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BIS(η-ALKYLCYCLOPENTADIENYL)-MOLYBDENUM AND -TUNGSTEN CHEMISTRY: MIXED VALENCE, AMBIDENTATE TETRAOXO- AND TETRATHIO-MOLYBDATO AND -TUNGSTATO DERIVATIVES, AND RELATED DIHYDRIDO AND DICHLORO COMPOUNDS

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Summary

The new compounds $[Mo(\eta\text{-}C_5H_4R)_2(\mu\text{-}O)_2MoO_2]_2$, R = H, Me or Bu^n, $[Mo(\eta\text{-}C_5H_4R)_2(\mu\text{-}S)_2MoS_2]_2$, R = H, Me or Bu^n, $[W(\eta\text{-}C_5H_5)_2(\mu\text{-}O)_2WO_2]_2$, $[W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2MoS_2]$, $[Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}O)_2WO_2]_2$, $[W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2WS_2]$, $[Mo(\eta\text{-}C_5H_4R)_2X_2]$, where R = Me or Bu^n and X = H or Cl, $[Mo(\eta\text{-}C_5H_4R)_2\text{-}(\mu\text{-}O)(\mu\text{-}X)SO_2]$, where R = Me or Bu^n and X = O or S, have been prepared and their properties are described.

Introduction

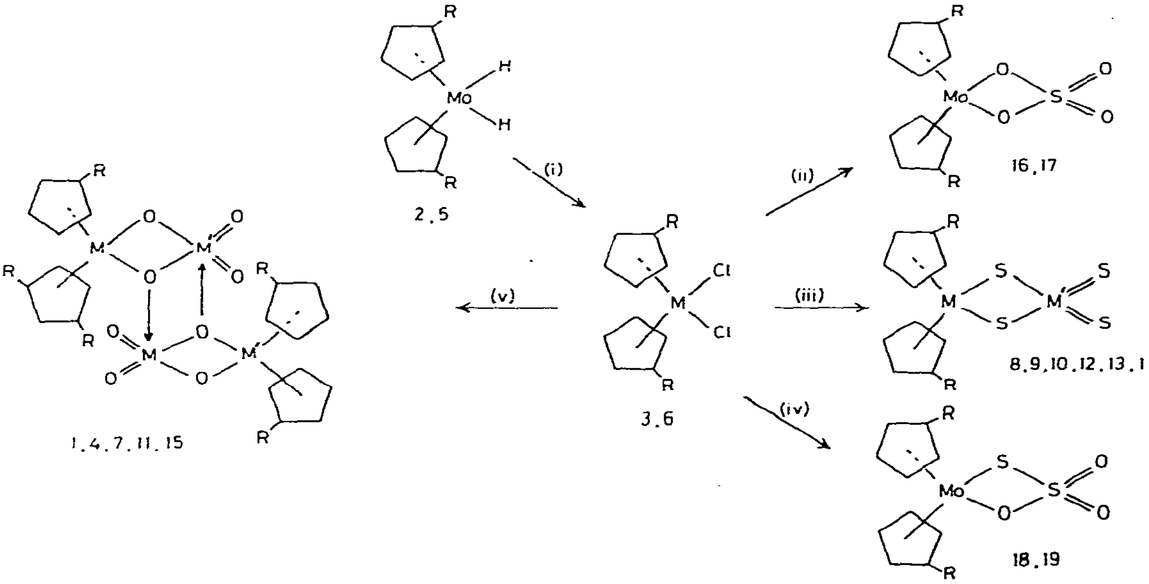
We have described a variety of η-cyclopentadienylmolybdenumoxo compounds which were prepared as part of a programme to develop an understanding of the role of the metal in catalytic olefin oxygenation processes [1—3]. The study showed that compounds of stoicheiometry $Mo_2(\eta\text{-}C_5H_5)_2O_4$ could exist as both orange dimeric and red tetrameric isomers [3]. The structure of the orange isomer was shown to be *cis*-$[MoO(\eta\text{-}C_5H_5)]_2(\mu\text{-}O)_2$ [3]. Related oxothio and thio compounds $[MoO(\eta\text{-}C_5H_5)]_2(\mu\text{-}S)_2$ and $[MoS(\eta\text{-}C_5H_5)](\mu\text{-}S)_2$ have also been described [4,5]. In a continuing development of the study of organometallic-oxo derivatives we realised the possibility of synthesising further isomers of stoicheiometry $M(\eta\text{-}C_5H_5)_2O_4$ with the structure $M(\eta\text{-}C_5H_5)_2(\mu\text{-}O)_2\text{-}MO_2$. These would be analogous to the known sulphato compound $Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}O)_2SO_2$ [6]. The synthesis and properties of these new cyclopentadienyloxo-molybdenum and -tungsten derivatives and thio analogues is described below. A brief communication of part of the work has appeared [7].

