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π-CYCLOPENTADIENYLOXOCHLOROMOLYBDENUM ALKOXIDES

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SUMMARY

Some π-cyclopentadienyloxochloromolybdenum alkoxides have been prepared by the interaction of di-π-cyclopentadienyloxomolybdenum dichloride with various primary and secondary alcohols and by the interaction of oxodichloromolybdenum dialkoxides with either cyclopentadiene or its sodium derivative. They have the general formulae, $\pi\text{-}C_5H_5MoOCl_2(OR)$ and $\pi\text{-}C_5H_5MoOCl(OR)_2$, where R is Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, or i-C_5H_{11}. The thermal stabilities and IR spectra are described.

INTRODUCTION

While a large number of derivatives of π-cyclopentadienylmolybdenum (VI) have been reported[1-9], there are only a few examples of π-cyclopentadienyl complexes of transition metals having one or more alkoxy groups attached to the metal atoms. These include the alkoxy derivatives of π-cyclopentadienyl complexes of titanium[10-11], zirconium[12], uranium and thorium[13]. Though tetraalkoxyoxomolybdenum(VI) and dialkoxyoxodichloromolybdenum(VI)[14] are known, there is no reference in the literature to π-cyclopentadienyl derivatives of molybdenum(VI) alkoxides. We recently described studies on mono and dialkoxy derivatives of π-cyclopentadienyloxochlorotungsten derivatives[15-16] and we now report the preparation and some properties of π-cyclopentadienyloxodichloromolybdenum monoalkoxides of general formula, $\pi\text{-}C_5H_5MoOCl_2(OR)$ and π-cyclopentadienyloxomonochloromolybdenum dialkoxides of general formula, $\pi\text{-}C_5H_5MoOCl(OR)_2$. Their preparation is represented by the following eqns.:

$$(\pi\text{-}C_5H_5)_2MoOCl_2 + ROH \rightarrow \pi\text{-}C_5H_5MoOCl_2(OR) + C_5H_6$$

$$(\pi\text{-}C_5H_5)_2MoOCl_2 + 2\,ROH + (C_2H_5)_3N \rightarrow \pi\text{-}C_5H_5MoOCl(OR)_2 + (C_2H_5)_3N\cdot HCl + C_5H_6$$

$$MoOCl_2(OR)_2 + C_5H_6 \rightarrow \pi\text{-}C_5H_5MoOCl(OR)_2 + HCl$$

$$MoOCl_2(OR)_2 + NaC_5H_5 \rightarrow \pi\text{-}C_5H_5MoOCl(OR)_2 + NaCl$$

where R is CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9 and i-C_5H_{11}.

The compounds are diamagnetic.

EXPERIMENTAL

All reactions were carried out under anhydrous conditions and at reduced pressure. Dry tetrahydrofuran was further purified by distillation in presence of lithium aluminium hydride. $MoOCl_4$[17] was further purified by sublimation under vacuum at 140–145° and fresh NaC_5H_5[18] was used. Magnetic measurements were carried out on a Gouy Magnetic Balance. IR spectra were recorded on a Perkin–Elmer Infrared spectrometer Model 137.

Di-π-cyclopentadienyloxomolybdenum dichloride was prepared by refluxing 5.2 ml (0.063 mole) cyclopentadiene with 6.4 g (0.025 mole) $MoOCl_4$ in 100 ml THF. Volatiles were removed under reduced pressure, and the residue was treated with aqueous ammonia. The solid obtained was crystallized from diethyl ether or THF and dried over P_2O_5.

The compound $(\pi\text{-}C_5H_5)_2MoOCl_2$ was also prepared by the interaction of NaC_5H_5 with $MoOCl_4$. To 9.6 g (0.037 mole) $MoOCl_4$ in 150 ml THF was added (0.07 mole) NaC_5H_5 and the contents were refluxed for 4–5 h at 90–95°. The cooled mixture was filtered and the residue was washed with THF. The filtrate and the washings on drying under reduced pressure yielded a dark brownish mass, which was crystallized from ether or THF to give reddish brown crystals of $(\pi\text{-}C_5H_5)_2\text{-}MoOCl_2$. (Found: C, 38.3; H, 3.1; Cl, 22.6; Mo, 30.6. $C_{10}H_{10}Cl_2MoO$ calcd.: C, 38.37; H, 3.22; Cl, 22.68; Mo, 30.65%.)

