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Reactions of Tungsten Oxy-dichlorodialkoxides with Cyclopentadiene and Sodium Cyclopentadienide

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The formation of π-cyclopentadienyl tungsten oxychlorodialkoxides as a result of the interaction between cyclopentadiene or its sodium derivative with tungsten oxy-dichlorodialkoxides, having the general formula $C_5H_5WOCl(OR)_2$, where R is CH_3, C_2H_5, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CH$, $CH_3CH_2CH_2$ and $CH_3CH_2CH_2CH_2$ along with the thermal stabilities and infrared spectra of the above products, has been studied and reported.

Though a large number of cyclopentadienyl compounds having alkyl,[1] aryl,[2] acetyl,[3] carbonyl,[4] nitrosyl,[1] and hydride[5] groups linked to the transition metal atoms have been reported, only a few cyclopentadienyl complexes having one or more alkoxy groups attached to the metal atoms in the π-cyclopentadienyl complexes are known, and these include the alkoxy derivatives of cyclopentadienyl compounds of titanium,[6a,b] zirconium,[7] uranium and thorium.[8] Recently we have prepared mono- and di-alkoxy derivatives of π-biscyclopentadienyl tungsten oxydichloride by its interaction with various alcohols with and without the use of triethylamine.[9,10] The present communication deals with the preparation of π-cyclopentadienyl compounds of tungsten oxydichlorodi-alkoxides[11] (by the interaction of cyclopentadiene and its sodium derivative with tungsten oxydichloro dialkoxides in presence of tetrahydrofuran as solvent) and their characterisation.

$$WOCl_4 + 2ROH \xrightarrow{C_6H_6} WOCl_2(OR)_2 + 2HCl$$

$$WOCl_2(OR)_2 + C_5H_6 \xrightarrow{THF} C_5H_5WOCl(OR)_2 + HCl$$

$$WOCl_2(OR)_2 + NaC_5H_5 \xrightarrow{THF} C_5H_5WOCl(OR)_2 + NaCl$$

Where R is CH_3, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_3H_7$ and $n\text{-}C_4H_9$. During these studies the removal of both chlorine atoms from $WOCl_2(OR)_2$ by treatment with cyclopentadiene as well as sodium cyclopentadienide has been attempted and even on refluxing the reactants for 24 hr it has been found that only one chlorine atom is replaced by cyclopentadienyl group.

Results and Discussion

Infrared spectra of the compounds taken in KBr, Nujol mull and $CHCl_3$ on Perkin Elmer Cord Model-137 between 4000—650 cm^{-1} is given in Table 1. The absorption at 3050—3100 cm^{-1} and 2910—2950 cm^{-1} in IR spectra of the compounds indicate the presence of C–H stretching frequencies,[12] the absorption bands at 1650—1740 cm^{-1} show the (π-C_5H_5) ring stretching while the C–C bands (asymmetric ring breathing) is evident at 1400—1450 cm^{-1}, which resemble those located in cyclopentadiene itself.[13] In the above IR spectra the vibrational bands observed at 1190 cm^{-1} indicate methoxy, at 1140, 1160 cm^{-1} indicate ethoxy, at 1110, 1170 cm^{-1} indicate isopropoxy while n-butoxy group are evident at 1090, 1120—

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TABLE 1. INFRARED SPECTRA OF π-CYCLOPENTADIENYL TUNGSTEN OXY-CHLORODIALKOXIDES (cm^{-1})