Results and discussion

Treatment of the compound $Mo(\eta\text{-}C_5H_5)_2Cl_2$ with aqueous solutions of dipotassium molybdate gave an orange-brown compound of stoicheiometry corresponding to $Mo_2(\eta\text{-}C_5H_5)_2O_4$, **1**. The compound was virtually insoluble in all solvents studied including dimethylsulphoxide. In order to improve the solubility it was decided to synthesize the alkyl-cyclopentadienyl analogues. Towards this end the compound $Mo(\eta\text{-}C_5H_4Me)_2H_2$, **2**, was prepared from NaC_5H_4Me, $MoCl_5$ and $NaBH_4$ using the same reaction conditions as for the unsubstituted analogue $Mo(\eta\text{-}C_5H_5)_2H_2$ [8]. The compound **2** forms air-sensitive, yellow crystals and appears to be closely analogous to the parent compound except that it is much more soluble, for example, in petroleum ether. The compound **2** reacts with chloroform giving the expected dichloro derivative $Mo(\eta\text{-}C_5H_4Me)_2Cl_2$, **3**, as light green crystals. These are soluble, in contrast to the only very slightly soluble parent analogue, e.g. in dichloromethane.

The compound **3** reacts readily with aqueous solutions of dipotassium molybdate giving on orange-brown precipitate whose stoicheiometry corresponds to $Mo_2(\eta\text{-}C_5H_4Me)_2O_4$, **4**. This compound was also insoluble in all solvents studied Therefore, potassium-η-butylcyclopentadienide was prepared and used to synthesise the compound $Mo(\eta\text{-}C_5H_4Bu^n)_2H_2$, **5**, by the method described for the unsubstituted analogue [8]. The compound **5** forms golden-yellow, air-sensitive crystals which melt around −30°C to a golden-brown oil. On treatment with chloroform **5** reacts giving the dichloro derivative $Mo(\eta\text{-}C_5H_4Bu^n)_2Cl_2$, **6**, as lustrous green crystals. These are very soluble in dichloromethane.

Addition of **6** to hot aqueous solutions of ammonium molybdate gave a pale brown solid. This could be recrystallised from dichloromethane giving



SCHEME 1

(i) **2**, R = Me, **5**, R = Bu^n; $CHCl_3$ at r.t. for 1 h gives **3**, R = Me; **6**, R = Bu^n respectively. (ii) K_2SO_4 in water at 90°C; **16**, R = Me; **17**, R = Bu^n. (iii) Typically, M = Mo, $(NH_4)_2MoS_4$ and H_2S in NH_4OH aq. at 60°C for 30 min; M = M′ = Mo, **8**, R = H, **9**, R = Me, **10**, R = Bu^n; M = M′ = W, **12**, R = H; **13**, R = H, M = Mo, M′ = W; **14**, R = H, M = W, M′ = Mo. (iv) $Na_2S_2O_3$ in acetone/water **18**, R = Me; **19**, R = Bu^n. (v) Typically, K_2MoO_4 in water at 90°C for 30 min; for M = M′ = Mo, **1**, R = H; **4**, R = Me, **7**, R = Bu^n; for M = M′ = W, **11**, R = H; for M = Mo, M′ = W, **15**, R = H.

