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NOVEL CYCLOOCTATETRAENE COMPLEXES OF TITANIUM, ZIRCONIUM AND HAFNIUM

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SUMMARY

Reactions of cyclooctatetraene with tetrachlorides of titanium, zirconium and hafnium have been studied and novel compounds of formula $MCl_2(C_8H_7)_2$ (M = Ti, Zr or Hf) have been isolated in which the cyclooctatetraene behaves as the anion, $C_8H_7^-$.

INTRODUCTION

Cyclooctatetraene is known to form addition compounds[1-4] in which a metal is attached to the C_8H_8 ring. The first substitution reaction of cyclooctatetraene with molybdenum tetrachloride oxide, $MoOCl_4$, which gave a novel compound $MoOCl_2(C_8H_7)_2$ was recently reported by us[5]. We have now studied the substitution reactions of cyclooctatetraene with tetrachlorides of titanium, zirconium, and hafnium, which give complexes of the general formula $MCl_2(C_8H_7)_2$ (where M = Ti, Zr or Hf) in which the cyclooctatetraene is present as the anion, $C_8H_7^-$.

EXPERIMENTAL

Precautions were taken to exclude moisture. Benzene dried over and distilled from sodium was further purified by azeotropic distillation with ethyl alcohol. Tetrachlorides of titanium and zirconium were prepared by the chlorination of these metals, and hafnium tetrachloride was obtained by the reduction of hafnium dioxide followed by chlorination. Freshly distilled cyclooctatetraene purum (Fluka AG, Buchs) was used. Infrared spectra (in potassium bromide) were recorded on a Perkin–Elmer Model 137 spectrophotometer and the peaks are listed in Table 1.

Preparation of di(cyclooctatetraenyl)hafnium dichloride, $HfCl_2(C_8H_7)_2$

When 0.55 g of cyclooctatetraene was added to 0.85 g of hafnium tetrachloride in 100 ml of dry benzene the mixture immediately became light brown but there was no evolution of hydrogen chloride. On refluxing the colour changed to dark brown and hydrogen chloride was evolved. Refluxing was continued (48 h) until there was no further evolution of hydrogen chloride. Volatile materials were removed under reduced pressure to leave a dark-brown solid, which was repeatedly washed with

TABLE 1

INFRARED SPECTRA (IN CM^{-1}) OF $TiCl_2(C_8H_7)_2$, $ZrCl_2(C_8H_7)_2$, AND $HfCl_2(C_8H_7)_2$ IN POTASSIUM BROMIDE

$TiCl_2(C_8H_7)_2$	$ZrCl_2(C_8H_7)_2$	$HfCl_2(C_8H_7)_2$
695 s	695 s	695 s
750 m	750 m	752 s
900 w	900 w	
1050 w	1070 w	800 s
	1395 m	900 w
1370m	1450 m	1080 m
		1400 m
1450 w	1490 w	1450 m
1635 s	1615 s	1600 m
2400 w	2400 s	1700 m
3000 m	3000 (br)	2400 s
		3020 m

benzene and subsequently dried under reduced pressure to give dark brown crystalline compound (yield 92%) the analysis for which corresponded with $HfCl_2(C_8H_7)_2$. (Found: C, 42.00; Cl, 15.41; Hf, 39.00. $C_{16}H_{14}Cl_2Hf$ calcd.: C, 42.15; Cl, 15.59; Hf, 39.18%.)

Reactions of cyclooctatetraene with titanium tetrachloride and zirconium tetrachloride were carried out similarly and data for the products are given in Table 2.

TABLE 2

DATA ON THE PREPARATION, PROPERTIES, AND ANALYSIS OF $TiCl_2(C_8H_7)_2$ AND $ZrCl_2(C_8H_7)_2$

Compound	MCl_4[a] taken (g)	COT[b] added (g)	C_6H_6 added (ml)	Reaction (h)	Colour	Yield (%)	Decomp. temp. (°C)	Analysis found (calcd.)(%)		
								M	Cl	C
$TiCl_2(C_8H_7)_2$	1.80	1.98	50	36	Brownish-black	95	245	14.70 (14.74)	21.82 (21.86)	59.10 (59.12)
$ZrCl_2(C_8H_7)_2$	1.45	1.28	40	41	Mushroom	92	235	24.75 (24.78)	19.32 (19.37)	52.00 (52.16)

[a] M = Ti or Zr. [b] COT = cyclooctatetraene.

RESULTS AND DISCUSSION

Reactions between different proportions (2/1, 3/1 or 4/1) of cyclooctatetraene and metal chlorides were tried. Analysis of the product in each case showed that two moles of cyclooctatetraene reacted with only one mole of titanium, zirconium or hafnium tetrachloride with the evolution of two moles of hydrogen chloride. The reactions may be represented as:

$$MCl_4 + 2\ C_8H_8 \rightarrow MCl_2(C_8H_7)_2 + 2\ HCl\ (M = Ti,\ Zr\ or\ Hf)$$

Sharp changes in colour were observed after the addition of cyclooctatetraene to these metal chlorides; the colourless solution of titanium tetrachloride on the addition of cyclooctatetraene immediately changed to pink, then to red and finally to brownish black on refluxing.

In the case of zirconium and hafnium tetrachlorides the colour changed first to light brown and then on refluxing to mushroom and dark brown, respectively. The evolution of hydrogen chloride was detected immediately on refluxing in the case of titanium complex whereas in the case of zirconium and hafnium evolution of hydrogen chloride was observed only after about 15 min. All the three complexes are slightly soluble in chloroform; the titanium complex, $TiCl_2(C_8H_7)_2$ is also partially soluble in benzene and carbon tetrachloride. These complexes are quite stable in air, and are not decomposed by water or dilute acids. The hafnium complex is stable up to 230° but starts to decompose at higher temperatures. The decomposition temperatures for the titanium and zirconium complexes are given in Table 2.

We have recently obtained similar results in the preparation of complexes from cycloheptatriene and titanium tetrachloride[6], zirconium tetrachloride[6], or hafnium tetrachloride[7], or tantalum pentachloride[8]. In both the cyclooctatetraene and cycloheptatriene complexes M–C σ-bonding seems to be involved, as indicated by bands ~ 750 cm^{-1}.

Infrared spectra

The infrared spectra of the above complexes were studied in the region 670–4000 cm^{-1}. The bands of medium intensity at ~ 3000 cm^{-1} can be assigned to C–H stretching frequency and those at ~ 1635 cm^{-1} may be due to C=C stretching. The bands at ~ 690 cm^{-1} (s), ~ 1400 cm^{-1} (m) and 1450 cm^{-1} (m) are probably due to ring distortion. The bands at ~ 900 cm^{-1} can be associated with C–C stretching. Metal–oxygen double bonds are indicated by a stretching frequency at ~ 980 cm^{-1} [9], and the absence of a band in this region in the spectra of our compounds shows that the metal chlorides do not undergo hydrolysis during the course of the reactions. The bands at ~ 750 cm^{-1} may be associated with the metal–C_8H_7 linkages.

From the close similarity between the IR spectra of cyclooctatetraene in its D_{2d} structure[10] and that of the above compounds it appears that cyclooctatetraene is present in these compounds as cyclooctatetraenyl anion in its D_{2d} (tub) conformation.

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