Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOVEL BEHAVIOUR OF CYCLOHEPTATRIENE. II

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(Received November 3rd, 1969; in revised form December 22nd, 1969)

SUMMARY

The reactions of cycloheptatriene with metal chlorides and oxychlorides of Groups IV and VI have been shown to give new types of compounds having the formulae $MCl_2(C_7H_7)_2$ (where M=Ti, Zr) and $MOCl_2(C_7H_7)_2$ (where M=Mo or W), in which the cycloheptatrienyl group is present as an anion.

INTRODUCTION

All the complexes of cycloheptatriene described until recently were either addition compounds or contained the cycloheptatrienyl cation[1-6], but our recent studies on the reaction of cycloheptatriene with tantalum pentachloride showed that cycloheptatrienyl can behave also as an anion[7]. The present investigations deal with the reactions of cycloheptatriene with metal chlorides of Group IV and oxychlorides of Group VI, in which new complexes are formed which have the formulae $MCl_2(C_7H_7)_2$ (M=Ti, Zr) and $MOCl_2(C_7H_7)_2$ (M=Mo or W); in these complexes the cycloheptatrienyl is again present as an anion.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Molybdenum oxide tetrachloride was prepared by the method of Colten *et al.*[8]. Tungsten oxide tetrachloride was prepared by refluxing the oxide of the metal with thionyl chloride. The resultant product after drying under reduced pressure and sublimation, gave tungsten oxide tetrachloride as scarlet needles. Zirconium tetrachloride was obtained by direct chlorination of the metal. Titanium tetrachloride (B.D.H.) was distilled before use. Benzene was dried by distillation over sodium and further purified by azeotropic distillation. Infrared spectra (in Nujol mull) were recorded on a Perkin–Elmer Model 137 spectrophotometer, and details are given in Table 1.

Preparation of dicycloheptatrienylmolybdenum oxide dichloride

To 2.4 g of molybdenum oxide tetrachloride in 250 ml of dry benzene were added 1.74 g of cycloheptatriene. The mixture was refluxed until the evolution of hydrogen chloride ceased. The bluish-black compound thus obtained was dried

TABLE 1

IR SPECTRA (cm^{-1}) OF THE COMPOUNDS FORMED BY THE REACTION OF CYCLOHEPTATRIENE WITH $TiCl_4$, $ZrCl_4$, $MoOCl_4$ AND $WOCl_4$

$MoOCl_2(C_7H_7)_2$	$WOCl_2(C_7H_7)_2$	$TiCl_2(C_7H_7)_2$	$ZrCl_2(C_7H_7)_2$
722 m	800 m	720 vw	722 m
805 m	875 w	800 w	810 w
880 vw	970 m	870 (sh)	850 vw
975 m	1025 m	1000 (sh)	1020 m
1025 m	1080 m	1020 m	1150 m
1085 m	1255 m	1150 vw	1375 s
1160 m	1350 (sh)	1300 vw	1465 s
1256 w	1375 m	1375 s	1500 vw
1300 vw	1460 s	1435 s	1530 vw
1350 (sh)	1540 w	1500 vw	1555 vw
1375 s	1550 w	1515 vw	1660 m
1460 s	1560 w	1550 m	1750 vw
1540 w	1670 m	1560 m	2175 vw
1550 w	1715 w	1630 m	2400 m
1560 w	2175 vw	1700 vw	3000 s
1670 m	2400 m	1720 vw	3480 vw
2175 vw	3000 s	2160 vw	
2400 m	3550 m	2385 s	
3000 s	3900 vw	3000 s	
3550 vw		3900 vw	
3900 vw			

under reduced pressure. (Found: C, 45.80; Cl, 19.60; Mo, 26.15. $C_{14}H_{14}Cl_2MoO$ calcd.: C, 46.03; Cl, 19.45; Mo, 26.29%.) The complex does not melt, but decomposes at 220°. The tungsten analogue was prepared in a similar manner. Details are given in Table 2.

TABLE 2

DETAILS OF THE PREPARATION, PROPERTIES AND ANALYSES OF $ZrCl_2(C_7H_7)_2$ (I) AND $WOCl_2(C_7H_7)_2$ (II)

Compound	Reactants and solvent			Colour	Decomposition temp. (°C)	Yield (%)	Analysis: found (calcd.) (%)		
	MCl_4 or $MOCl_4$ (g)	C_7H_8 (g)	Benzene (ml)				C	Cl	Metal
I	2.2	1.8	250	Light brown	160	95	48.75 (48.79)	20.60 (20.63)	26.52 (26.50)
II	2.1	1.14	200	Dark brown	>320	94	36.85 (37.07)	15.60 (15.67)	40.50 (40.60)

Preparation of dicycloheptatrienyltitanium dichloride

1.82 g of cycloheptatriene was added to 1.85 g of titanium tetrachloride in 200 ml of dry benzene, and the mixture was refluxed until the evolution of hydrogen chloride ceased. The mixture was cooled to room temperature, and the solid formed was dried under reduced pressure to brownish-black crystals, decomposing at 290°.

(Found: C, 55.88; Cl, 23.58; Ti, 15.90. $C_{14}H_{14}Cl_2Ti$ calcd.: C, 55.84; Cl, 23.60; Ti, 15.92%.)

The zirconium analogue was prepared similarly and details are given in Table 2.

RESULTS AND DISCUSSION

Cycloheptatriene could give rise to three species, *viz.* $C_7H_7^+$, $C_7H_7^-$ and $C_7H_7^{\cdot}$. Only the cation, $C_7H_7^+$, has all its electrons in bonding orbitals and a closed shell and hence it should be the most stable of the three species. Clearly, however, the $C_7H_7^-$ anion can also be present in complexes and is quite stable.

The formation of the compounds prepared can be represented by the following equations:

$$MCl_4 + 2\,C_7H_8 \rightarrow MCl_2(C_7H_7)_2 + 2\,HCl \quad (M{=}Ti, Zr) \tag{1}$$

$$MOCl_4 + 2\,C_7H_8 \rightarrow MOCl_2(C_7H_7)_2 + 2\,HCl \quad (M{=}Mo, W) \tag{2}$$

Various ratios (2/1, 3/1, 4/1) of cycloheptatriene and metal halides and oxyhalides have been tried, but in all cases only two chlorines were replaced. Addition of cycloheptatriene to titanium tetrachloride caused a rapid formation of a light brown-coloured complex. On refluxing it changed to brown and finally to brownish-black. In this case the evolution of hydrogen chloride started immediately on refluxing the solution, whereas with the molybdenum, tungsten and zirconium compound the evolution of hydrogen chloride began after 1–3 h.

Interpretation of IR Spectra

In all the compounds the bands of medium intensity in between 1630 to 1675 cm^{-1} may be due to C=C stretching and those bands of strong intensity at 3000 cm^{-1} can be attributed to C–H stretching vibrations. The metal $-C_7H_7$ band appears at $\sim$800 cm^{-1}. Extra bands at $\sim$975 cm^{-1} in case of compounds of molybdenum and tungsten may be due to M=O vibrations.

ACKNOWLEDGEMENTS

One of the authors (K.M.S.) thanks the Council of Scientific and Industrial Research, New Delhi, India, for the award of a Research Fellowship.

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