brown microcrystals of stoicheometry $Mo_2(\eta\text{-}C_5H_4Bu^n)_2O_4$, **7**. These were also soluble in chloroform and ethanol. The compound **7** appears to be decomposed by dimethylsulphoxide. During the course of this work, Dr. Sala-Pala was studying the hydrolytic decomposition of the trihydrido cation $[Mo(\eta\text{-}C_5H_4Me)_2H_3]^+$ and from such a reaction mixture he inadvertently obtained brown crystals whose infra-red spectrum was identical to that of analytically pure **4** [9]. The crystal structure of the brown crystals showed the tetrameric molecule represented in Scheme 1. Thus compound **4** consists in essence of identical dimeric units $Mo(\eta\text{-}C_5H_4Me)(\mu\text{-}O)_2MoO_2$ held together by two triply bridging oxygens. The details for the crystal structure determination have been published elsewhere [7,10].

The infrared spectra of the compounds **1**, **4** and **7** are closely similar (see the Experimental section) and they all show bands assignable to Mo—O—Mo and Mo=O vibrations. We conclude that the compounds **1** and **7** have structures shown in the Scheme which are in essence the same as shown for compound **4**.

Treatment of the dichloro derivative $Mo(\eta\text{-}C_5H_5)_2Cl_2$ in aqueous ammonia with diammonium tetrathiomolybdate followed by saturation of the solution with dihydrogen sulphide gives a bright orange-red air-stable solid which is very slightly soluble in dichloromethane. Analysis shows stoicheiometry corresponding to $Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2MoS_2$, **8**. Similarly, treatment of **3** and **6** with ammonium tetrathiomolybdate gives the compounds $Mo(\eta\text{-}C_5H_4Me)_2(\mu\text{-}S)_2MoS_2$, **9** and $Mo(\eta\text{-}C_5H_4Bu^n)_2(\mu\text{-}S)_2MoS_2$, **10**, respectively. Compound **9** is quite soluble in dimethylsulphoxide and liquid sulphur dioxide. The crystal structure of **9** has been determined and is represented in Scheme 1; full details of the X-ray determination and resulting structural data have been published elsewhere [10].

The similarity of the IR spectra and other physical properties of the compounds **8**, **9** and **10** suggest that they have essentially the same basic structure.

The chemistry of the bis-η-cyclopentadienyltungsten system often parallels that of the molybdenum analogue and so as expected we were able to prepare the tungsten analogue of **1**, namely $W_2(\eta\text{-}C_5H_5)_2O_4$, **11**.

The compound **11** was insoluble in all solvents studied. The IR spectrum shows bands assignable to W—O—W and W=O vibrations. We propose **11** to have the same tetranuclear structure as **7**.

The tungsten analogue of **8**, namely $W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2WS_2$, **12** is also readily prepared from $W(\eta\text{-}C_5H_5)_2Cl_2$ and ammoniacal tetrathiotungstate as an air stable bright orange-red microcrystalline compound.

We have also been able to prepare the mixed metal isomers $Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2WS_2$, **13**, and $W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2MoS_2$, **14**. Apart from appearance and stoicheiometry the principal evidence supporting the structure proposed for **12**, **13** and **14** arises from the IR spectra and analogy with the previous chemistry. The infrared data are given in the Experimental section.

The compound $Mo(\eta\text{-}C_5H_4Me)_2WO_4$, **15** has also been prepared by reaction between **3** and ammonium tungstate.

