Bis-π-cyclopentadienyl Complexes of Molybdenum and Tungsten containing Trihalogenostannyl-, Oxo-, Sulphato-, and Thiosulphato-ligands

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The complexes $(\pi\text{-}C_5H_5)_2M(SnX_3)X$, where M = Mo or W and X = Cl or Br are described. They react with chlorine or bromine respectively forming the salts $[(\pi\text{-}C_5H_5)_2MX_2]^+SnX_3^-$. The complexes $(\pi\text{-}C_5H_5)_2M{=}O$ (M = Mo or W), $(\pi\text{-}C_5H_5)_2MoSO_4$, and $(\pi\text{-}C_5H_5)_2MoS_2O_3$ have also been prepared.

HERE we describe the preparation of complexes containing trihalogenostannyl-, oxo-, and sulphato-ligands, and their reactions.

Chemical Studies.—Treatment of hot aqueous solutions of the dihalides $(\pi\text{-}C_5H_5)_2MX_2$, (I, M = Mo or W, X = Cl or Br) with an excess of the corresponding stannous halide SnX_2 in hydrohalogenic acid HX results in an immediate colour change and formation of crystalline precipitates. These are soluble in liquid sulphur dioxide from which they may be crystallised by addition of ether. Elemental analysis and, in some cases, molecular-weight determination, suggest the stoicheiometry $C_{10}H_{10}$-$MSnX_4$ (II), see the Table. The mass spectra were $^{184}WSnBr_4]^+$ at *m/e* 746; the other complexes (II) showed no bands higher than those corresponding to the ions $[(\pi\text{-}C_5H_5)_2MX_2]^+$.

Treatment of the pure compounds (II) in dichloromethane with chlorine or bromine affords microcrystalline products which are insoluble in most solvents and although they dissolve in water and dimethyl sulphoxide the solutions slowly decompose. The analysis of the washed precipitates was consistent with the stoicheiometry $C_{10}H_{10}MSnX_5$ (III). The e.s.r. spectra of the complexes (III) in dimethyl sulphoxide are identical with those reported previously for the corresponding cations $[(\pi\text{-}C_5H_5)_2MX_2]^+$ [1] We, therefore, suggest that the

Analytical and spectroscopic data *

Compound	Colour	C	H	Halogen
$(\pi\text{-}C_5H_5)_2Mo(SnCl_3)Cl$ [a]	Green	24·8 (24·7)	2·3 (2·1)	28·5 (29·1)
$(\pi\text{-}C_5H_5)_2Mo(SnBr_3)Br$ [b]	Green	18·3 (18·1)	1·8 (1·5)	48·6 (48·1)
$(\pi\text{-}C_5H_5)_2W(SnCl_3)Cl$ [c]	Dark blue	20·8 (20·9)	1·8 (1·8)	25·1 (24·7)
$(\pi\text{-}C_5H_5)_2W(SnBr_3)Br$	Dark blue	16·1 (16·0)	1·6 (1·3)	41·8 (42·5)
$(\pi\text{-}C_5H_5)_2MoSO_4$	Dark green	36·9 (37·3)	2·7 (3·1)	
$(\pi\text{-}C_5H_5)_2MoS_2O_3$	Red	35·1 (35·5)	3·3 (3·0)	
$[(\pi\text{-}C_5H_5)_2MoCl_2]^+SnCl_3^-$	Brown	23·7 (23·0)	2·1 (1·9)	33·6 (34·0)
$[(\pi\text{-}C_5H_5)_2WCl_2]^+SnCl_3^-$	Orange	20·5 (19·7)	1·9 (1·7)	29·2 (29·1)
$[(\pi\text{-}C_5H_5)_2WBr_2]^+SnBr_3^-$	Mauve	16·4 (14·4)	1·5 (1·2)	48·4 (48·0)
$(\pi\text{-}C_5H_5)_2Mo{=}O$	Green	49·6 (49·6)	4·5 (4·2)	
$(\pi\text{-}C_5H_5)_2W{=}O$	Red-purple	36·1 (36·4)	3·2 (3·1)	

* Required % in parentheses.

[a] *M*(acetone) 482 (487); ^{1}H n.m.r. 4·36, s, $\pi\text{-}C_5H_5$. [b] *M*(acetone) 659 (665). [c] *M*(acetone) 565 (567); ^{1}H n.m.r. 4·38, s, $\pi\text{-}C_5H_5$.

compounds (III) are ionic and have the formulation $[(\pi\text{-}C_5H_5)_2MX_2]^+SnX_3^-$.

