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STUDIES ON DI-π-CYCLOPENTADIENYLALKOXYDICHLOROTUNGSTEN COMPOUNDS

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SUMMARY

Di-π-cyclopentadienyltrichlorotungsten has been treated with various primary and secondary alcohols in benzene medium to give the compounds $(\pi\text{-}C_5H_5)_2$-$WCl_2(OR)$, in which R is CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9 and iso-C_5H_{11}. Infrared spectra, thermal stabilities and some physical characteristics of these compounds are reported.

INTRODUCTION

Since the preparation of di-π-cyclopentadienyltrichlorotungsten by Cotton and Wilkinson[1], extensive studies on its hydrides and other related derivatives have been carried out by various workers[2-5], but there is no reference in literature to cyclopentadienyltungsten compounds containing alkoxy groups. Recently we have reported the preparation of some π-cyclopentadienyloxochlorotungsten compounds containing mono- and dialkoxy groups from the reaction of various primary and secondary alcohols with di-π-cyclopentadienyloxodichlorotungsten[6,7]. We now describe the action of various primary and secondary alcohols on $(\pi\text{-}C_5H_5)_2WCl_3$ in presence of benzene to give the compounds, $(\pi\text{-}C_5H_5)_2WCl_2(OR)$, where R = Me, Et, Pr, iso-Pr, Bu, iso-Bu or isopentyl.

We expected that treatment of the complex $(\pi\text{-}C_5H_5)_2WCl_3$ with an excess of an alcohol would lead to replacement of one cyclopentadienyl group by an alkoxy group resulting in the formation of compounds analogous to those reported earlier[7]. Instead an alkoxy group replaces a chlorine atom. Attempts to replace more than one chlorine atom by prolonged refluxing of the complex with an excess of alcohol, alone or in presence of triethylamine, were unsuccessful.

Analytical data along with some characteristics of the compounds are given in Table 1. The compounds which are generally green-orange in colour, though extremely sensitive to moisture, are stable in dry and inert atmosphere. They are soluble in tetrahydrofuran, dioxane, halogenated solvents and partially soluble in hydrocarbons. They decompose without melting, generally above 100°. They are insoluble in water, but are readily hydrolysed on heating or on treatment with dilute acids and alkalies to give yellow resinous mass. The compounds are nonvolatile and

TABLE 1

DI-π-CYCLOPENTADIENYLALKOXYDICHLOROTUNGSTEN DERIVATIVES, $(C_5H_5)_2WCl_2(OR)$

R	Reaction time (h)	Alcohol added (ml)	Yield (%)	Colour	Dec. p. (°C)	Analysis, found (calcd.) (%)		
						W	Cl	OR
Me	4.5	20	80	Orange green	105	44.1 (44.09)	17.1 (17.00)	7.50 (7.49)
Et	6	20	85	Yellow green	109	42.6 (42.65)	16.4 (16.44)	10.50 (10.52)
Pr	8	25	75	Green	135	41.2 (42.29)	15.9 (15.94)	
iso-Pr	7	30	90	Orange green	123	41.3 (41.29)	16.0 (15.94)	13.4 (13.38)
Bu	9	30	80	Green	167	40.0 (40.02)	15.4 (15.41)	
iso-Bu	11	25	70	Green	154	40.1 (40.02)	15.4 (15.41)	
iso-C_5H_{11}	12	20	75	Deep green	195	38.6 (38.61)	14.9 (14.98)	

do not sublime even under vacuum, when kept for 3–4 days, they slowly decompose, and the chlorine contents decrease considerably. The methoxy, ethoxy and isopropoxy derivatives turn chromic acid solution (12% H_2SO_4, 1*N* $K_2Cr_2O_7$) green.

The isopropoxy derivative was also prepared by the alcohol interchange method[14], *i.e.* by the action of isopropyl alcohol on dicyclopentadienylethoxydichlorotungsten in benzene, with the ethyl alcohol removed azeotropically.

RESULTS AND DISCUSSION

Details of the infrared spectra of the compounds (recorded on a Perkin–Elmer Infracord Model-137) in KBr, nujol and $CHCl_3$, are given in Table 2; they show the presence of C–H stretching frequencies in the region, 3010–3115 cm^{-1}, C–H bending at 810–820 cm^{-1} and the C–C absorption bands (antisymmetric ring breathing) at 1410–1450 cm^{-1}, and the characteristic π-cyclopentadienyl band[8] at 1010–1115 cm^{-1}.

