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ALKYL, ARYL AND CARBOXYL DERIVATIVES OF DI-π-CYCLOPENTADIENYLTUNGSTEN OXIDE DICHLORIDE

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SUMMARY

Treatment of di-π-cyclopentadienyltungsten oxide dichloride with the appropriate Grignard reagents, organolithium compounds or the sodium salt of the appropriate carboxylic acids gives products of the formula $(C_5H_5)_2WO(R)_2$, where R is CH_3, C_2H_5, C_6H_5, $C_6H_5CH_2$, C_6H_5CO and CH_3COO, C_3H_7COO and C_6H_5-COO. Infrared spectra, thermal stabilities, and some other properties of the compounds are discussed.

INTRODUCTION

Earlier attempts at preparation of organometallic compounds of tungsten[1-3] resulted only in the coupling of Grignard reagents. The first tungsten "arene" compounds were reported by Hein *et al.*[4]. Alkyl and aryl derivatives of π-cyclopentadienyl compounds of chromium, molybdenum, tungsten and iron[5], titanium[6,7], zirconium[8], cobalt[9], manganese[10], ruthenium[11], nickel[12,13], palladium[14] and platinum[15] have been made, as have some carboxylates of cyclopentadienyl derivatives of lanthanides[16], but alkyl, aryl, and carboxyl derivatives of di-π-cyclopentadienyltungsten oxide dichloride[17] (I) have not been previously reported. Recently we prepared di-π-cyclopentadienyltungsten oxide dichloride, (I), by treatment of $WOCl_4$ with cyclopentadiene or its sodium derivative in tetrahydrofuran; the green crystalline compound obtained possessed all the characteristics of a "sandwich" metallocene[18].

In a previous communication we reported the preparation of the mono- and di-alkoxycyclopentadienyltungsten oxide chloride compounds[19,20] by treatment of (I) with various primary and secondary alcohols, with or without triethylamine. The present communication deals with derivatives of (I) in which the covalently bonded chlorine atoms have been replaced by alkyl, aryl or carboxyl ligands; these compounds undergo displacement reactions similar to those of dicyclopentadienyl compounds of other transition metal complexes[21], and have the formula $(\pi\text{-}C_5H_5)_2WO(R)_2$, where R is alkyl, aryl or carboxyl.

The following are the various methods used for the preparation of these compounds:

(1) *The Grignard method*[22,23]. Alkyl and aryl derivatives of (I) have been prepared from Grignard reagents in both diethyl ether and tetrahydrofuran,

$$(\pi\text{-}C_5H_5)_2WOCl_2 + 2\,RMgI \rightarrow (\pi\text{-}C_5H_5)_2WO(R_2) + 2\,MgClI$$

$$(R = Me, Et, Ph \text{ or } CH_2Ph)$$

(2) *The organolithium method*[23]. Alkyl and aryl derivatives of (I) have been obtained in good yield from alkyl- and aryl-lithium compounds with (I) in diethyl ether or higher boiling solvents:

$$(\pi\text{-}C_5H_5)_2WOCl_2 + 2\,RLi \rightarrow (\pi\text{-}C_5H_5)_2WO(R)_2 + 2\,LiCl$$

$$(R = Me, Et, Ph, CH_2Ph, COPh)$$

(3) *The sodium salt method.* Both aliphatic and aromatic carboxyl derivatives have been prepared in almost quantitative yield by treatment of (I) with sodium salts of carboxylic acids in dry benzene,

$$(\pi\text{-}C_5H_5)_2WOCl_2 + 2\,NaO_2CR \rightarrow (\pi\text{-}C_5H_5)_2WO(O_2CR)_2 + 2\,NaCl$$

$$(R = Me, Et, Pr, Ph)$$

EXPERIMENTAL

All operations were carried out in nitrogen under anhydrous conditions. Tetrahydrofuran was refluxed with potassium hydroxide and then distilled over lithium aluminium hydride. Tungsten oxytetrachloride was prepared by refluxing WO_3 with thionyl chloride, and evaporating the reddish solution under reduced pressure (30–40 mm) to give red crystals, which on sublimation under reduced pressure (10–15 mm) gave pure scarlet needles of $WOCl_4$.

Bi-π-cyclopentadienyltungsten oxide dichloride[17,19] (I) was prepared by the action of sodium cyclopentadienide or liquid cyclopentadiene on $WOCl_4$ in tetrahydrofuran. The mixture was refluxed with stirring for 6–8 h, then evaporated under reduced pressure to leave a deep-green residue, which was subsequently recrystallized from light petroleum (b.p. 60–80°).

