Mono-η-cyclopentadienylmolybdenum Chemistry. Some Oxo-, Oxohalogeno-, Halogeno-, Thio-, η-Disulphido-, and Thiohalogeno-derivatives

By **Mark J. Bunker** and **Malcolm L. H. Green**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The new compounds $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$ and $[Mo(\eta\text{-}C_5H_4R)Cl_3(OH)]$, where R = Pr^i or Bu^n, $[\{Mo(\eta\text{-}C_5H_4R)(\mu\text{-}O)O\}_2]$, R = Me, Pr^i, or Bu^n, $[\{Mo(\eta\text{-}C_5H_5)OI\}_2(\mu\text{-}O)]$, $[Cl(\eta\text{-}C_5H_5)Mo(\mu\text{-}SMe)_3Mo(\eta\text{-}C_5H_5)Cl_2]$, $[Cl(\eta\text{-}C_5H_5)Mo(\mu\text{-}OH)(\mu\text{-}SMe)_2Mo(\eta\text{-}C_5H_5)Cl_2]$, and $[\{Mo(\mu\text{-}C_5H_4Bu^n)Cl_2\}_2(\mu\text{-}S_2)]$ have been prepared and characterised.

THE cyclopentadienyl ligand combines inertness towards addition or substitution reactions with stereochemical compactness and the ability to bond with transition metals in a wide variety of oxidation states and ligand environments.

Several years ago we showed that mono-η-cyclopentadienylmolybdenum oxides could be prepared[1-3] and we have continued to study the synthesis and reactivity of compounds of this type. It is our hope that study of organo-transition-metal oxides may eventually lead to insight into mechanisms of transition-metal catalysed oxygenation of olefins.

RESULTS

Treatment of $[\{MoOCl_3\}_n]$ in diethyl ether with tri-n-butylcyclopentadienyltin gives a yellow-brown solution, examination of a small sample of which showed it to contain the compound $[Mo(\eta\text{-}C_5H_5)OCl_2]$. However, this was not normally isolated and the reaction mixture was immediately treated with hydrogen chloride gas causing precipitation of fine red microcrystals of the known compound $[Mo(\eta\text{-}C_5H_5)Cl_4]$, (1).[1] This route can provide the compound (1) conveniently and on a substantial laboratory scale (20 g). Treatment of $[\{MoOCl_3\}_n]$ with thallium cyclopentadienide in tetrahydrofuran (thf) also provides the compound (1) in reasonable yield. The ' tin-σ-cyclopentadienylating agent ' is to be preferred since it is more convenient and economic to prepare in substantial quantities. Also, the tin reagent gives greater yields of (1) than does the thallium reagent.

The methylcyclopentadienyl reagent $Sn(\eta\text{-}C_5H_4Me)Bu^n{}_3$ also reacts readily with $[\{MoOCl_3\}_n]$, giving the compound $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$, (2). When $[\{MoOCl_3\}_n]$ is treated with the compounds $Sn(\sigma\text{-}C_5H_4R)Bu^n{}_3$ (R = Pr^i or Bu^n), then the hydroxytrichloro-derivatives $[Mo(\eta\text{-}C_5H_4R)Cl_3(OH)]$, where R = Pr^i (3) or Bu^n (4), respectively, are prepared in high yields. The microanalysis data are consistent with the empirical stoicheiometries given for the compounds (1)—(4). The i.r. spectra of the compounds (3) and (4) show bands assignable to the Mo—OH system (see Table).

The e.s.r. spectra of (1), (2), (3), and (4) were characteristic of a d^1 molybdenum compound. For example, solutions of (3) in dichloromethane saturated with hydrogen chloride gas showed an equally spaced and intense sextet with $\langle g \rangle = 1.992$, $\langle a \rangle = 3.92$ mT and a more intense central singlet. The fine structure may be assigned to coupling with the nuclei ^{95}Mo and ^{97}Mo (combined abundance 25.18%, spin $\frac{5}{2}$). Whereas (1) and (2) are almost insoluble in common organic solvents, the compounds (3) and (4) are soluble in dichloromethane, chlorobenzene, and slightly soluble in toluene. It was possible to crystallise (3) and (4) to give crystals of excellent appearance but they were unsuitable for *X*-ray diffraction studies.

