich) solutions with a Brucker AC-200 spectrometer at 200.13 and 50.33 MHz, respectively, at a probe temperature of 293 K. For both nuclei the chemical shifts were measured relative to tetramethylsilane = 0.0 ppm as internal standard. The assignment of the relevant proton resonances was made from the relative chemical shifts and interactions and bi-dimensional homonuclear shift correlation (COSY) experiments.[6,7] The assignment of the relevant $^{13}$C resonances was made from the relative chemical shifts and spin–spin splittings observed in the proton undecoupled $^{13}$C spectra.

Mass-spectrometric measurements were performed on a VG ZAB 2F mass spectrometer (VG Analytical, Manchester, UK) operating under electron ionization conditions (70 eV, 200 μA, ion-source temperature 180 °C). Metastable ions were studied by means of mass-analysed ion kinetic energy (MIKE) spectroscopy.

The sublimation points of the complexes were determined at $(1–2) \times 10^{-1}$ mm Hg in a microsublimator immersed in a silicone oil filled thermostat Haake F3 (Haake, Karlsruhe, Germany).

## RESULTS AND DISCUSSION

Compounds of the type $[(Me_3SiCp)_2Hf(OR)_2]$ and $[(Me_3SiCp)_2HfCl(OR)]$ (where R = Me, Et) have previously been described by Hoke and Stern[8] using a procedure different from that followed by us. In fact, they were synthesized in THF solvent in moderate yields of 61% and 72% for R = Et and Me respectively. As a twofold excess of the alcohol (methanol or ethanol), with respect to a stoichiometric quantity, was utilized for the synthesis of the derivatives in question, the final products were separated as clear oils of solvato-adducts $[(Me_3SiCp)_2Hf(OR)_2 \cdot ROH]$. Unsolvated complexes could only be obtained by sublimation. Triethylamine, a strong organic base, was used to absorb the HCl eliminated. On the other hand, when hexane was used as a solvent, the reaction was carried out in suspension via sodium alcoholate instead of an alcohol + organic base. In this case after 3.5 days of stirring at room temperature, the yield is higher (91%), but only a mono-substituted product (if R = Me) or an inseparable mixture of mono- and di-substituted derivatives (R = Et) could be obtained.

In our opinion the organolithium route is more convenient for the synthesis of analogous complexes. We achieved the synthesis of $Cp_2Hf(OR)_2$, where R = –OBL, *endo*-ONBL or *exo*-ONBL. In fact organolithium derivatives can be easily obtained from the corresponding alcohol and buthyl-lithium. The resulting solution is used directly in subsequent procedures. The reaction is complete in 6 h, first at room temperature and then under reflux in THF/toluene solvent mixture. Under such conditions both initial reagents are in solution and it is not necessary to use an excess of nucleophile. The products are obtained in higher yields of 82–87% as yellowish powders.

### Infrared spectra

The molecules of the complexes in question are quite large; hence their IR spectra show quite complex absorption patterns. Nevertheless, their assignment is fairly straightforward. The main characteristic absorption bands of $\eta$-$C_5H_5$ ligands are present: $\nu_s$(C–H) 3100 cm$^{-1}$; $\delta_{as}$ (C–H)$_{\text{in-plane}}$ 1020 cm$^{-1}$; $\nu_{as}$(C–H)$_{\text{out-of-plane}}$ 1013–1016, 855–860, 838–844 cm$^{-1}$; $\delta_s$(C–H) 823–825 cm$^{-1}$ (frequency intervals designate the location of the correspond-