For comparative purposes we also prepared the purple, air stable sulphato compounds $Mo(\eta\text{-}C_5H_4R)_2(\mu\text{-}O)_2SO_2$, R = Me, **16** or Bu^n, **17**, by treatment of aqueous solutions of the appropriate dichloride with sodium sulphate solutions. The thiosulphate derivatives have also been synthesised, i.e. $Mo(\eta\text{-}C_5H_4R)(\mu\text{-}O)(\mu\text{-}S)SO_2$, R = Me, **18** or Bu^n, **19**. The monomeric nature of the compounds is

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

	Compound	Colour	Analytical data (%) ^{a}			^{1}H NMR ^{b} or IR data
			C	H	Cl or S	
1	$[Mo(\eta\text{-}C_5H_5)_2MoO_4]_2$	orange brown	30.7 (31.1)	2.5 (1.5)		
2	$Mo(\eta\text{-}C_5H_4Me)_2H_2$	yellow	56.5 (55.8)	6.3 ^{c} (6.65)		5.4, 5.63, $\underline{8}$, c, $2\eta\text{-}C_5H_4$; 7.96, $\underline{6}$, s, 2 Me; 18.36, $\underline{2}$, s, 2 MoH ^{d}
3	$Mo(\eta\text{-}C_5H_4Me)_2Cl_2$	green	44.1 (44.45)	4.5 (4.35)	22.2 (21.9)	4.4—5.5, $\underline{8}$, c, 2 C_5H_4; 7.94, $\underline{6}$, s, 2 Me ^{e}
4	$[Mo(\eta\text{-}C_5H_4Me)_2MoO_4]_2$	brown	34.4 (34.8)	3.6 (3.4)		
5	$Mo(\eta\text{-}C_5H_4Bu^n)_2H_2$	yellow	63.5 (58.3)	8.3 ^{f} (8.0)		5.5, 5.7, $\underline{8}$, c, A_2B_2, $2\eta\text{-}C_5H_4$; 7.8—9.3, $\underline{18}$, c, 2 Bu^n; 18.7, $\underline{2}$, s, 2 H ^{d}
6	$Mo(\eta\text{-}C_5H_4Bu^n)_2Cl_2$	green	52.4 (52.8)	6.9 (6.4)	17.3 (17.3)	4.58, $\underline{8}$, c, $2\eta\text{-}C_5H_4$; 7.7, 8.4, 8.98, $\underline{18}$, c, 2 Bu^n. ^{e}
7	$[Mo(\eta\text{-}C_5H_4Bu^n)_2MoO_4]_2$	brown	43.6 (43.4)	5.9 (5.3)		4.53, 4.75, $\underline{8}$, A_2B_2 of two $\eta\text{-}C_5H_4$; 7.65, 8.41, 9.07, $\underline{18}$ (4 : 8 : 6), c, 2 Bu^n. ^{e}
8	$Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2MoS_2$	orange-red	27.2 (27.7)	2.5 (2.2)	27.7 ^{g} (28.4)	3.82, m-C_5H_5. ^{h}
9 ^{i}	$Mo(\eta\text{-}C_5H_4Me)_2(\mu\text{-}S)_2MoS_2$	dark red	29.2 (30.1)	2.8 (2.9)	26.3 (26.8)	

