ELSEVIER Journal of Organometallic Chemistry 492 (1995) 235–239

Journal of Organometallic Chemistry

Arene–transition metal complexes as precursors of hard coatings prepared by the chemical vapour deposition technique ☆

K. Hankó, G. Vass, L. Szepes *

Department of General and Inorganic Chemistry, Eötvös Loránd University, Pázmány P. sétány 2, 1117 Budapest, Hungary

Received 27 October 1994

Abstract

Chemical aspects of hard coating preparation by chemical vapour deposition were studied in the temperature range 300–600°C using bis(arene)chromium and (cyclopentadienyl)zirconium or hafnium tetrahydroborate compounds as precursors. Chromium carbide was deposited from bis(benzene)chromium (**I**), bis(toluene)chromium (**II**) and bis(*p*-xylene)chromium (**III**); in another set of experiments, thin films of zirconium carbide–boride as well as zirconium and hafnium carbide from (cyclopentadienyl)zirconium tris(tetrahydroborate) (**IV**) bis(cyclopentadienyl)zirconium bis(tetrahydroborate) (**V**) and bis(cyclopentadienyl)hafnium bis(tetrahydroborate) (**VI**) were prepared. In both cases mass spectrometry fragmentation patterns have been invoked to rationalize trends in the deposition temperature and chemical composition of the obtained thin films.

Keywords: MOCVD; Zirconium; Chromium; Arene; Hafnium; Mass spectrometry

1. Introduction

The industrial demands for hard coatings are increasing because of their good resistance of wear and corrosion. Such coatings are for example the transition metal carbides, borides and carbide–borides.

Organometallic precursors are important starting materials for hard coating formation by chemical vapour deposition (CVD), because processes can be conducted at substantially lower temperatures than in the case of inorganic reactants [1]. For example, chromium carbide coatings are deposited at 1050°C by the industrial CVD process using chromium halides and methane [2], and only at 600°C or lower temperature by using organochromium precursors [3,4].

The deposition temperature during the CVD process depends not only on the pressure and flow conditions but also on the nature of the ligand and the strength of the metal–ligand bond.

We have prepared chromium carbide thin films from bis(arene)chromium compounds (namely bis(benzene)chromium (**I**), bis(toluene)chromium (**II**) and bis(*p*-xylene)chromium (**III**)) as precursors, and in another set of experiments zirconium boride–carbide as well as zirconium and hafnium carbide coatings from (cyclopentadienyl)zirconium or hafnium tetrahydroborate compounds ((cyclopentadienyl)zirconium tris(tetrahydroborate) (**IV**), bis(cyclopentadienyl)-zirconium bis(tetrahydroborate) (**V**) and bis(cyclopentadienyl)hafnium bis(tetrahydroborate) (**VI**)) as precursors.

In both cases, mass spectrometry fragmentation patterns have been invoked to rationalize trends in the deposition temperature and chemical composition of the obtained thin films.

2. Experimental details

2.1. Synthesis

The bis(arene)chromium compounds were prepared according to Fischer's [5] method reported in the literature:

$$3\mathrm{CrCl_3} + 2\mathrm{Al} + \mathrm{AlCl_3} + 6\mathrm{Ar} = 3[\mathrm{Cr(Ar)_2}]^+[\mathrm{AlCl_4}]^- \quad (1)$$

$$2[\mathrm{Cr(Ar)_2}]^+ + \mathrm{S_2O_4^{2-}} + 4\mathrm{OH^-} = 2\mathrm{Cr(Ar)_2} + 2\mathrm{SO_3^{2-}} + 2\mathrm{H_2O} \quad (2)$$

where Ar = benzene (**I**), toluene (**II**) or *p*-xylene (**III**).

☆ Paper presented at the 1st Journal of Organometallic Chemistry Conference, München, 1993.

* Corresponding author.

SSDI 0022-328X(94)05313-8

In the preparation of the toluene and the *p*-xylene compound a slight modification has been applied: there was no need to use mesitylene as a catalyst, because reaction (1) was completed in 2–3 h also without its use. As a consequence, no bis(mesitylene)chromium byproduct was formed. In reaction (2) the aromatic solvent was replaced by cyclohexane; so the crude product could be purified much more easily.

The dark-brown, very air-sensitive compounds were identified by elemental analysis and mass spectrometry.