Treatment of the chloride $(\pi\text{-}C_5H_5)_2MoCl_2$ with an excess of aqueous sodium sulphate gives dark green crystals of stoicheiometry $C_{10}H_{10}MoSO_4$ (IV), see the Table. This compound is soluble in liquid sulphur dioxide and slightly soluble in hot water and concentrated hydrochloric acid. The i.r. spectrum shows bands at 1267 and 1153 cm^{-1} which may be assigned to symmetric and antisymmetric S=O stretching frequencies. The mass spectrum shows a parent ion band at $m/e = 324$ corresponding to the ion $[(\pi\text{-}C_5H_5)_2MoSO_4]^+$; other peaks occurred at $m/e = 276$, 244, 228, and 179 which may be assigned to the fragments $C_{10}H_{10}MoSO^+$, $C_{10}H_{10}MoO^+$, $C_{10}H_{10}Mo^+$, and $C_5H_5MoO^+$ respectively.

Treatment of the compound $(\pi\text{-}C_5H_5)_2MoCl_2$ with aqueous sodium thiosulphate gives dark red needles whose analysis is consistent with the stoicheiometry $C_{10}H_{10}MoS_2O_3$ (V). The mass spectrum shows a parent ion peak at $m/e = 340$, corresponding to the fragment $[(\pi\text{-}C_5H_5)_2MoS_2O_2]^+$. Further bands occurred at $m/e = 276$, 244, 228, and 179; these may be assigned to the fragments $C_{10}H_{10}MoSO^+$, $C_{10}H_{10}MoO^+$, $C_{10}H_{10}Mo^+$, and $C_5H_5MoO^+$.

There are also strong bands at $m/e = 260$ and 175 for which there are no corresponding bands in the mass spectrum of the sulphate analogue (IV). It therefore seems reasonable to assign these bands to sulphur containing species, such as $C_{10}H_{10}MoS^+$ and $C_5H_5MoS^+$.

Aqueous solutions of the dichlorides $(\pi\text{-}C_5H_5)_2MCl_2$, M = Mo or W, with an excess of concentrated sodium hydroxide give copious green precipitates. These are soluble in dichloromethane and tetrahydrofuran. Analysis is consistent with the stoicheiometry $(\pi\text{-}C_5H_5)_2M{=}O$ (VI).

The mass spectra of both the compounds (VI) show strong bands corresponding to the parent ions $[(\pi\text{-}C_5H_5)_2M{=}O]^+$, at $m/e = 330$ for $M = {}^{184}W$ and at $m/e = 244$ for $M = {}^{98}Mo$. The i.r. spectra of the complexes are closely similar; both show absorptions characteristic of π-cyclopentadienyl groups and both possess strong bands at 793—868 cm^{-1} (M = Mo) and 799—879 cm^{-1} (M = W) which may be assigned to M=O stretching frequencies.[2]

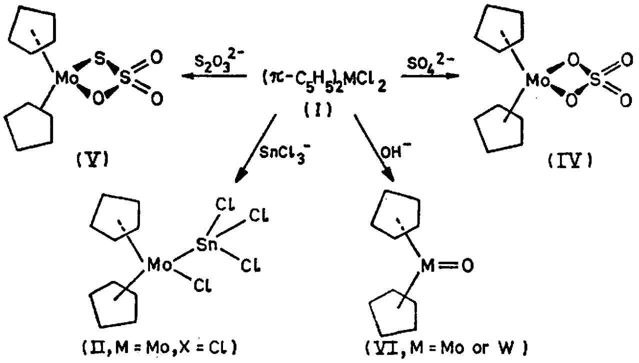
It was found that the oxo-compounds (VI) were a convenient starting material for the preparation of the previously described dithiol derivatives $(\pi\text{-}C_5H_5)_2M(SH)_2$[3] using the following reaction:

$$(\pi\text{-}C_5H_5)_2M{=}O + 2H_2S \rightleftharpoons (\pi\text{-}C_5H_5)_2M(SH)_2 + H_2O$$

DISCUSSION

The data given above suggest the structures for the compounds (II) shown in the Scheme. The crystal structure of the complex (II, M = Mo, X = Br) has been determined and provides confirmatory evidence for these structures.[4] Since the SnX_3 ligand and the ligand in the complexes (II) would be expected to be held quite close together it was of interest to look for evidence of direct interaction between the two. The i.r. spectra provided no clear evidence for or against such an interaction.