Alkyl group present in $C_5H_5WOCl(OR)_2$	(π-Cp) C–H str.	(π-Cp) ring str.	(π-Cp) C–C str.	(π-Cp) C–H def.	Alkoxy group str.	(π-Cp) C–H out-of-plane def.	(π-Cp) out-of-plane def.
Methyl	3060 s, 2930 m	1740 s, 1650 m	1450 s	1372 m	1190 w	1092 w, 1012 s	750 s
Ethyl	3055 m, 2910 m	1730 s, 1640 s	1450 m	1360 s	1160 w	1140 m, 1010 w	810 m
i-Propyl	3080 s, 2935 m	1710 s, 1630 w	1440 w	1310 s	1170 m	1110 w, 1015 w	820 m
n-Propyl	3090 m, 2915 m	1740 m, 1610 s	1410 s	1300 w	1190 w	1040 m, 980 w	780 s
n-Butyl	3100 s, 2950 m	1710 m, 1600 m	1450 w	1340 s	1210 s	1020 w, 1010 s	770 m

s=strong, m=medium, w=weak, Cp=C_5H_5 Spectra were taken in Nujol mull, KBr pellets and $CHCl_3$ as solvent.

TABLE 2. DECOMPOSITION TEMPERATURES OF π-CYCLOPENTADIENYL TUNGSTEN OXY-CHLORODIALKOXIDE COMPOUNDS

$C_5H_5WOCl(OR)_2$	R				
	CH_3	C_2H_5	*i*-C_3H_7	*n*-C_3H_7	*n*-C_4H_9
Decomposition temperature °C	90	105—106	110	113	135

TABLE 3. π-CYCLOPENTADIENYL TUNGSTEN OXY-CHLORODIALKOXIDES

Alkyl group present in $C_5H_5WOCl(OR)_2$	Colour	Mp °C	Yield % (theoretical)	Time of reaction (hr)	Amt. of alcohols added (m*l*)	Amt. of THF added (m*l*)	Tungsten %		Chloride %		Alkoxy group	
							Found	Calcd	Found	Calcd	Found	Calcd
Methyl	Green	86—87	75	10	70	35	51.4	50.69	9.9	9.78	17.3	17.12
Ethyl	Green	96—97	70	12	80	40	47.1	47.07	9.0	9.07	23.1	23.05
i-Propyl	Deep-green	105—106	60	12	60	45	43.9	43.92	8.4	8.46	28.1	28.23
n-Propyl	Deep-green	135	65	10	60	40	43.8	43.92	8.3	8.46	—	—
n-Butyl	Brown green	140.5	70	11 12	50	50	41.1	41.16	7.9	7.91	—	—

* Where the atomic weights in the above calculated results are: W, 183.85; Cl, 35.45; O, 16.00; C, 12.01; H, 1.008.

1160 cm^{-1} frequencies[14,15] and these are given in Table 1.

The above details of the IR spectra show the presence of alkoxy groups attached to the tungsten atom as is the case with other π-cyclopentadienyl transition metal compounds.[6-9]

The above products which are green in colour, are very sensitive to moisture though stable in inert atmosphere and in vacuum. They are soluble in THF, acetone, dioxane, dimethoxyethane, and miscible in hot dilute acids and alkalies and form a resinous mass when in contact with hot water. These compounds do not sublime under reduced pressure (5 mmHg) and decompose at high temperatures. They change the orange chromic acid (12% H_2SO_4, N-$K_2Cr_2O_7$) to green colouration. The compounds containing lower alkoxide groups have been found to be thermally less stable than those containing higher alkoxide groups. The temperatures at which various compounds undergo decomposition as shown by (i) the change in their colour from green to dirty yellow, and (ii) the decrease in their weights, have been recorded with a Koffler heating block apparatus as given in Table 2.

From infrared spectra and elemental analysis, the following formula is proposed for the compounds, $C_5H_5WOCl(OR)_2$, where R is CH_3 to C_4H_9 groups. The interaction of cyclopentadiene and sodium cyclopentadienide with $WOCl_2(OR)_2$ involves the replacement of electronegative radical (Cl^-) by another electronegative radical ($C_5H_5^-$). It has been further observed that the interaction between $WOCl_2(OR)_2$ and excess of sodium cyclopentadienide does not result in the replacement of more than one chlorine atom by cyclopentadienyl group and this observation is at variance with the results reported by earlier workers.[6-9]