The zirconium and hafnium compounds were synthesized according to procedures reported in the literature [6–8]:

$$(\eta^5\text{-}C_5H_5)_2MCl_2 + 2LiBH_4 = (\eta^5\text{-}C_5H_5)_2M(BH_4)_2 + 2LiCl \qquad (3)$$

where M = Zr, Hf;

$$(\eta^5\text{-}C_5H_5)ZrBr_3 + 3LiBH_4 = (\eta^5\text{-}C_5H_5)Zr(BH_4)_3 + 3LiBr \qquad (4)$$

The white crystalline moisture-sensitive compounds were also identified by elemental analysis and mass spectrometry.

2.2. Chemical vapour deposition

A standard horizontal low pressure hot-wall CVD reactor of 2.5 cm diameter and 25 cm length was used. The pressure was about 20 Pa in the reactor during the experiments. Deposition was made on previously cleaned and baked (500°C in vacuum) glass surfaces.

3. Results

3.1. Bis(arene)chromium compounds

Thin film deposition was studied between 300 and 600°C using bis(arene)chromium compounds. The optimum temperatures obtained in our apparatus are summarised in Table 1.

The films formed are silvery grey, having metallic lustre, insoluble in hot concentrated acids (concentrated HCl, and concentrated HNO_3). The composition of the films was found to be chromium carbide by X-ray photoelectron spectroscopy (XPS). The C 1s and Cr 2p3/2 region of the x-ray photoelectron spectra are shown in Fig. 1.

Table 1
Chemical vapour deposition of bis(arene)chromium compounds

Precursor	Deposition temperature (°C)	Composition of thin films
$(C_6H_6)_2Cr$	600	Chromium carbide
$(C_6H_5CH_3)_2Cr$	380	Chromium carbide
$(p\text{-}C_6H_4(CH_3)_2)_2Cr$	330	Chromium carbide

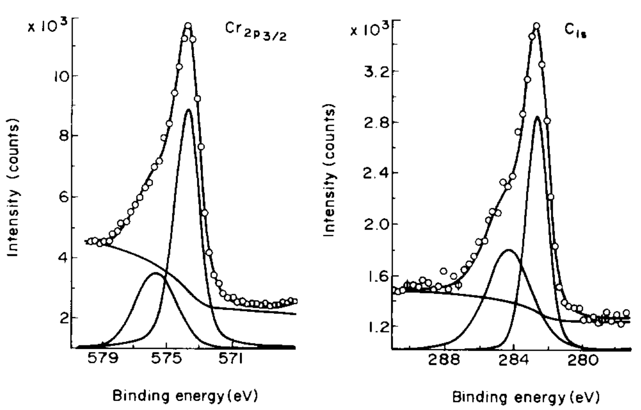

Fig. 1. C 1s and Cr $2p_{3/2}$ region of the X-ray photoelectron spectrum of a chromium carbide film deposited from bis(toluene)chromium precursor

The XPS peaks in Table 2, were assigned using literature data [4]. The oxygen originates from the residual gases of the CVD apparatus.

3.1.1. Mass spectrometry

Tables 3–5 show the 70 eV electron impact mass spectra of the bis(arene)chromium compounds and that of the corresponding free ligands. The mass spectrum of bis(benzene)chromium suggests that the major fragmentation pattern involves stepwise loss of the aromatic ligand. The reactive carbon-containing species, needed for the deposition of chromium carbide, are

Table 2
Assignment of X-ray photoelectron spectroscopy peaks

Elements	Binding energy (eV)	Species
C 1s	282.6 ± 0.17	Chromium carbide
	284.6 ± 0.35	Free carbon (graphite)
O 1s	530.7 ± 0.18	Chromium(III) oxide
Cr $2p_{3/2}$	573.8 ± 0.15	Chromium metal
	575.7 ± 0.25	Chromium carbide
	576.3 ± 0.21	Chromium(III) oxide

Table 3
Mass spectra of bis(benzene)chromium and of benzene

Intensity (complex) [9]	m/z	Ion	Intensity (ligand) [10]
–	39	$C_3H_3^+$	13
100	52	Cr^+	
15	77	$C_6H_5^+$	17
45	78	$C_6H_6^+$	100
	104	$CrC_{12}H_{12}^{2+}$	–
50	130	$CrC_6H_6^+$	–
38	208	$CrC_{12}H_{12}^+$	–

Table 4
Mass spectra of bis(toluene)chromium and of toluene

Intensity (complex)	m/z	Ion	Intensity (ligand) [10]
8	39	$C_3H_3^+$	13
100	52	Cr^+	
7	65	$C_5H_5^+$	11
14	77	$C_6H_5^+$	–
65	91	$C_7H_7^+$	100
68	92	$C_7H_8^+$	79
11	144	$CrC_7H_8^+$	–
5	236	$CrC_{14}H_{16}^+$	–