10	$Mo(\eta\text{-}C_5H_4Bu^n)_2(\mu\text{-}S)_2MoS_2$	orange red	37.3 (38.4)	4.65 (4.6)	21.9 (22.8)	5.00, $\underline{8}$, c broad, $2\eta\text{-}C_5H_4$; 7.63, 8.5, 9.33, $\underline{18}$ (4 : 8 : 6), c, $2Bu^n$. [i]
11	$[W(\eta\text{-}C_5H_5)_2WO_4]_2$	orange-brown	22.7 (22.8)	2.00 (1.9)		
12	$W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2WS_2$	bright yellow	18.1 (18.6)	2.2 (1.5)	17.6 [j] (19.8)	3.78, $\eta\text{-}C_5H_5$. [h]
13	$Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2WS_2$	orange-red	21.8 (22.3)	1.9 (1.9)	24.3 (23.8)	
14	$W(\eta\text{-}C_5H_5)_2(\mu\text{-}S)_2MoS_2$	orange-red	22.0 (22.3)	1.9 (1.9)	23.9 (23.8)	
15	$[Mo(\eta\text{-}C_5H_4Me)_2WO_4]_2$	brown	28.7 (28.0)	2.8 (3.0)		
16	$Mo(\eta\text{-}C_5H_4Me)_2(\mu\text{-}O)_2SO_2$	purple	40.5 (41.1)	3.9 (4.0)	8.9 (9.2)	
17	$Mo(\eta\text{-}C_5H_4Bu^n)_2(\mu\text{-}O)_2SO_2$	purple	50.1 (49.8)	6.5 (6.0)	7.1 (7.4)	4.6, 8, $\underline{c}$, 2 C_5H_4; 7.6, 8.5, 9.2, $\underline{18}$ (4 : 8 : 6), c, 2 Bu^n. [k]
18	$Mo(\eta\text{-}C_5H_4Me)_2(\mu\text{-}O)(\mu\text{-}S)MoO_2$	orange	39.3 (39.2)	3.9 (3.9)	17.3 (17.5)	4.43, 4.75, 4.99, $\underline{8}$ (typical for an ABCD group) 2 C_5H_4; 8.04; 6, s, 2 Me. [i]
19	$Mo(\eta\text{-}C_5H_4Bu^n)(\mu\text{-}O)(\mu\text{-}S)SO_2$	orange-brown	48.3 (47.9)	6.1 (5.8)	14.0 (14.2)	4.30, $\underline{1}$ (4 lines) 4.70, $\underline{2}$, c, 4.94, (4 lines) the whole being a typical ABCD system assignable to 2 C_5H_4 groups; 7.69, $\underline{2}$, t, CH_2; 8.46, $\underline{8}$, c, $2(CH_2)$; 9.02, $\underline{6}$, t, 2 Me. [e]

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[a] Found (calc.). [b] Given as: chemical shift (τ), relative intensity, multiplicity, (J in Hz), assignment. [c] $\nu(Mo{-}H)$ = 1850 cm^{-1}. [d] In C_6D_6. [e] In $CDCl_3$. [f] $\nu(Mo{-}H)$ = 1830 cm^{-1}. [g] Mo: 42.0 (42.3) %. [h] In $(CD_3)_2SO$. [i] In SO_2. [j] W: 57.3 (60.1) %. [k] In $C_6D_5NO_2$. [l] Electronic spectrum in Me_2SO: 432 (ϵ = 1.5 × 10^3), 297 (3 × 10^3), 277 mμ (3 × 10^3).

shown by determination of their molecular weight.

The compounds **18** and **19** are sufficiently soluble for determination of their ^1H NMR spectra. These show that the hydrogens of the C_5H_4R groups occur as a ABCD system. This is consistent with the presence of the (μ-O)(μ-S) system rather than a (μ-O)$_2$ system: the former does not have the plane of symmetry containing the metal—ring centroid. The data characterising the new compounds, **1**—**19** are given in Table 1 and the Experimental section, and with the exceptions given above are not further discussed. The structures proposed fot the new compounds are shown in Scheme 1. Compounds related to **1**—**15** are those containing the trinuclear anions $[Ni(WS_4)_2]^{2-}$, $[Co(WO_2S_2)_2]^{2-}$, and $[(S)_2Mo(\mu\text{-}S_2)Mo(S)_2]^{2-}$ which contain the anions $[WO_2S_2]^{2-}$, $[WS_4]^{2-}$, and $[MoS_4]^{2-}$ as ligands [11].

It seems likely that a wide variety of η-cyclopentadienyltransition metaloxo derivatives can exist ranging from mono oxomonomers such as $Mo(\eta\text{-}C_4H_4)_2O$ [6,12] and $[Mo(\eta\text{-}C_5H_5)(dmpe)O]^+PF_6$ [13] to oligomeric compounds such as **1**, **4** and **7** and even to the cyclopentadienylated heteropolymolybdates recently described by Klemperer [14].

Experimental

All preparations and manipulations were carried out in vacuum or under an inert atmosphere. Solvents were dried and distilled before use. Infrared spectra were determined as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. ^1H NMR spectra were determined on JEOL C-60HL or Bruker 90 MHz instruments. Mass spectra were determined by using an MS9 spectrometer.

The compounds $M(\eta\text{-}C_5H_5)_2Cl_2$, M = Mo or W, were prepared as previously described [8].