This compound has also been prepared in our laboratories by the UV irradiation of a mixture of $MoOCl_4$ with monomer cyclopentadiene.

Preparation of $\pi\text{-}C_5H_5MoOCl_2(OR)$ compounds

The mixture of 4.14 g (0.01 mole) of $(\pi\text{-}C_5H_5)_2MoOCl_2$ 30 ml ethanol and 50 ml dry benzene was refluxed at 110° with stirring for 4–5 h. The greenish blue product obtained by evaporation of the resultant mixture under reduced pressure (10 mm) was extracted with THF and the extract evaporated under reduced pressure (5 mm). The residue on crystallization from petroleum ether (60–80°) yielded a greenish blue product. (Found: Cl, 23.8; Mo, 32.7; OC_2H_5, 15.3. $C_7H_{10}Cl_2MoO_2$ calcd.: Cl, 23.85; Mo, 32.71; OC_2H_5, 15.38%.) This compound is soluble in THF, acetone (brown solution), soluble in CH_2Cl_2, $CHCl_3$ and CCl_4 (green solution) but is insoluble in ether and benzene. It is very sensitive to moisture and is hydrolysed by dilute alkalies.

Methoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and isoamyloxy compounds were prepared similarly by refluxing $(\pi\text{-}C_5H_5)_2MoOCl_2$ with suitable alcohols. Their characteristics and analytical data are given in Table 1.

Preparation of $\pi\text{-}C_5H_5MoOCl(OR)_2$ compounds

(*a*). *From $(\pi\text{-}C_5H_5)_2MoOCl_2$.* An alcoholic solution containing 4.13 g (0.010 mole) of $(\pi\text{-}C_5H_5)_2MoOCl_2$ in 40 ml benzene and 30 ml ethanol was refluxed for about 4 h at 110–115°. After the addition of 7.5 ml triethylamine, the mixture was refluxed for a further 10–12 h at 130°, then cooled. Triethylamine hydrochloride was filtered off under anhydrous conditions, and the filtrate was fractionally distilled and then evaporated under reduced pressure. The deep green residue was crystallized from petroleum ether (40–60°) to give greenish blue crystals of $\pi\text{-}C_5H_5MoOCl\text{-}(OC_2H_5)_2$.

TABLE 1

π-CYCLOPENTADIENYLALKOXYOXODICHLOROMOLYBDENUM COMPOUNDS, π-$C_5H_5MoOCl_2(OR)$

R	Colour	Yield (%)	Time of reaction (h)	Amount of alcohols added (ml)	Amount of C_6H_6 added (ml)	Analysis found (calcd.) (%)		
						Mo	Cl	OR
CH_3	Brownish green	80	4–5	30	40	34.4 (34.33)	25.2 (25.26)	11.2 (11.18)
C_2H_5	Light green	85	5–6	35	50	32.6 (32.6)	24.1 (24.13)	15.5 (15.46)
n-C_3H_7	Green	75	6	40	50	31.1 (31.16)	22.6 (22.70)	
i-C_3H_7	Light green	78	7	40	45	31.2 (31.16)	22.7 (22.70)	19.3 (19.35)
n-C_4H_9	Blue greenish	80	9	30	60	29.8 (29.79)	22.0 (22.01)	
i-C_4H_9	Blue greenish	60	10	25	55	29.7 (29.79)	22.1 (22.01)	
i-C_5H_{11}	Deep blue greenish	65	12–13	25	40	28.5 (28.53)	21.1 (21.08)	

Methoxy and higher dialkoxy derivatives of $(\pi\text{-}C_5H_5)_2MoOCl_2$ were prepared by using appropriate alcohols under similar conditions. Their characteristics and analytical data are given in Table 2.

TABLE 2

π-CYCLOPENTADIENYLDIALKOXYOXOCHLOROMOLYBDENUM COMPOUNDS, π-$C_5H_5MoOCl_2(OR)_2$

R	Colour	Yield (%)	Time of reaction (h)	Amount of THF added (ml)	Analysis found (calcd.) (%)		
					Mo	Cl	OR
CH_3	Greenish orange	90	5	50	38.54 (38.54)	13.6 (13.66)	24.1 (24.09)
C_2H_5	Orange red	80–85	7–8	60	33.3 (33.35)	12.3 (12.32)	31.6 (31.61)
n-C_3H_7	Green	70	6	60	30.2 (30.35)	11.2 (11.21)	
i-C_3H_7	Greenish brown	75	5–6	50	30.3 (30.35)	11.2 (11.21)	37.7 (37.71)
n-C_4H_9	Green	60	10	60	27.9 (27.88)	10.3 (10.29)	
i-C_4H_9	Green	65	10–11	70	27.7 (27.88)	10.2 (10.29)	
i-C_5H_{11}	Greenish blue	55	14–15	60	24.7 (24.74)	9.5 (9.51)	

