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Bis(η^5-cyclopentadienyl)hafnium Complexes containing σ-bonded Alkynyl Groups

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The synthesis of the stable compounds $Cp_2Hf(C{\equiv}C-R)_2$ *(R = phenyl, cyclohexhyl, n-hexyl, 2,2-diphenylethyl and 2-cyano-2,2-diphenylethyl) from* Cp_2HfCl_2 *and* $NaC{\equiv}C-R$ *in dioxane is described. The properties of these compounds are discussed and compared with those of the analogous titanium and zirconium derivatives. The compounds were characterized by elemental microanalysis and by infrared, electronic and* ^1H *NMR spectroscopy.*

Introduction

The organometallic chemistry of titanium has been extensively developed over the past three decades, while that of zirconium is only now beginning to be developed and that of hafnium has been very little explored. Several hafnium compounds containing cyclopentadienyl and alkyl or aryl ligands have been studied [1–3], and Jenkins *et al.* [4] briefly mention the synthesis and some properties of an alkynyl compound of hafnium formulated as $Cp_2Hf(C{\equiv}C-C_6H_5)_2$; no further information on this compound has been reported.

Although there is a very close parallel between zirconium and hafnium derivatives and their chemistry is very similar, there are surprising differences in the behaviour of some of their compounds [1, 5] so that the chemistry of hafnium should be examined more closely.

We have shown previously that several air and moisture stable bis(η^5-cyclopentadienyl) bis(alkynyl)-titanium(IV) and -zirconium(IV) complexes can be prepared [6, 7]. We describe here the synthesis and properties of some new stable complexes of the type Cp_2HfR_2 (Cp = cyclopentadienyl; R = phenylethynyl (PE), cyclohexylethynyl (CHE), n-octynyl (HE), 4,4-diphenylbutynyl (DPB), 4-cyano-4,4-diphenylbutynyl (DPPN)), in order to contribute to the knowledge of compounds of Group IVA metals containing alkynyl groups as ligands.

Some similarities and differences between these compounds and the titanium and zirconium analogues have been considered.

Results and Discussion

The compounds were obtained by the reaction of sodium alkylnylide and Cp_2HfCl_2. When this reaction is carried out in anhydrous ether at room temperature, the yield is very low (2–15%) whereas the analogous titanium and zirconium derivatives can be obtained by this method with a good yield [6, 7]. Several solvents and temperatures of reaction have been tried and the best results have been obtained for dioxane at 50 °C (yield 60–65%). When higher temperatures or other solvents (such as boiling THF) were used a mixture of reaction products which could not be separated was obtained.

On the other hand the use of Cp_2HfBr_2 or $Cp_2Hf(ClO_4)_2$ as starting materials either did not lead to better yields, or the compounds obtained were oils which could not be crystallized.

The compounds are stable to air and moisture, diamagnetic, soluble in most of the usual organic solvents, and insoluble in water. They are hydrophobic, and can stay several days in water without alteration.

In presence of HCl gas in diethylether or HBr in aqueous acetone the metal–carbon σ-bond is broken with formation of Cp_2HfX_2 (X = Cl, Br) and the respective acetylenic hydrocarbon in good yield.

Infrared Spectra

The IR spectra of all the compounds show the absence of bands corresponding to σ-bonded cyclopentadienyl group vibrations excluding the possibility of a σ-bond between the cyclopentadienyl group and the metal in these compounds. However, the characteristic absorption frequencies of η^5-bonded

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TABLE I. ν(C≡C) and ν(C≡N) Stretching Frequencies and Electronic Spectral Data of the Compounds.[a]

Compound	ν(C≡C) (cm^{-1})	ν(C≡N) (cm^{-1})	λ_{max} (nm) (log ϵ)
Cp_2HfCl_2			266 (3.34), 308 (2.98)
$Cp_2Hf(PE)_2$[b]	2083 w (2122)		280 (4.86)
$Cp_2Hf(CHE)_2$	2096 w (2113)		266 (4.80)
$Cp_2Hf(HE)_2$	2100 w (2117)		278 (4.81)
$Cp_2Hf(DPPN)_2$	2100 w (2120)	2180m (2240)	256 (4.84)
$Cp_2Hf(DPB)_2$	2095 w (2109)		254 (4.84)

[a] ν(C≡C) and ν(C≡N) values of starting acetylenic compounds are given in parentheses. [b] See ref. 4. [c] m = medium, w = weak.