Bis(η-cyclopentadienylmolybdenum)(μ-dioxo)dioxomolybdenum, 1

The compound $Mo(\eta\text{-}C_5H_5)_2Cl_2$ (2.0 g, 6.7 mmol) in water (25 cm^3) was treated with dipotassium molybdate (4.3 g, 16.6 mmol) in water (25 cm^3) at 90°C. The mixture was refluxed for 15 min, giving a yellow-brown precipitate. After cooling the precipitate was collected, washed with water and dried in vacuo, yield 90%.

The tungsten analogue **11** was similarly prepared from $W(\eta\text{-}C_5H_5)_2Cl_2$ (2.0 g) in water (100 cm^3) and dipotassium tungstate (4.0 g in 50 cm^3 of water), yield 70%.

Dihydridobis(η-methylcyclopentadienyl)molybdenum, 2

Sodium methylcyclopentadienide (112.5 g, 1.1 mol) in dry tetrahydrofuran (1600 cm^3) was treated with sodium borohydride (1.5 g, 0.36 mol) and pentachloromolybdenum (1.0 g, 0.11 mol). The precise manner of mixing the components and the subsequent isolation of product is that described in detail elsewhere for the unsubstituted analogue $Mo(\eta\text{-}C_5H_5)_2H_2$ [8]. The yield of the compound $Mo(\eta\text{-}C_5H_4Me)_2H_2$ was ca. 11.0 g, 40% based on $MoCl_5$.

Dichlorobis(η-methylcyclopentadienyl)molybdenum, 3

The compound $Mo(\eta\text{-}C_5H_4Me)_2H_2$ (12.0 g, 0.47 mol) in toluene/chloroform mixture (1/1, 200 cm^3) at r.t. was left for 12 h. The initially yellow solution rapidly turned green and then deposited large dark-green crystals. These were collected, washed with petroleum ether (40—60°C) and dried in vacuo, yield 14.5 g, yield ca. 90%.

Bis(η-methylcyclopentadienyl)molybdenum(μ-dioxo)dioxomolybdenum, 4

The compound Mo(η-C_5H_4Me)$_2$Cl$_2$ (1.1 g, 3.4 mmol) in water (60 cm^3) at 80°C was treated with dipotassium molybdate (2.0 g dissolved in the minimum volume of warm water). The mixture was boiled for 15 min, and a brown precipitate separated. This was washed with water (4 X 10 cm^3) and dried in vacuo, yield ca. 80%.

Bis(η-n-butylcyclopentadienyl)(dihydrido)molybdenum, 5

n-Butylcyclopentadiene was prepared in 53% yield by reaction between sodium cyclopentadienide in liquid ammonia with n-butyliodide.

n-Butylcyclopentadiene (30 cm^3) was added in a dropwise manner to potassium sand (10 g) in tetrahydrofuram (100 cm^3). The reaction mixture was stirred under reflux for 3 h. The resulting solution of potassium n-butylcyclopentadienide was used in the following manner.

Potassium n-butylcyclopentadienide (from 30 cm^3 of $C_5H_5Bu^n$) in dried tetrahydrofuran (200 cm^3) at —117°C was treated with pentachloromolybdenum (11 g, 50.0 mmol) and sodiumborohydride (4.5 g, 119 mmol). The mixture was refluxed for 3 h and the product was isolated using the acid extraction procedure described in detail elsewhere [8], giving the title compound, 2.7 g, ca. 20% yield. The compound could be crystallised from light petroleum ether (30—40°C) at —70°C as golden-yellow crystals. The crystals melt at —30°C giving a golden-brown oil.

Bis(η-n-butylcyclopentadienyl)(dichloro)molybdenum, 6

The compound Mo(η-$C_5H_4Bu^n$)$_2$H$_2$ (1.0 g, 2.9 mmol) in petroleum ether (10 cm^3, 30—40°C) was treated with carbontetrachloride (10 cm^3). After 2 h the solvent was removed, giving green crystals. These were recrystallised from toluene/petroleum ether (30—40°C), 1.1 g, yield ca. 90%.