(*b*). *From* $MoOCl_2(OR)_2$. 2.73 g (0.01 mole) $MoOCl_2(OC_2H_5)_2$[14] in 40 ml dry benzene was treated with (0.025 mole) sodium cyclopentadienide or 2.1 ml (0.025 mole) cyclopentadiene and the mixture after stirring was refluxed for 6 h at 110–115°. The resulting green blue solution was evaporated to dryness under reduced pressure (20 mm). The residue was extracted with methylene dichloride then dried under reduced pressure (5 mm) at room temperature. Crystallization from petroleum ether/acetone 1/1 gave blue green crystals.

The product was identical obtained by the method (*a*), above.

Other related dialkoxy derivatives with $R=CH_3$, n-C_3H_7 n-C_4H_9, i-C_4H_9 and i-C_5H_{11} groups, were similarly prepared and their characteristics and analytical data are given in Table 2.

Preparation of isopropoxy derivative of π-$C_5H_5MoOCl(OR)_2$ *by alcohol interchange method*

A suspension of 3.5 g of π-$C_5H_5MoOCl(OC_2H_5)_2$, 30 ml isopropyl alcohol and 40 ml dry benzene, was refluxed for 7–8 h at 110°. Ethanol liberated in the reaction mixture was then azeotropically removed along with the benzene during a period of 6 h. Removal of all volatile material gave a residue, which was dried under reduced pressure (5 mm) to give a deep greenish product. This was crystallized from petroleum ether (40–60°) to give green crystals of π-C_5H_5MoOCl(i-$OC_3H_7)_2$. (Found: Cl, 10.7; Mo, 29.0; i-OC_3H_7, 25.6. $C_{11}H_{19}ClMoO_3$ calcd.: Cl, 10.72; Mo, 29.0; i-OC_3H_7, 25.69%.)

The IR spectrum and the analytical data show the above compound to be π-C_5H_5MoOCl(i-$OC_3H_7)_2$.

RESULTS AND DISCUSSION

In the IR spectra of these compounds, in KBr pellets or nujol, shown in Tables 3 and 4 the presence of π-C_5H_5 rings is revealed by single C–H stretching bonds

TABLE 3

IR SPECTRA OF π-$C_5H_5MoOCl_2(OR)$ COMPOUNDS (cm^{-1})

R	π-C_5H_5	Mo=O	Mo–O–R
CH_3	3070 m, 1670 w, 1610 w, 1570 w, 1417 s, 1105 s, 820 m	970 m	1190 w
C_2H_5	3090 s, 1730 w, 1690 w, 167 vw, 1610 vw, 1420 s, 1109 m, 814 s	965 s	1150 s
n-C_3H_7	3105 s, 1710 w, 1680 w, 1650 w, 1430 s, 1110 w, 810 vw	955 m	1135 m
i-C_3H_7	3095 m, 1690 w, 1670 w, 1650 vw, 1610 vw, 1440 s, 1090 m, 805 m	960 s	1140 m
n-C_4H_9	3110 m 1610 w, 1605 w, 1590 w, 1435 s, 1105 w, 795 m	960 m	1140 s
i-C_4H_9	3095 s, 1715 w, 1680 w, 1650 w, 1445 s, 1095 m, 820 s	965 s	1145 s
i-C_5H_{11}	3115 m, 1710 w, 1630 w, 1590 vw, 1415 s, 1090 s, 815 m	990 s	1165 m

TABLE 4

IR SPECTRA OF π-$C_5H_5MoOCl(OR)_2$ COMPOUNDS (cm^{-1})