Table 5
Mass spectra of bis(*p*-xylene)chromium and of *p*-xylene

Intensity (complex)	m/z	Ion	Intensity (ligand) [10]
95	52	Cr^+	–
10	77	$C_6H_5^+$	13
65	91	$C_7H_7^+$	100
< 10	92	$C_7H_8^+$	75
	105	$C_8H_9^+$	30
53	106	$C_8H_{10}^+$	61
53	158	$CrC_8H_{10}^+$	–
100	264	$CrC_{16}H_{20}^+$	–

formed presumably via aromatic C–C bond cleavage while, in the case of **II** and **III**, fragments $C_6H_5^+$ (**II**) and $C_7H_7^+$ (**III**) are probably formed by single C–C bond breaking.

Table 6 summarizes some neutral and the ionic C–C bond dissociation energies in the aromatic ligands (D and D^+ respectively) calculated by use of thermochemical data found in the literature [11–18]. In the case of benzene, this is simply the aromatic C–C bond dissociation energy while, in the remaining cases, data can be related to the fission of C_6H_5–CH_3 as well as $CH_3C_6H_4$–CH_3 bonds in the neutral and ion.

In the case of *p*-xylene, no neutral bond dissociation energy is available. However, it can be estimated by using the energy difference between $D(C_6H_5–CH_3)$ and $D^+(C_6H_5–CH_3)^+$ (50 kJ mol^{-1}). If the same difference also applies to *p*-xylene, the estimated value of $D(CH_3C_6H_4–CH_3)$ is 417 kJ mol^{-1}.

Table 6
Specific carbon–carbon bond dissociation energies in the ligands of bis(arene)chromium compounds

Compound	Deposition temperature (°C)	D(C–C) (kJ mol^{-1})	D^+(C–C) (kJ mol^{-1})
$(C_6H_6)_2Cr$	600	518 [11]	–
$(C_6H_5CH_3)_2Cr$	380	425 [12–14]	375 [12,17]
$(p\text{-}C_6H_4(CH_3)_2)_2Cr$	330	417 [a]	367 [12,16,18]

[a] Estimated value.

Table 7
Chemical vapour deposition of (cyclopentadienyl)zirconium and hafnium tetrahydroborates

Precursor	Deposition temperature (°C)	Composition of thin films
$(\eta^5\text{-}C_5H_5)Zr(BH_4)_3$	350	Zirconium boride–carbide [19]
$(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$	600	Zirconium carbide
$(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$	600	Hafnium carbide

It is evident from the data in Table 6 that the trend in deposition temperatures is very similar to that of bond dissociation energies. This experimental finding is in agreement with our previous suggestion, based on mass spectrometry fragmentation patterns, that reac-

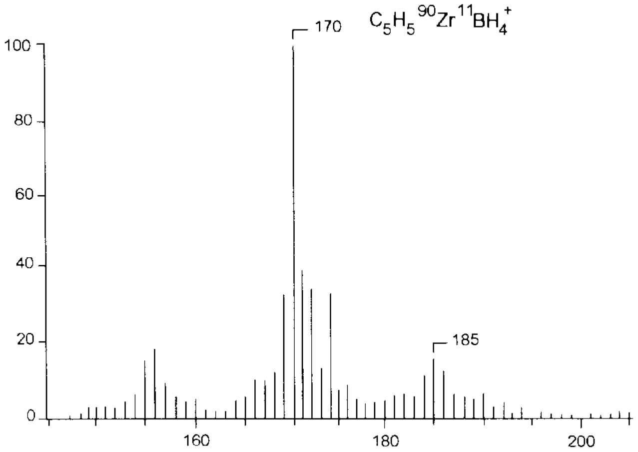

Fig. 2. 70 eV mass spectrum of (cyclopentadienyl)zirconium tris(tetrahydroborate) (**IV**).