Bis(η-butylcyclopentadienyl)molybdenum(μ-dioxo)dioxomolybdenum, 7

The compound Mo(η-$C_5H_4Bu^n$)$_2$Cl$_2$ (0.5 g, 1.2 mmol) in water (50 cm^3) was treated with dipotassium molybdate (0.5 g, 2.1 mmol) in water (10 cm^3). The mixture was heated for 15 min, giving a brown suspension. This was collected washed with water and dried. Recrystallisation from dichloromethane at —78°C gave a brown microcrystalline product, 0.36 g, yield ca. 60%.

Bis(η-cyclopentadienyl)molybdenum(μ-dithio)dithiomolybdenum, 8

The compound Mo(η-C_5H_5)$_2$Cl$_2$ (0.5 g) in water (30 cm^3) at 90°C was treated with diammonium tetrathiomolybdate (0.5 g) in water (10 cm^3) at 90°C. An orange precipitate appeared almost immediately. After 30 min this was collected, washed with water (3 X 10 cm^3) and dried in vacuum. The compound could be recrystallised from hot dimethylsulphoxide (at 80°C), yield 80%.

The tungsten analogue 12 was similarly prepared from W(η-C_5H_5)$_2$Cl$_2$ (0.5 g) and diammonium tetrathiotungstate in water, yield 60%.

Bis(η-methylcyclopentadienyl)(η-dithio)dithiomolybdenum, 9

Diammonium tetrathiomolybdate (3.0 g, 11.5 mmol) in aqueous ammonia (0.880, 10 cm^3) was added to Mo(η-C_5H_4Me)$_2$$Cl_2$ (3.5 g, 10.7 mmol) in aqueous ammonia (0.880, 15 cm^3). The mixture was then situated with dihydrogensulphide. An orange-red precipitate separated rapidly. This was separated, washed with water (2 X 50 cm^3) and dried. The compound could be recrystallised from liquid sulphur dioxide and dimethylsulphoxide as deep red crystals, yield 4.1 g, ca. 80%.

Bis(η-n-butylcyclopentadienyl)molybdenum(μ-dithio)dithiomolybdenum, 10

The compound Mo(η-$C_5H_4Bu^n$)$_2$$Cl_2$ (2.0 g, 4.9 mmol) in ethanol (20 cm^3) was treated with aqueous ammonia (0.880, 150 cm^3) and the ethanol was removed under reduced pressure. The resulting solution was treated with diammonium tetrathiomolybdate (1.27 g, 5.0 mmol) dissolved in aqueous ammonia (0.880, 15 cm^3). An orange precipitate separated which was collected, washed with water and dried in vacuo. The compound was recrystallised from hot saturated solutions in dimethylsulphoxide, yield 1.1 g, ca. 40%.

Bis(η-methylcyclopentadienyl)molybdenum(μ-dithio)dithiotungsten, 13

The compound Mo(η-C_5H_4Me)$_2$$Cl_2$ (1.0 g, 3.1 mmol) and ammonium tetrathiotungstate (1.4 g, 3.2 mmol) were reacted in the identical manner to that described above for the compound Mo(η-C_5H_4Me)$_2$(μ-S)$_2$$MoS_2$, giving the title compound in ca. 60% yield.

Bis(η-cyclopentadienyl)tungsten(μ-dithio)dithiomolybdenum, 14

The compound Mo(η-C_5H_5)$_2$$Cl_2$ (0.5 g, 1.68 mmol) in aqueous ammonia (20 cm^3 of 0.880 *M* solution) at 90°C was treated with dipotassium molybdate (0.5 g, 2.1 mmol) in water (10 cm^3) at 90°C. The mixture was treated with dihydrogen sulphide for 30 min and a bright orange precipitate separated. This was collected, washed with water then ethanol (10 X 5 cm^3) and dried in vacuo, yield 65%.