TABLE 1

CHARACTERISTICS OF π-$(C_5H_5)_2WO(R)_2$ COMPOUNDS

Compound, Colour	Method of prepn.	Solvent used	Solvent amount (ml)	Reaction time	Yield (%)	M.p. (°C) with decompn.	Stability (in air)
π-$(C_5H_5)_2WO(CH_3)_2$ waxy orange-yellow	1,2	THF/ether	120	7–8	15	53	Unstable
π-$(C_5H_5)_2WO(C_2H_5)_2$ waxy orange-yellow	1,2	THF/ether	110	9	10	47	Unstable
π-$(C_5H_5)_2WO(C_6H_5)_2$ waxy orange	1,2	Ether	80	8	70	115	3–4 h
π-$(C_5H_5)_2WO(C_6H_5CH_2)_2$ deep orange	1,2	Dibutyl ether	75	9	75	125	1–2 days
π-$(C_5H_5)_2WO(C_6H_5CO)_2$ brown	2	Dimethylaniline	70	3–4	55	131	2–3 days
π-$(C_5H_5)_2WO(CH_3COO)_2$ brown	3	Benzene	100	4	90	135	Stable
π-$(C_5H_5)_2WO(C_2H_5COO)_2$ reddish brown	3	Toluene	110	4	80	130	Stable
π-$(C_5H_5)_2WO(C_3H_7COO)_2$ reddish brown	3	THF	120	5	85	125	Stable
π-$(C_5H_5)_2WO(C_6H_5COO)_2$ light brown	3	Benzene	150	3–5	75	102	Very stable

TABLE 2

ANALYTICAL DATA OF π-$(C_5H_5)_2WO(R)_2$ COMPOUNDS

R	Tungsten (%)		Carbon (%)		Hydrogen (%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
Methyl	51.0	51.05	39.8	40.02	4.4	4.45
Ethyl	47.4	47.39	43.2	43.31	5.2	5.20
Phenyl	37.9	37.94	54.4	54.53	4.1	4.16
Tolyl	35.8	35.88	56.2	56.24	3.8	3.93
Benzoyl	34.0	34.03	53.4	53.36	3.8	3.73
Acetate	41.1	41.02	38.6	38.63	3.7	3.71
Propionate	38.6	38.61	40.4	40.35	4.2	4.23
Butyrate	36.5	36.46	42.8	42.87	4.8	4.79
Benzoate	32.1	32.12	50.4	50.37	3.6	3.52

TABLE 3

INFRA RED SPECTRA OF π-$(C_5H_5)_2WO(R)_2$ COMPLEXES (cm^{-1})

Cp = cyclopentadienyl; s = strong, m = medium, w = weak.

Compound	Data
$Cp_2WO(CH_3)_2$	3080 w, 2935 s, 1430 m, 1385 s, 1190 w, 1115 s, 1090 w, 915 m, 730 m, 675 m
$Cp_2WO(C_2H_5)_2$	3105 m, 2920 w, 1520 s, 1460 w, 1400 m, 1370 m, 1120 s. 1050 w, 910 m, 725 w
$Cp_2WO(C_6H_5)_2$	3500 m, 3015 s, 1650 m, 1570 m, 1480 s, 1430 w, 1110 m, 1020 m, 735 s, 695 m
$Cp_2WO(C_6H_5CH_2)_2$	3020 m, 1680 m, 1570 s, 1450 w, 1430 s, 1360 m, 1340 m, 1110 s, 910 w, 775 m
$Cp_2WO(C_6H_5CO)_2$	3010 m, 1795 w, 1640 s, 1575 m, 1460 s, 1335 s, 1260 m, 1105 m, 830 s, 750 m
$Cp_2WO(CH_3COO)_2$	3025 s, 2810 m, 1710 m, 1570 w, 1430 s, 1360 w, 1115 s, 950 m, 810 w, 690 m
$Cp_2WO(C_3H_7COO)_2$	3100 s, 2930 w, 2010 m, 1450 m, 1430 s, 1380 w, 1215 m, 1120 s. 1090 w, 750
$Cp_2WO(C_6H_5COO)_2$	3010 m, 1700 s, 1610 w, 1560 s, 1510 m, 1425 s, 1310 s, 1280 w, 1040 s, 750 m

Alkyl and aryl derivatives by the Grignard method

Stoichiometric quantities of (I) and appropriate Grignard reagents were used in the preparation of these compounds.

(I) (4.01 g, 0.61 mole) and THF (100 ml) were placed in a three-necked flask, fitted with a condenser and a $CaCl_2/P_2O_5$ guard tube, and the suspension was stirred to give a homogeneous solution. The Grignard reagent made from methyl iodide (3.0 ml, 0.02 mole) and magnesium ribbon (0.5 g, 0.02 g-atom) in THF (50 ml) was added dropwise during one hour, and the mixture was refluxed at 80–90° and stirred vigorously for 14–16 h. The orange-yellow solution so formed was filtered through cotton plug and a G-4 sintered glass disc and the residue was washed with THF. The filtrate was distilled under reduced pressure (15–20 mm) to give a waxy orange-yellow substance, which turned brown in contact with air. The product, formed in about 15% yield, sublimed at 50–54° with decomposition to give a dark brown liquid, and dissolved in common organic solvents to give brown solutions, possibly as a result of decomposition.

Other derivatives prepared by this method were diethyl, diphenyl and ditolyl complexes. Some of their characteristics and analytical data together with infrared spectra, are given in Tables 1, 2 and 3.