Rapid hydrolysis of (1) gave the red compound previously described[2] as the tetramer $[\{Mo(\eta\text{-}C_5H_5)O_2\}_4]$, (5). Prolonged hydrolysis of (1), in the manner described previously, gave the known compound $[\{Mo(\eta\text{-}C_5H_5)O_2\}_2]$, (6). Large orange crystals of (6), grown from acetonitrile, were found suitable for a crystal-structure determination. The structure, which has been described in detail elsewhere,[4] is shown in the Scheme.

Similarly, hydrolysis of (2), (3), or (4) gives in the first instance red crystalline compounds. Analyses were consistent with the empirical formulation $Mo(\eta\text{-}C_5H_4R)O_2$, where R = Me (7), Pr^i (8), or Bu^n (9), respectively. The compounds (7), (8), and (9) are soluble in dichloromethane and (9) is very soluble in toluene. Crystals of (7), (8), or (9) were not found suitable for crystal-structure determination. Also, their solutions slowly decompose at room temperature (24 h) and convert to orange solutions from which orange crystalline compounds of the same empirical formula may be isolated. For example, ^1H n.m.r. spectra show a steady and quantitative rearrangement of (9) to the orange isomer. We designate the orange isomers as $[\{Mo(\eta\text{-}C_5H_4R)(\mu\text{-}O)O\}_2]$, where R = Me (10), Pr^i (11); and Bu^n (12). The i.r. spectra of (7), (8), and (9) (Table) show general similarities to the corresponding red compound described tentatively by Cousins and Green[2] as the tetramer $[\{Mo(\eta\text{-}C_5H_5)O_2\}_4]$. The conversion of (9) to (12) in dichloromethane limited the accuracy of the determination of the molecular weight of (9). However, initial values for the molecular weight of (9) in dichloromethane gave *ca.* 900 decreasing to 600 within about 1 h. The calculated value of the molecular wieght of (9) is 996.56. Thus the red isomers (6), (7), (8), and (9) are very probably tetrameric. Their i.r. spectra show bands assignable to both terminal and bridging oxo-groups (see Table). The ^1H n.m.r. spectra show the four $\eta\text{-}C_5H_4R$ groups in the molecule to be equivalent. Also, for the compound (8) the equivalence of the two methyl groups of the isopropyl substituent shows the availability of a plane of symmetry through the molecule. This conclusion is supported by the observation that the compounds (7), (8), and (9) show an AA'BB' rather than ABCD pattern for the C_5H_4 hydrogens. Attempts to obtain the mass spectra of (7), (8), and (9) gave an identical spectrum to that obtained for (10), (11), and (12). This might arise either from rearrangement of (7), (8), and (9) to (10), (11), and (12) respectively, or be due to the presence of traces of (10), (11), or (12) as impurities. We note that it was not found possible to completely separate the red isomers from the orange isomers even by rapid recrystallisation.

On the basis of evidence we tentatively favour a structure for the red isomers (5), (7), (8), and (9) shown in the Scheme. This structure is closely related to that found for the compound $[\{Ti(\eta\text{-}C_5H_5)OCl_4\}_4]$.[5]

It has been previously found that the compound $[\{Mo(\eta\text{-}C_5H_5)O_2\}_2(\mu\text{-}O)]$, (13), can be prepared by adventitious oxygenation of solutions of various $Mo(\eta\text{-}C_5H_5)$ derivatives [1] but yields were unsatisfactory. After examination of a range of potential oxygen-transfer reagents, such as dioxygen, olefin oxides, and alkyl peroxides, it was found that treatment of (6) with silver oxide gave rise to formation of (13) in good yield. Solutions of (13) in benzene showed no reaction with cyclohexane. However, addition of triphenylphosphine to (13) in toluene resulted in a smooth transfer of oxygen giving triphenylphosphine oxide, and the compound (5) was recovered from the reaction mixture in high yield.