Bis(η-methylcyclopentadienyl)molybdenum(μ-dioxo)dioxotungsten, 15

The compound Mo(η-C_5H_4Me)$_2$$Cl_2$ (0.75 g, 2.3 mmol) in water (60 cm^3) at 80°C was treated with dipotassium tungstate (0.75 g, 2.3 mmol) in water (10 cm^3). A brown crystalline compound separated. This was collected, washed with water (4 X 10 cm^3) and dried in vacuo, ca. 80%.

Bis(η-methylcyclopentadienyl)molybdenum(μ-dioxo)sulphurdioxo, 16

The compound Mo(η-C_5H_4Me)Cl_2 (0.5 g, 1.6 mmol) in water (50 cm^3) was added to disodium sulphate (1.0 g) in water (10 cm^3). The mixture was allowed to stand and the initial green colour turned to red. After 1 h purple needle crystals separated and after 2 h these were collected, washed with water and dried in vacuo, yield 0.48 g, ca. 90%.

The n-butyl analogue, 17, was similarly prepared starting from 6 (0.5 g) in acetone (10 cm^3) and disodium sulphate (0.5 g in 20 cm^3 of water) at 60°C for 1.5 h, yield 65%.

Bis(η-methylcyclopentadienyl)molybdenum(μ-oxo)(μ-thio)sulphurdioxo, 18

The compound $Mo(\eta\text{-}C_5H_4Me)_2Cl_2$ (0.6 g, 1.8 mmol) in water (60 cm^3) was added to disodium thiosulphate (1.0 g) in water (15 cm^3). The initially green solution turned pink and after a further 15 min a brown precipitate separated. This was collected and washed with water. Recrystallisation was from hot acetonitrile (80° C) or sulphur dioxide/diethyl ether, yield 0.65 g, ca. 85%. The n-butyl analogue was similarly prepared from 6 (1.0 g in 20 cm^3, acetone/water (4/1)) and disodium thiosulphate (0.8 g in 6 cm^3 water) at 60°C for 30 min, yield 70%.

Infrared data

Selected data are presented in regions where M=O, Mo—O—Mo, Mo=S and Mo—S—Mo vibrations are found. Data is presented as: Compound number: peak position (cm^{-1}), approximate intensity, assignment as superfix, etc. 1: 918s [a], 900s [a], 880s [a], 843s [a], 740s [b], 509s [c], 380 [d]; 4: 917s [a], 885s [a], 854s [a], 736vs [b], 510vs [c], 376s [d], 285s [d]; 7: 912s [a], 890s [a], 730s [b], 630s [c]; 8: 510s [e], 500s [e]; 9: 514s [e], 500s [e]: 10: 514s [e], 495s [e]; 11: 940m [f], 890s [f], 725m [g]; 15: 937vs [f], 885s [f], 750s [h], 504vs [i]. [a] Mo=O stretching frequency. [b] Mo—O—Mo stretch (sym.). [c] Mo—O—Mo stretch (asym.). [d] MoO_2 def. [e] Mo=S of MoS_2. [f] W=O of WO_2. [g] W—O—W. [h] Mo—O—W (sym.). [i] Mo—O—W (asym.).

Mass spectral data

Only in a few cases were peaks due to parent ions observed. However, there were in many compounds peaks assignable to substantial fragments and we note the most prominent of these as evidence for the proposed formulations. The data is presented as compound number; *m/e*, assignment (*P* represents the parent molecule); etc. The *m/e* is quoted for the ^{98}Mo and ^{37}Cl isotopes only but for all peaks quoted there was also present a recognisable pattern due to the other isotopes of molybdenum. Data: 2: 258, P^+; 243, $P^+ - Me$: 3: 330, P^+; 293, $P^+ - Cl$; 256, $P^+ - 2\ Cl$; 4: 272, $Mo(\eta\text{-}C_5H_5)_2O$; 256 $Mo(\eta\text{-}C_5H_4Me)_2$: 5: 342, P^+; 6: 414, P^+: 7.340, $Mo(\eta\text{-}C_5H_4Bu^n)_2$: 10: 404, $Mo(\eta\text{-}C_5H_4Bu^n)_2S_2^+$; 16: 354, P^+.

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