R	π-C_5H_5	Mo=O	Mo=O=R
CH_3	3050 m, 1710 w, 1650 vw, 1625 w, 1410 vs, 1105 m, 870 s	980 s	1160 w
C_2H_5	3065 s, 1710 w, 1610 w, 1605 w, 1440 vs, 1120 m, 840 s	965 m	1130 s
n-C_3H_7	3085 s, 1750 w, 1700 vw, 1650 vw 1445 s, 1100 m, 820 s	970 s	1140 m
i-C_3H_7	3105 m, 1700 w, 1680 w, 1630 w, 1410 s, 1125 s, 835 m	985 s	1170 w
n-C_4H_9	3090 m, 1730 w, 1610 w, 1590 w, 1425 s, 1090 m, 810 s	965 s	1160 s
i-C_4H_9	3100 s, 1700 w, 1650 w, 1610 w, 1410 s, 1105 w, 825 s	940 m	1175 m
i-C_5H_{11}	3070 m, 1710 w, 1690 w, 1650 w, 1420 s, 1095 m, 810 m	963 s	1145 w

(3010–3120 cm^{-1}), C–C bands (asymmetric ring breathing) (1415–1445 cm^{-1}), and bands from C–H deformation of $C_5H_5^-$ ring (1010–1125 cm^{-1}). The bands at 810–825 cm^{-1} are attributable to C–H bending (out of plane deformation) as observed in cyclopentadiene itself[20]. The vibrational bands at 1190 cm^{-1} are attributable to methoxy, at 1140–1160 cm^{-1} to ethoxy, and at 1110 and 1170 cm^{-1} to isopropoxy groups, while the bands at 1090, 1120–1160 cm^{-1} show the presence of butoxy and higher alkoxy groups in these compounds as with other metal alkoxy compounds[21–23]. Absorption bands at 960 cm^{-1} show the presence of the Mo=O bond[24–25]. The weak bands in the region of 1600–1750 cm^{-1} do not conclusively indicate the presence of any fundamental frequency of π-cyclopentadienyl metal compounds[26].

The compounds, π-$C_5H_5MoOCl_2(OR)$ and π-$C_5H_5MoOCl(OR)_2$ are bluish green and are sensitive to moisture. They decompose without melting and do not sublime under vacuum. Table 5 gives the temperatures at which these compounds

TABLE 5

DECOMPOSITION TEMPERATURES AND LOSS IN WEIGHT (%) OF π-CYCLOPENTADIENYLOXOCHLOROMOLYBDENUM ALKOXIDES

R	$C_5H_5MoOCl_2(OR)$		$C_5H_5MoOCl(OR)_2$	
	Decompn. temp. (°C)	Loss in weight (%)	Decompn. temp. (°C)	Loss in weight (%)
CH_3	87	41	83	40
C_2H_5	105	44	97	46
n-C_3H_7	113	49	207	50
i-C_3H_7	110	48	105	50.5
n-C_4H_9	139	53	130	55
i-C_4H_9	135	51.5	129	54
i-C_5H_{11}	147	54.5	137	58.5

undergo decomposition as indicated (*i*) by the change in colour from green blue to black blue, and (*ii*) by the decrease in their weights (recorded on a Koffler Block). It will be seen that the thermal stabilities of the above compounds increase as the size of the alkoxy group increases from OCH_3 to OC_5H_{11}.

The complexes are soluble in THF, acetone, dioxane, dimethoxy ether, dichloromethane, carbon disulphide, trifluoroacetic acid, and partly in benzene and diethyl ether.

The complexes are readily hydrolysed when treated with hot or dilute alkalies. They react rapidly with concentrated hydrochloric acid, and on warming red brown crystals of $(\pi\text{-}C_5H_5)_2MoOCl_2$ are deposited. They reduce acidified potassium dichromate (12.5% H_2SO_4, *N* $K_2Cr_2O_7$).

The diamagnetic character of these compounds suggests that the Mo metal atom in these compounds is in hexa-valent oxidation state. Further the presence of Mo=O bond at $\sim 960\ cm^{-1}$ in the IR spectra of these compounds indicates the presence of molybdenum–oxy grouping as found in $MoOCl_4$ molecule itself[25].

IR spectra, physical properties together with elemental analysis suggest the following formulae for these compounds: $\pi\text{-}C_5H_5MoOCl_2(OR)$ and $\pi\text{-}C_5H_5MoOCl(OR)_2$, where R is CH_3 to C_5H_{11} groups. The IR spectra of the above compounds also suggest that the linkage between $C_5H_5^-$ rings to the metal atom retains the character of delocalised π-bonds, while the alkoxide groups are probably attached to the metal atom by σ-bonds, as is the case with other transition metal complexes[10–13].

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