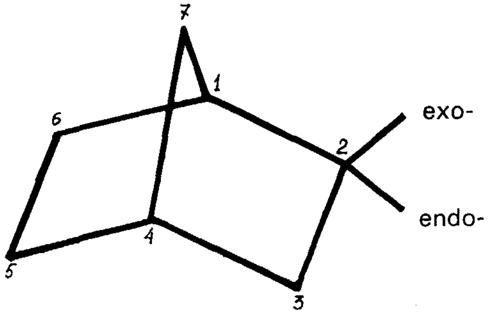

**Figure 1** The bicyclo[2.2.1]heptane framework.

ing bands for three complexes). Low intensity of a band at 1125 cm$^{-1}$, corresponding to Cp-ring breathing, enables us to suppose that the Hf–Cp bond[9] has considerable ionic character. The alicyclic framework of the alkoxo ligands is revealed by strong bands at 2983, 2956 and 2873 cm$^{-1}$ (**1**), 2954 and 2870 cm$^{-1}$ (**2**) and 2951 and 2870 cm$^{-1}$ (**3**); thus the vibration at 2983 cm$^{-1}$ could be assigned to one of the terminal methyl groups C–H stretching modes in an OBL ligand (1,7,7-positions; see Fig. 1),, while the other is present together with alicyclic $\nu_{C\text{-}H}$ ones. Absorbances at 1168–1180 cm$^{-1}$ are assigned to the characteristic $\nu_{C\text{-}O}$ frequencies. A strong band, present in the spectra of all three complexes in the region 799–802 cm$^{-1}$, and which is absent from the spectra of both $Cp_2HfCl_2$ and the alcohols, may be ascribed to Hf–O bond stretching.[10]

## NMR spectra

Well-defined proton and $^{13}C$ spectra confirm the diamagnetism of the synthesized hafnium complexes, typical of distorted tetrahedral $d^0$ systems. The NMR spectra are also in agreement with the proposed symmetrical formulations, having the cyclopentadienyl and bicyclic species in a ratio of 1 : 1. In addition, coordination of the alkoxo moiety is unambiguously assigned by

(1) the disappearance of any O–H resonance in the proton spectra of all hafnium complexes;
(2) the marked downfield shift observed for both protons ($H_2$) and carbons ($C_2$) close to the coordinated oxygens in hafnium complexes (and the less pronounced chemical shifts at $C_1$ and $C_3$) when compared with those of the free ligands (see Fig.1; Table 2).

This latter effect is in accordance with the acidic character of $Hf^{4+}$ ion, which draws electron density from the ligand framework to balance its positive charge.

The residual pattern of the bicyclo moiety looks very similar to that of the ligand. The most upfield signal (a doublet of triplets) most likely arises from one of the two $H_3$ protons, because of the coupling with $H_2$, as evidenced in the diagram in Fig. 2. In addition $H_2$ is further coupled with two more protons, $H_1$ and the second $H_3$. The proton spectrum of **1** also shows the cyclopentadienyl protons at 5.96 ppm (see Table 2).

The mono- and bi-dimensional H spectra of **2** are shown in Fig. 2 as an example.

## Mass spectra

All spectra exhibit the expected eight-line isotope pattern of the molecular ion and the mass values of hafnium containing ions are referred to the $^{176}Hf$ isotope. The mass spectra and fragmentation patterns are reported in Figs 3 and 4.

For both *endo*- and *exo*-ONBL derivatives of hafnocene, the fragmentation patterns are quite complex, but nearly the same.[11] As may be estimated, the primary mass losses (Fig. 3) are due to

**Table 2** Selected $^1H$ and $^{13}C$ spectral data for hafnium complexes compared with those of the free ligands in benzene-$d_6$ solutions[a]

| | $^1H$ NMR | | | $^{13}C\{^1H\}$ NMR | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | O—H | C—$H_2$ | Cp—H | $C_{Cp}$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
| [(1*S*)-*endo*]-(−)Borneol | 1.95 (d) | 3.78 (m) | — | — | 49.7 | 76.9 | 39.3 | 45.5 |
| [$Cp_2Hf$(*endo*-OBL)$_2$] | — | 4.27 (m) | 6.00 (s) | 110.6 | 50.8 | 86.8 | 40.6 | 45.7 |
| (+)*endo*(−)Norborneol | 2.80 (bs) | 4.05 (m) | — | — | 42.9 | 72.7 | 39.6 | 37.6 |
| [$Cp_2Hf$(*endo*-ONBL)$_2$] | — | 4.37 (m) | 5.96 (s) | 110.6 | 44.1 | 82.1 | 41.2 | 37.7 |
| (+)*exo*(−)Norborneol | 2.77 (bs) | 3.60 (d) | — | — | 44.5 | 74.6 | 42.3 | 35.8 |
| [$Cp_2Hf$(*exo*-ONBL)$_2$] | — | 3.90 (d) | 5.97 (s) | 110.5 | 45.4 | 84.1 | 44.3 | 35.8 |

[a] Multiplicities in parentheses: s, singlet; bs, broad singlet; d, doublet; m, multiplet.