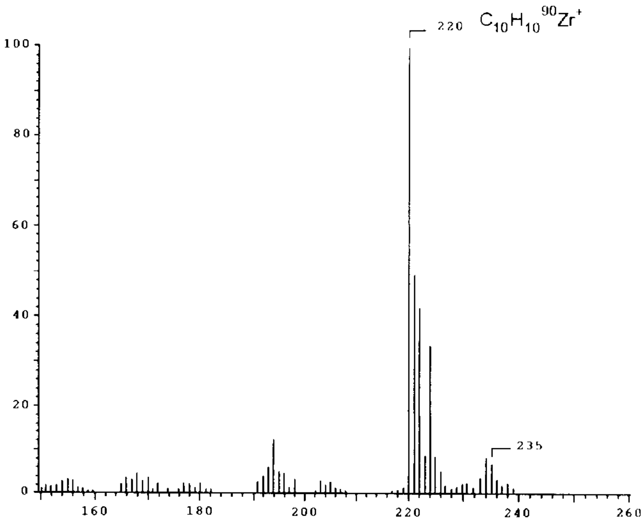

Fig. 3. 70 eV mass spectrum of bis(cyclopentadienyl)zirconium bis(tetrahydroborate) (**V**).

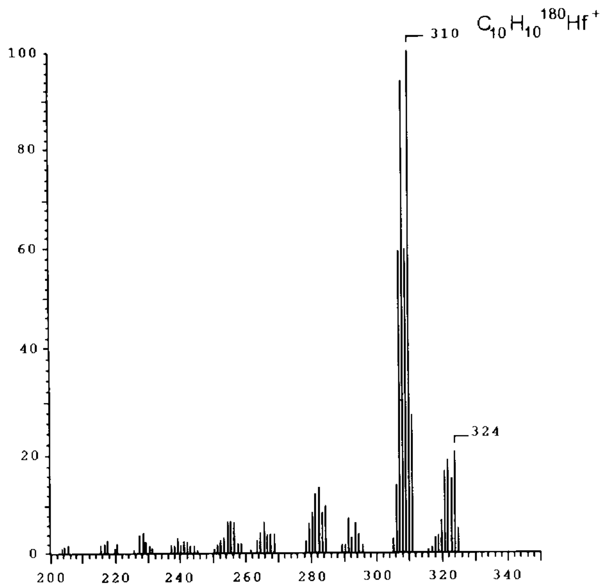

Fig. 4. 70 eV mass spectrum of bis(cyclopentadienyl)hafnium bis(tetrahydroborate) (**VI**).

tive carbon-containing species can be formed via aromatic C–C bond cleavage in the case of precursor **I**, while, in the other cases (**II** and **III**), single C–C bond rupture may occur.

3.2. Zirconium and hafnium compounds

In another set of experiments, hard coating formation by using (cyclopentadienyl)zirconium or hafnium tetrahydroborate precursors has been studied in the temperature range 300–600°C. The optimum deposition temperatures together with the compositions of the thin films are reported in Table 7.

The chemical composition of the thin films was determined by XPS and electron probe microanalysis methods. The coatings obtained in this way have a metallic lustre and show considerable chemical resistance against hot concentrated nitric acid.

3.2.1. Mass spectrometry

The 70 eV electron impact mass spectra of the above compounds (Figs. 2–4) contain very weak molecular ions. Fragments formed by loss of one or two BH_4 groups dominate the spectra, resulting in the corresponding base peaks: $C_5H_5ZrBH_4^+$ (**IV**), $C_{10}H_{10}Zr^+$ (**V**) and $C_{10}H_{10}Hf^+$ (**VI**). It is note worthy that the elemental compositions of the fragments are similar to those of thin films, as far as the film composing elements are concerned. This indicates that—from a chemical composition point of view—relative ion stabilities reflected by the mass spectrum can be considered as influential factors governing the film formation.

4. Conclusions

Low temperature CVD experiments performed on bis(arene)chromiums (**I–III**) and (cyclopentadienyl)zirconium or hafnium tetrahydroborates (**IV–VI**) showed that mass spectrometry information concerning the precursors can be related in two ways to the CVD processes.

(1) In the case of bis(arene)chromium compounds, noticeable connection seems to exist between the decomposition temperature and the energy demand of the primary bond dissociation, leading to formation of reactive carbon-containing species.

(2) In the case of (cyclopentadienyl)zirconium or hafnium tetrahydroborate precursors, the chemical composition of the films can be related to the elemental composition of the mass spectral base peaks.

The extension of the above relations to other compounds needs further systematic studies. However, the available data show that mass spectrometry investigation of the precursors may give preliminary information concerning the expected results of CVD experiments.

Acknowledgements

We thank K. Ujszászy for the mass spectra of **II** and **III**. We are grateful to the University of Tübingen for the mass spectrometry measurements of precursors **IV** and **V** as well as for the XPS analysis of the related thin films.

This research has been supported by the Hungarian National Research Fund (Contract number OTKA 2161).

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