The methoxy gives rise to the band at 1190 cm^{-1}, the ethoxy to that at 1140–1160 cm^{-1}, the isopropoxy to that at 1110–1170 cm^{-1}, the butoxy to those at 1090, 1120–1160 cm^{-1} and the isopentyloxy group to those at 1110 and 1040 cm^{-1} [9,10]. The absorption band at 1610–1670 cm^{-1} are probably associated with the C–O linkages of the alkoxy groups. The IR spectra indicate that the π-bonding between cyclopentadienyl rings and tungsten metal atom is retained, while the alkoxy groups are probably attached to the tungsten metal atom by σ-bonds, as in other transition metal compounds[11–13].

The compounds containing lower alkoxy groups have been found to be thermally less stable than those containing higher alkoxy groups. The decomposition of various compounds at different temperatures can be observed from (*i*) the change in their colour from greenish yellow to brownish grey and (*ii*) by the decrease in their weights. The decomposition temperatures of these compounds are given in Table 1.

TABLE 2

INFRARED SPECTRA OF DI-π-CYCLOPENTADIENYLALKOXYDICHLOROTUNGSTEN COMPOUNDS, $(C_5H_5)_2WCl_2(OR)$

s = strong, w = weak, m = medium, v = very, sh = shoulder.

Compounds for R =						
Me	Et	Pr	iso-Pr	Bu	iso-Bu	iso-C_5H_{11}
3050 m	3040 s	3017 s	3010 m	3015 s	3020 w	3015 s
2990 w	1580 m	1590 m	1720 s	1700 w	1710 w	1700 w
1650 m	1560 s	1450 s	1600 m	1650 vw	1560 w	1660 w
1540 w	1460 m	1410 w	1550 w	1570 m	1550 w	1610 w
1440 w	1320 m	1250 w	1290 w	1140 s	1160 vw	1540 w
1280 vw	1220 s	1160 w	1112 w	1110 w	1115 w	1450 s
1190 m	1200 s	1035 m	1070 m	1090 s	810 w	1370 m
1110 vm	1160 m	990 w	720 w	815 vw	770 w	1110 w
960 sh	1060 s	810 w	690 m	720 w		1100 s
615 w	970 m	765 s				1040 w
	820 s					820 m
	790 s					720 w
	750 s					

EXPERIMENTAL

All reactions were carried out under reduced pressure and anhydrous conditions. Tetrahydrofuran was dried over potassium hydroxide and then distilled in presence of lithium aluminium hydride. Dry alcohols were further purified by azeotropic distillation in presence of benzene. Freshly sublimed tungsten hexachloride was used. Depolymerized cyclopentadiene obtained from its dimer was used in the preparation of sodium cyclopentadienide[15].

The compounds were decomposed with perchloric acid; the tungsten was determined as the 8-hydroxyquinolate, and the chlorine as silver chloride. The alkoxy groups ($-OCH_3$, $-OC_2H_5$ and $O\text{-iso-}C_3H_7$) in the compounds were determined by chromic acid method[16-17].

Preparation of di-π-cyclopentadienyltrichlorotungsten

To 3.4 g (0.01 mole) tungsten hexachloride in 150 ml tetrahydrofuran sodium cyclopentadienide (0.023 mole) in 50 ml tetrahydrofuran was added with stirring. The content was refluxed at 80–90° for 7–8 h, and the dark-brown product was filtered off and dried under reduced pressure (5 mm) to yield a red-brown oily mass. This was crystallized from chloroform to give dark-red crystals of di-π-cyclopentadienyltrichlorotungsten.

Preparation of di-π-cyclopentadienylethoxydichlorotungsten

A mixture of 4.2 g (0.01 mole) of di-π-cyclopentadienyltrichlorotungsten, 20 ml ethanol, and 30 ml dry benzene was stirred and refluxed (at about 100°) for 3–4 h. The greenish orange product obtained by evaporation of the resultant mixture under reduced pressure (15 mm) was extracted with tetrahydrofuran, and the extract was evaporated again under reduced pressure (10 mm). The residue on crystallization from petroleum ether (60–80) gave a greenish-orange compound corresponding to the composition $(C_5H_5)_2WCl_2(OC_2H_5)$. Since the compound is very susceptible to the action of air and moisture, it was always kept under dry and reduced atmosphere.

Methoxy and higher alkoxy derivatives such as propoxy, butoxy and pentyloxy were prepared similarly. Details are given in Table 1.

Preparation of the isopropoxy derivative by alcohol interchange

A suspension of $(\pi\text{-}C_5H_5)_2WCl_2(OC_2H_5)$ (4.0 g) 30 ml isopropyl alcohol and 40 ml dry benzene, was refluxed for about 6 h and the resulting greenish-orange solution was then fractionally distilled, the liberated ethanol being first removed as an azeotrope. The residue was dried under reduced pressure (5 mm) to give a deep green product which on crystallization from petroleum ether (40–60°) yielded orange-yellow crystals.

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