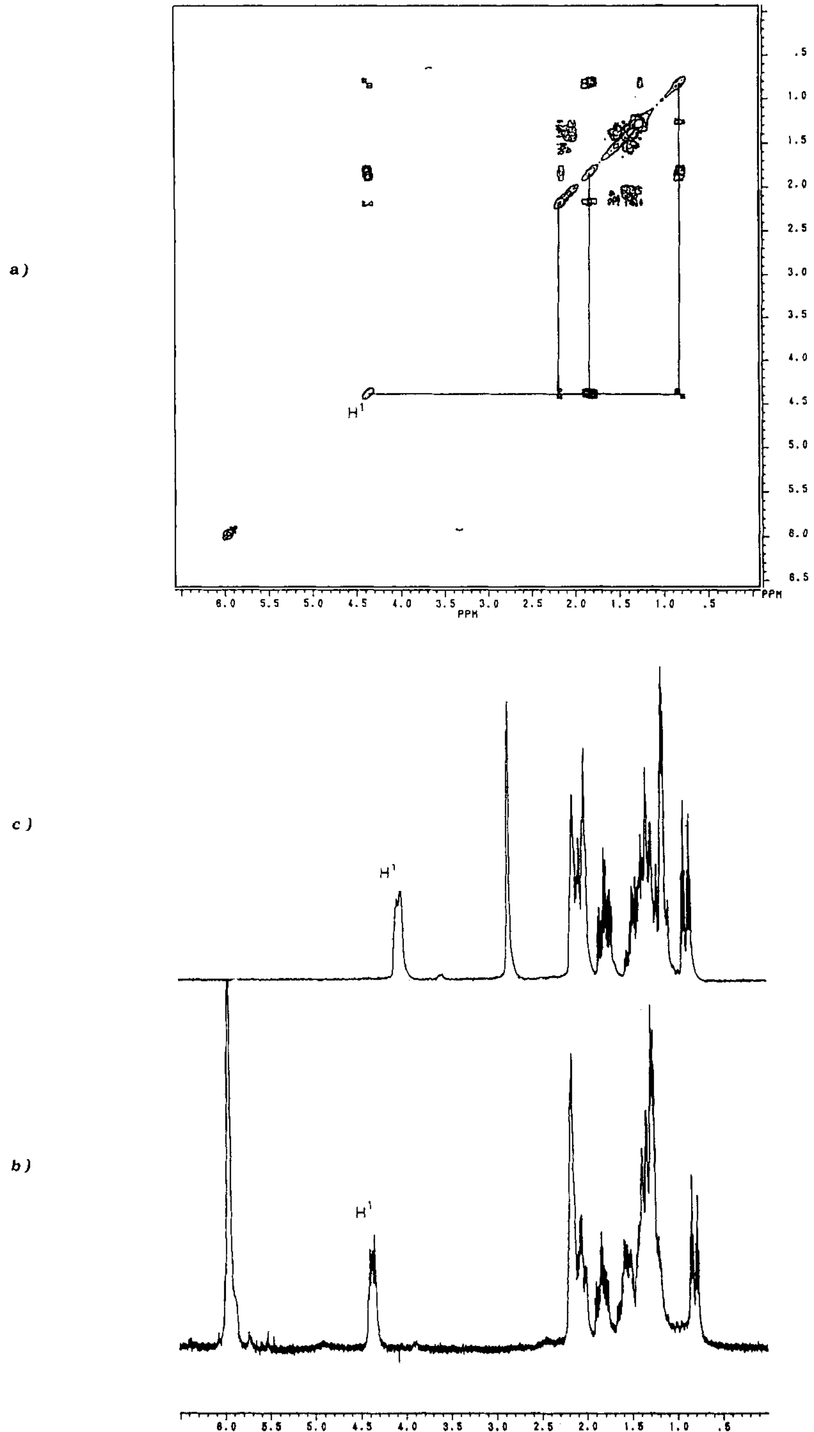

**Figure 2** (a) Proton 200 MHz COSY45 contour plot map of [Cp$_2$Hf(*endo*-ONBL)$_2$] over the 0.5–4.8 ppm region; note coupling of H$_2$ with three other protons corresponding to H$_1$, H$_3$ (axial) and H$_3$ (equatorial). (b) Monodimensional $^1$H spectrum of [Cp$_2$Hf(*endo*-ONBL)$_2$]. (c) Monodimensional $^1$H spectrum of *endo*(−)norborneol; note disappearance of the O—H signal and downfield shift of H$_2$ in the hafnium complex with respect to signals in the free ligand spectrum.