Alkyl and aryl derivatives by the organolithium method

Phenyllithium, made from bromobenzene (10 ml, 0.06 mole) and lithium (0.4 g, 0.05 g-atom) in ether (70 ml), was added to (I) (8.02 g, 0.02 mole) in ether (100 ml) with stirring during 30 min. The mixture was stirred and refluxed gently (50–55°) for 10–11 h, then left to settle. The clear orange solution was filtered, and distilled under reduced pressure (30–35 mm) to leave a light-brown residue. Crystallization of this from light petroleum (b.p. 60–80°) gave light brown crystals, m.p. 80–86° with decomposition. The yield was 50–52%.

Dimethyl, diethyl, ditolyl and dibenzoyl derivatives were prepared similarly. The products were identical in composition and other characteristics to those made from Grignard reagents. Details are given in Tables 1, 2 and 3.

Carboxyl derivatives by the sodium salt method

A mixture of (I) (4.1 g, 0.01 mole) and sodium acetate (1.64 g, 0.02 mole) in benzene (100 ml) was stirred and refluxed at 95–100° for 6–7 h. The initial green suspension turned to a brown solution, which was filtered and evaporated under reduced pressure (30–35 mm) to give a reddish-brown residue. Crystallization from light petroleum ether (b.p. 40–60°) gave light brown crystals of $(C_5H_5)_2WO(CH_3COO)_2$, m.p. 135° with decomposition. The yield was about 85%.

Dipropionate, dibutyrate and dibenzoate derivatives of (I) were also prepared by the same method. Their characteristics, analytical data and infrared spectra are listed in Tables 1, 2 and 3.

Analyses

The tungsten in the compounds was estimated as 8-hydroxyquinolinate after heating the compounds with perchloric acid. Carbon and hydrogen were determined by micro-analytical methods, while the presence of cyclopentadienyl, alkyl, aryl or carboxyl groups was inferred from the infrared spectra.

Properties

The alkyl and aryl compounds are readily soluble in light petroleum and other common organic solvents to give brown solutions. The alkyl compounds sublime readily under vacuum, but with deomposition. They possess a peculiar odour and are decomposed in air. The higher alkyl compounds could not be prepared because they were too unstable. The aryl derivatives are brown in colour, stable in an inert atmosphere and not miscible with water. Both alkyl and aryl derivatives form oily resins when treated with dilute acids or alkalies.

The carboxyl derivatives are quite stable compounds with sharp melting points, and are soluble in common organic solvents except diethyl ether. They are not acted upon by cold or hot water, but dilute acids or alkalies convert them into black products of indefinite composition. Diacetate and dibenzoate derivatives sublime under reduced pressure.

The compounds have different thermal stabilities, which depends upon the nature of the groups present. They are best stored in sealed tubes at low temperatures.

DISCUSSION

In the infrared spectra of these compounds taken in nujol, KBr and in $CHCl_3$, between 4000–650 cm^{-1}, the methyl group is identified by its absorption frequencies at about 2900–2960 cm^{-1} and the symmetrical methyl–methyl deformation at 1370–1385 cm^{-1}. The presence of an ethyl group is indicated by the $C-CH_3$ asymmetric deformation at about 1373 cm^{-1}. The phenyl group is indicated by the C–C stretching vibrations between 1615–1485 cm^{-1}. The π-cyclopentadienyl character is indicated by C–H stretching absorptions at 3110–3012 cm^{-1}, C–C vibrational bands at 1430–1415 cm^{-1} and a characteristic absorption due to the π-C_5H_5 ring[24] at 1110–1115 cm^{-1}. The presence of C–O stretching in the case of the benzoyl derivative is shown by the characteristic band at 1715 cm^{-1}.

Carboxylate ions are indicated by the strong absorptions at 1615–1540 cm^{-1}, arising from the asymmetric O–C–O stretching, and at 1400–1300 cm^{-1}, arising from the symmetric stretching, and by an intense band at 1540–1420 cm^{-1}, while absorption bands around 1040 ± 15 cm^{-1} and 925 ± 30 cm^{-1} indicate a metal–acetate linkage[25,26]. From the IR spectra it seems probable that the alkyl, aryl and carboxyl groups are linked to the metal atom by covalent linkages whereas the cyclopentadienyl rings retain the delocalized π-bonds in the complexes; this is in keeping with the behaviour of other π-cyclopentadienyl transition metal complexes[5,6]. The highly unstable character of the alkyl and aryl derivatives obtained is in keeping with the facts observed by Jaffe and Doak[27].

During the preparations of alkyl and aryl compounds considerable decomposition occurs and a deep brown tar is formed even when the reactions are carried out under pure nitrogen. Among polar solvents, diethyl ether has been found to be the best medium, use of other polar solvents giving poorer yields. Alkyl derivatives higher than ethyl could not be prepared, possibly because of steric hindrance. Organolithium compounds are more reactive than the corresponding magnesium reagents, as is usual.

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