Experimental

All operations were carried out under anhydrous conditions with guard tubes containing silica gel. In some cases, a P_2O_5 and $CaCl_2$ (fused) guard tube had to be used in series with the silica gel tube under reduced pressure, using an oil vacuum pump. Tetrahydrofuran before use was first dried by refluxing with potassium hydroxide and then distilling from lithium aluminium hydride. Aromatic hydrocarbons were first dried with sodium wire and then distilled, whereas the alcohols were dried by usual methods including azeotropic distillation. Tungsten oxytetrachloride obtained as reddish crystals on refluxing WO_3 with thionyl chloride for 16—18 hr and after drying under reduced pressure, was finally sublimed under reduced pressure (5—10 mmHg) at 135—140°C to give scarlet red crystals. Sodium cyclopentadienide was always freshly prepared before use.

Preparation of Tungsten Oxy-dichlorodimethoxide. 70 m*l* methyl alcohol, 40 m*l* dry benzene and 3.42 g (0.1 mol) of tungsten oxytetrachloride were placed in a 500 m*l* round bottom flask fitted with a reflux condenser and a $CaCl_2$ guard tube, and refluxed at 65—70°C over an oil bath for 4—5 hr. From the colourless product so obtained, benzene was removed by distillation under reduced pressure (20—25 mmHg) and the compound finally dried under reduced pressure (15 mmHg).

Higher alkoxy derivatives ranging from ethoxy to *n*-butoxy of tungsten oxytetrachloride were similarly prepared by refluxing with suitable alcohols at requisite temperatures.

Preparation of Cyclopentadienyl Tungsten Oxy-chlorodiethoxide. *1) By Using Cyclopentadiene.* 2 m*l* (0.025 mol) of freshly depolymerized cyclopentadiene was added to a mixture of 3.6 g (0.01 mol) of tungsten oxydiethoxide and 50 m*l* THF, and the contents were refluxed at 100—110°C for 10—12 hr. After cooling, excess of THF was removed by distillation under reduced pressure. The dark greenish product on crystallization from petroleum ether (40—60°C) gave greenish crystals. The compound is soluble in chloroform, THF, carbon disulphide, but insoluble in ether and aromatic hydrocarbons. The compound is extremely sensitive to moisture and readily gets hydrolysed in dilute acids and alkalies. It melts with decomposition at 96—97°C to a dirty yellow mass.

Found: W, 47.1; Cl, 9.0; OC_2H_5, 23.1%. Calcd for $C_5H_5WOCl(OC_2H_5)_2$: W, 47.07; Cl, 9.07; OC_2H_5, 23.05%.

2) By Using Sodium Cyclopentadienide.[16] To freshly prepared sodium cyclopentadienide (0.04 mol; approx. 1 g Na; 3.4 m*l* C_5H_6) in 50 m*l* tetrahydrofuran, was added 7.22 g (0.02 mol) tungsten oxydichlorodiethoxide in 30 m*l* THF in a three necked round bottom flask. The mixture was vigorously stirred while being refluxed for 6—8 hr till the contents turned to greenish products. After filtering the products through a porous plug and a G-4 sinitered glass filter disc, the filtrate was distilled under reduced pressure. The analysis of the product corresponded to the composition of C_5H_5-$WOCl(OC_2H_5)_2$. The compound on crystallization from petroleum ether (60—80°C) yielded green crystals and was found to be identical to the product obtained by the reaction of cyclopentadiene with $WOCl_2(OC_2H_5)_2$.

The cyclopentadienyl derivatives of the methoxy and higher alkoxy compounds of tungsten were prepared by a similar procedure and under similar conditions, but at suitable temperatures. Their analytical data is given in Table 3.

Infrared spectra for all the above compounds are recorded in Table 1.

After decomposing the compounds with perchloric acid, tungsten was estimated as 8-hydroxyquinolate, chloride was estimated as silver chloride, and the alkoxy group was determined by chromic acid method.[17,18]

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