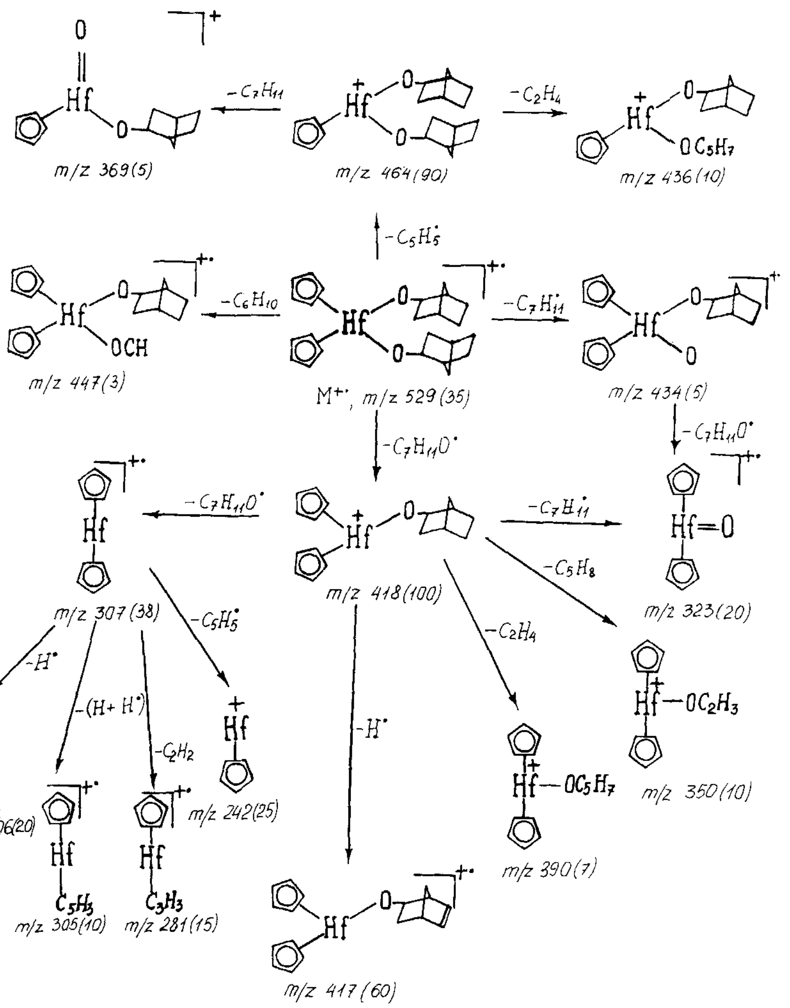

**Figure 3** Fragmentation pattern of [$Cp_2Hf$(*endo*-ONBL)$_2$].

cyclopentadienyl or norborneoxy ligand elimination with nearly the same probability, accompanied by side-processes of C–O bond cleavage or norbornane framework destruction. Therefore, the first process (i.e. —ONBL elimination) has little preference. In further steps, the MIKE spectroscopy results show a different number and composition of the destruction products for the fragments [$Cp_2Hf$(ONBL)]$^+$ and [$Cp_2Hf$(O)(ONBL)]$^+$, but this is only at first sight. It is interesting to note that, in both cases, exclusively the —ONBL ligand underwent further decomposition, while the Cp–Hf–Cp structures remained essentially unaffected. Such stability indicates a high Hf–Cp-ring bond strength and confirms the ionic character of this bond, already noted in the IR spectra. As has been mentioned above, the fragmentation of *endo*- (**2**) and *exo*- (**3**) isomers occurs by virtually the same channels; the only difference lies in inverted —ONBL framework decay in the [$Cp_2Hf$(ONBL)]$^+$ fragment.

In contrast to the case described above, the fragmentation pattern of complex **3** is simpler (Fig. 4). Evidently, —OBL ligand elimination is the dominant mass loss process. Considering the pattern as a whole, it should be noted that introduction of three methylic substituents the bicyclo-[2.2.1]heptane framework has a stabilizing effect, the decay of the latter was hardly observed and