TABLE II. Chemical Shifts (δ) of Hafnium Derivatives.[a]

Compound	C_5H_5	C_6H_5	CH_3	CH_2	CH
Cp_2HfCl_2[b]	6.46 s				
$Cp_2Hf(PE)_2$[c]	6.23 s	7.17 s			
$Cp_2Hf(CHE)_2$	6.30 s			1.60 m	
$Cp_2Hf(HE)_2$	6.32 s		1.05 m	1.30 m	
$Cp_2Hf(DPPN)_2$	6.00 s	7.38 m		3.08 d	
$Cp_2Hf(DPB)_2$	6.15 s	7.42 m		3.05 d	4.12 t

[a] s = singlet, d = doublet, m = multiplet, t = triplet. [b] See ref. 1. [c] See ref. 4.

cyclopentadienyl groups appear at 3100 cm^{-1} ν(C–H str.), 1450 cm^{-1} ν(C–C str.), 1010 cm^{-1} δ(C–H bend. in plane) and 810 cm^{-1} δ(C–H bend. out of plane).

The ν(C≡C) stretching frequency in the compounds shifts towards the lower frequencies with respect to those of the starting acetylenic compounds. This shift can be due to the increase of polarity of the acetylenic bond upon coordination to the metal. The influence of a d_π(metal) → p_π*(ligand) back-bonding on the ν(C≡C) frequency is improbable, because of the high oxidation state of the metal. The shifts observed for the hafnium derivatives are smaller than those of the corresponding compounds of titanium and zirconium [6, 7]. This fact could be due to a (presumably) longer Hf–C sigma-bond length with respect to those of Ti–C and Zr–C. Such a possibility is based on the structural data of the $(\eta^5\text{-}C_9H_7)M(CH_3)_2$ (M = Ti, Zr, Hf) derivatives, in which the M–C σ-bond length is significantly longer for the hafnium compound [5].

In addition, the ν(C≡N) stretching in the DPPN derivative shifts from 2240 to 2180 cm^{-1}; this could be explained by an interaction between the nitrile group and the metal. Similar shifts are also observed in the analogous titanium and zirconium derivatives [6, 7].

Table I summarizes the ν(C≡C) stretching frequencies of the compounds obtained together with the ν(C≡N) stretching frequency of the DPPN derivative.

^{1}H NMR Spectra

The ^{1}H NMR spectra of all the compounds show only a singlet corresponding to the cyclopentadienyl ring protons, which indicates a magnetic equivalence of them by a free rotation of the cyclopentadienyl rings.

In the analogous titanium and zirconium derivatives of DPPN, two or one multiplets appeared respectively for the cyclopentadienyl ring protons [6, 7]. The presumably increasing M-C≡ σ-bond length in the series Ti < Zr < Hf could explain the observed differences, since the steric hindrance of the DPPN ligand on the C_5H_5 rings should diminish with increasing M–C≡ distances.

The substitution of chlorine by the less electronegative alkynyl ligand leads to a higher shielding of the ring protons and causes a shift of the δ values of the cyclopentadienyl protons towards higher fields.

Table II lists the proton chemical shifts for the acetylenic compounds obtained.

Electronic Spectra

The electronic spectrum of Cp_2HfCl_2 shows between 180 and 800 nm two absorptions at 266 and 308 nm. In the alkynyl derivatives an absorption is observed that can only be assigned to a charge transfer ligand → metal transition, rather than to an internal transition of the cyclopentadienyl ring because of its position changes on changing the alkynyl ligand. The analogous titanium and zirconium derivatives show three electronic transitions in this range [6, 7].

Table I lists the electronic spectral data for the compounds.

Experimental

All reactions and manipulations were carried out under dinitrogen or in vacuum. All solvents were dried and purified by conventional methods. Before use they were freed from oxygen by repeated degassing and saturating with dinitrogen.

Elemental analyses for C, H, N were performed by Elemental Micro-Analysis Limited, Surrey (England). Infrared spectra in the region 4000–200 cm^{-1} were recorded as KBr discs or Nujol mulls on a Perkin–Elmer 325 spectrometer. ^1H NMR spectra were determined using a Perkin-Elmer R12 (60 MHz) spectrometer in deuterochloroform (with TMS as internal standard). Electronic spectra were recorded with a Unicam SP 1800 B using chloroform as solvent. Magnetic susceptibilities were determined by the Gouy method.