The sulphato- and thiosulphato-complexes (IV) and (V) presumably have the structures shown in the Scheme. The placement of the thiosulphato-ligand as S–O bonding rather than O–O is made on the basis of the mass spectrum, and the i.r. spectrum which shows bands at 1249 and 1128 cm^{-1} corresponding to symmetric and asymmetric stretches of an SO_2 system. Also the sulphur bonded structure would be expected in the light of the known chemistry of the bis(π-cyclopentadienyl)-molybdenum system.



SCHEME

EXPERIMENTAL

Inert atmosphere techniques were required for the oxo-compounds (VI) only. ^1H n.m.r. spectra were determined using a Japan Electron Optics Laboratory instrument operating at 60 MHz. Mass spectra were measured on a Perkin Elmer MS 9 instrument. I.r. spectra were determined as mulls using a Perkin-Elmer 337 spectrometer. E.s.r. spectra were recorded on a Varian V4500 spectrometer with 100 kHz modulation. Molecular weight determinations were made using a Mecrolab osmometer with the kind assistance of Mr D. Chapple. The dichlorides $(\pi\text{-}C_5H_5)_2MX_2$, M = Mo or W were prepared by published methods.[1]

Chloro(trichlorostannyl)bis(π-cyclopentadienyl)molybdenum.—Dichlorobis(π-cyclopentadienyl)molybdenum (2·0 g) in hot, concentrated hydrochloric acid (50 ml) was treated with an excess of stannous chloride (3·0 g) in concentrated hydrochloric acid (6 ml). A copious green-blue precipitate formed almost immediately which was separated, washed with dilute hydrochloric acid, water, and dried. Recrystallisation was from liquid sulphur dioxide–ether, *ca.* 90%. The other complexes (II) were similarly prepared from the corresponding stannous halides and hydrohalogenic acids.

Thiosulphatobis(π-cyclopentadienyl)molybdenum.—The dichloride $(\pi\text{-}C_5H_5)_2MoCl_2$ (1·3 g) in hot water (100 ml) was treated with sodium thiosulphate (3·0 g) in water (20 ml). The mixture became a clear burgandy colour and, after boiling for 10 min a red-brown precipitate formed. This

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[2] M. Cousins and M. L. H. Green, *J. Chem. Soc.* (*A*), 1969, 16.

[3] M. L. H. Green and W. E. Lindsell, *J. Chem. Soc.* (*A*), 1967, 1455.

[4] T. S. Cameron and C. K. Prout, following paper.

was collected, washed with water, and dried. The product was extracted with liquid sulphur dioxide, the solution was filtered and dichloromethane was added to the filtrate. As the sulphur dioxide evaporated red crystals of the pure *compound* appeared, *ca.* 75%.

Sulphatobis(π-cyclopentadienyl)molybdenum.—The compound $(\pi\text{-}C_5H_5)_2MoCl_2$ (1·0 g) in hot water (100 ml) was added to sodium sulphate (2·0 g) in hot water (50 ml) and the mixture was boiled (10 min) when the colour changed from dark green to pale green. The hot solution was separated from a little undissolved starting material and cooled giving a green precipitate which was collected and washed with water.

The precipitate was extracted with liquid sulphur dioxide and addition of dichloromethane to the extract gave dark green crystals of the pure *compound*, *ca.* 70%.

Oxobis(π-cyclopentadienyl)molybdenum.— Dichlorobis(π-cyclopentadienyl)molybdenum (0·4 g) in water (10 ml) was treated with sodium hydroxide (1·3 g). A green precipitate formed which was separated, washed with concentrated sodium hydroxide solution and solvent was removed *in vacuo*. The residue was extracted with *dry* tetrahydrofuran, the solution was filtered and concentrated. Addition of dry ether gave green air-sensitive crystals, *ca.* 50%.

The tungsten analogue was prepared similarly, yield *ca.* 60%.

Dithiolbis(π-cyclopentadienyl)molybdenum.—The oxo-compound (VI, M = Mo) (0·5 g) in dry dichloromethane (10 ml) was treated with dry hydrogen sulphide for 1½ min. The resulting deep red solution was purified by chromatography on an alumina column as described elsewhere,[3] *ca.* 55%.

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