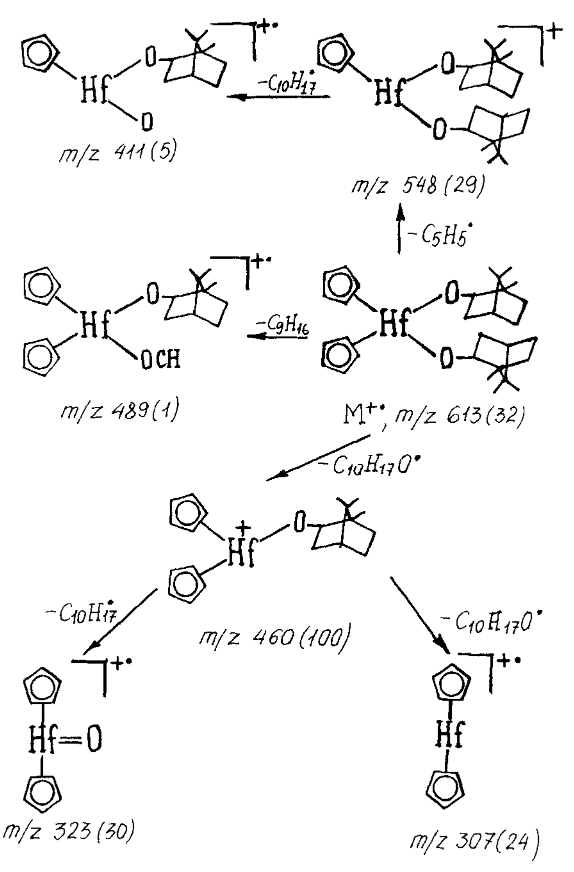

**Figure 4** Fragmentation pattern of $[Cp_2Hf(OBL)_2]$.

the 1,7,7-trimethylbicyclo[2.2.1]heptane framework was eliminated as an entity owing to C–O or Hf–O bond cleavage.

### Sublimation points

Sublimation point determinations were carried out in a microsublimator at $(1-2) \times 10^{-1}$ mm Hg. If the complexes had been purified by recrystallization with activated carbon, they sublimed without melting at relatively low temperatures, as indicated in Table 1. The behaviour of the complex **3** changed significantly in the absence of preliminary purification: it melted at 120 °C and then sublimed from the resulting oil at 140 °C. All sublimates were identified by $^1H$ and $^{13}C$ NMR and IR spectroscopies; the spectra showed further purification.

## CONCLUSIONS

We have synthesized the first representatives of a new family of volatile hafnium compounds with mono- and bi-cyclic shielding ligands, which were characterized by elemental analysis and a variety of spectroscopic methods (IR, $^1H$ and $^{13}C$ NMR, mass spectrometry, MIKE). Volatility at relatively low temperatures for hafnium compounds has been determined from the sublimation points. it should be noted that the behaviour of hafnocene derivatives with nonsubstituted bicyclic ligands when compared with those of substituted ones appears to be of quite different character. As expected, complex **1** exhibits greater volatility at lower temperature with respect to nonsubstituted analogues. Parallel to this, mass spectrometry shows that $[Cp_2Hf(OBL)_2]$ loses the hydrocarbon framework easily and completely. It should lead to lower carbon content in the resulting material (film or powder). We are considering this approach in contrast to the traditional use of complexes with small ligands and the minimum possible carbon content. These properties of the complex in question, coupled with its cheapness and availability, should promote its use for HfC or $HfO_2$ protective films. At the same time, $[Cp_2Hf(ONBL)_2]$ may also be of interest for the synthesis of graded coatings because of the great variety of its decomposition products.

The complex **1** was utilized as an MOCVD precursor for protective oxide coatings on different carbon-based materials (carbonized plastics, fibres, composites). This protection gives nearly 2–3-fold improvement in thermal and erosion resistance of the materials at 2573–3323 K. It is interesting to note that we have not used intermediate layers in order to balance the mismatch in thermal expansion coefficients of the substrate and the film. The desired effect was achieved by a graded layer C/HfOC/$HfO_2$ deposition.

Moreover, we have also found that the new complexes possess high activity as ethylene homogeneous polymerization catalysts. Polymers with interesting technological parameters were obtained.

We consider that further research on heavy transition metal complexes with mono- and bicyclic shielding ligands and their application for functional materials has a long-term perspective. This work is in progress and results will be described in forthcoming papers in this series.

*Acknowledgements* The authors would like to express their thanks to Dr G. Rossetto for his assistance in the research work organization and discussion, to Dr I. A. Grafova for sublimation point determinations and helpful discussion as well as to Mr S. Garon for his assistance in glass-blowing. One of us (AVG) expresses his gratitude to CNR-ICTIMA (Padua, Italy) for financial support and for his stay in Italy.

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