Phenylacetylene (Merck), cyclohexylacetylene (Merck) and n-octyne (Fluka) were obtained from commercial sources and distilled before use. Bis(cyclopentadienyl)hafnium dichloride and 4,4-diphenylbutyne (HDPB) were prepared by a published method [6, 8]. 2,2-diphenyl-4-pentynenitrile (HDPPN) was prepared as described by Salmon-Legagneur and Brunet [9] but with some modifications [10]. The sodium salts of acetylenic compounds were prepared as previously described [11].

General Method of Preparation

The bis(alkynyl)-bis(cyclopentadienyl)hafnium derivatives were prepared by reaction of a suspension of the corresponding sodium alkynylide in anhydrous dioxane and Cp_2HfCl_2 in a molar ratio of 2/1. The mixture was stirred for 8 hours at 50 °C filtered and concentrated to about 1/3 of the initial volume. Pentane or hexane was added and after 24 hours at 0 °C a precipitate appeared. The product was filtered, washed with pentane or hexane, and dried in vacuum.

Bis(cyclopentadienyl)-bis(phenylethynyl)hafnium(IV)

Sodium phenylethynylide (0.49 g, 4 mmol) and bis(cyclopentadienyl)hafnium dichloride (0.76 g, 2 mmol) yielded 0.67 g (65%) of the complex as a pale ochre microcrystalline solid. Jenkins *et al.* [4] have previously prepared the same compound from $Cp_2Hf[N(CH_3)_2]_2$ and phenylacetylene. The IR and ^1H NMR spectra of the compounds obtained by both methods are identical.

Bis(cyclopentadienyl)-bis(cyclohexylethynyl)hafnium(IV)

Sodium cyclohexylethynylide (0.52 g, 4 mmol) and bis(cyclopentadienyl)hafnium dichloride (0.76 g, 2 mmol) yielded 0.63 g (60%) of the complex as a yellowish white microcrystalline solid. (Found: C, 59.43; H, 6.35; $C_{26}H_{32}Hf$ calcd: C, 59.71; H, 6.12%).

Bis(cyclopentadienyl)-bis(octynyl)hafnium(IV)

Sodium octynylide (0.53 g, 4 mmol) and bis(cyclopentadienyl)hafnium dichloride (0.76 g, 2 mmol) yielded 0.67 g (64%) of the complex as a yellowish white microcrystalline solid. (Found: C, 58.98; H, 7.01. $C_{26}H_{36}Hf$ calcd; C, 59.26; H, 6.38%).

Bis(cyclopentadienyl)-bis(4-cyano-4,4-diphenylbutynyl) hafnium(IV)

Sodium 4-cyano-4,4-diphenylbutynylide (1.02 g, 4 mmol) and bis(cyclopentadienyl)hafnium dichloride (0.76 g, 2 mmol) yielded 0.97 g (63%) of the complex as a pale ochre microcrystalline solid. (Found: C, 68.32; H, 4.69; N, 3.58. $C_{44}H_{34}N_2Hf$ calcd: C, 68.70; H, 4.42; N, 3.64%).

Bis(cyclopentadienyl)-bis(4,4-diphenyl-butynyl)-hafnium(IV)

Sodium 4,4-diphenyl-butynylide (0.82 g, 4 mmol) and bis(cyclopentadienyl)hafnium dichloride (0.76 g, 2 mmol) yielded 0.86 g (60%) of the complex as a pale ochre microcrystalline solid. (Found: C, 69.89; H, 5.22. $C_{42}H_{36}Hf$ calcd: C, 70.15, H, 5.01%).

Reactions of bis(cyclopentadienyl)-bis(alkynyl)hafnium(IV) with HX

An ethereal solution of alkynyl derivative was placed in a flask. While HCl gas was bubbled through this solution the colour changed to colourless in 15 min; then pentane was added and bis(cyclopentadienyl)hafnium dichloride (90%) was filtered off. The filtrate was concentrated or distilled to give acetylenic hydrocarbon (40–70%).

In a similar experiment HBr in acetone was used and then Cp_2HfBr_2 was obtained (70%).

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