Analytical and spectroscopic data

Compound	Colour	Analysis [a]			E.s.r. and ^1H n.m.r. data [b]
		C	H	Halogen	
(2) $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$	Deep red	22.9 (22.7)	2.6 (2.2)		E.s.r. (Et_2O–HCl), r.t.: $\langle g\rangle = 199.8$, sextet, $\langle a\rangle$ 4.0 mT [c]
(3) $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_3(OH)]\cdot 0.5(1,2\text{-}C_2H_4Cl_2)$	Red	28.0 (28.2)	3.6 (3.8)	41.5 (41.7) [d]	E.s.r. (CH_2Cl_2), r.t.: $\langle g\rangle = 199.2$, sextet, $\langle a\rangle$ 3.91 mT [c]
(4) $[Mo(\eta\text{-}C_5H_4Bu^n)Cl_3(OH)]\cdot 0.5CH_2Cl_2$	Red	28.7 (29.8)	4.1 (3.95)	37.4 [e] (37.0)	E.s.r. (CH_2Cl_2), r.t.: $\langle g\rangle = 199.2$, sextet, $\langle a\rangle$ 3.92 mT [c]
(7) $[\{Mo(\eta\text{-}C_5H_4Me)O_2\}_4]$	Red	34.8 (34.8)	3.4 (3.4)		N.m.r.: complex multiplet, 3.72, *3 lines*, sep. 3 Hz and 4.39, *3 lines*, sep. 3 Hz, **4**, A_2B_2 of $\eta\text{-}C_5H_4$; 8.02, **3**, *s*, Me [f]
(8) $[\{Mo(\eta\text{-}C_5H_4Pr^i)O_2\}_4]$	Red	40.8 (40.9)	4.7 [g] (4.7)		N.m.r.: 4.06, **2**, *t* (*J* 2.7) and 4.41, **2**, *t*(*J* 2.7), C_5H_4; 7.05, **1**, *septet* (*J* 7.3), CH; 8.75, **6**, *d* (*J* 7.3), 2 Me [h]
(9) $[\{Mo(\eta\text{-}C_5H_4Bu^n)O_2\}_4]$	Red	43.3 (43.4)	5.35 [i] (5.3)		N.m.r.: 4.03, **2**, *t* (*J* 2.7) and 4.60, **2**, *t* (*J* 2.7), C_5H_4; 7.59, **2**, *t* (*J* 7.3), CH_2; 8.6, **4**, *c*, 2 H_2; 9.12, **3**, *t* (*J* 7.1), Me [j]
(10) $[\{Mo(\eta\text{-}C_5H_4Me)(\mu\text{-}O)O\}_2]$	Orange	34.8 (34.8)	3.4 (3.4)		N.m.r.: 4.06, **4**, *s*, $\eta\text{-}C_5H_4$; 7.78, **3**, *s*, Me [h,k]
(11) $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}O)O\}_2]$	Orange	40.9 (40.9)	4.8 [l] (4.7)		N.m.r.: 4.16, **2**, *t* (*J* 2.5) and 4.13, **2**, *t* (*J* 2.5), C_5H_4; 6.96, **1**, *septet* (*J* 6.8), CH; 8.66, **6**, *d* (*J* 6.8), 2 Me [h]
(12) $[\{Mo(\eta\text{-}C_5H_4Bu^n)(\mu\text{-}O)O\}_2]$	Orange	43.5 (43.4)	5.3 [m] (5.3)		N.m.r.: 4.25, **4**, *s* (*br*), C_5H_4; 7.50, **2**, *t* (*J* 7.5), CH_2; 8.6, **4**, *c*, 2 CH_2; 9.14, **3**, *t* (*J* 6.7), Me [h]
(14) $[\{Mo(\eta\text{-}C_5H_5)OI\}_2(\mu\text{-}O)]$	Emerald green	19.3 (19.3)	1.6 (1.6)	41.8 [n] (40.7)	N.m.r.: 3.45, **5**, *s*, C_5H_5 [j]
(16) $[Cl(\eta\text{-}C_5H_5)Mo(\mu\text{-}SMe)_3Mo(\eta\text{-}C_5H_5)Cl_2]$	Orange-red	27.7 (27.4)	3.4 [o] (3.7)		N.m.r.: 4.09, **5**, *s*, $\eta\text{-}C_5H_5$; 4.71, **5**, *s*, $\eta\text{-}C_5H_5$; 7.56, **3**, *s*, Me; 7.59, **3**, *s*, Me; 7.75, **3**, *s*, Me
(17) $[Cl(\eta\text{-}C_5H_5)Mo(\mu\text{-}OH)(\mu\text{-}SMe)_2Mo(\eta\text{-}C_5H_5)\text{-}Cl_2]$	Orange-red [p]				
(18) $[\{Mo(\eta\text{-}C_5H_4Bu^n)Cl_2\}_2(\mu\text{-}S_2)]$	Orange-black [p]				

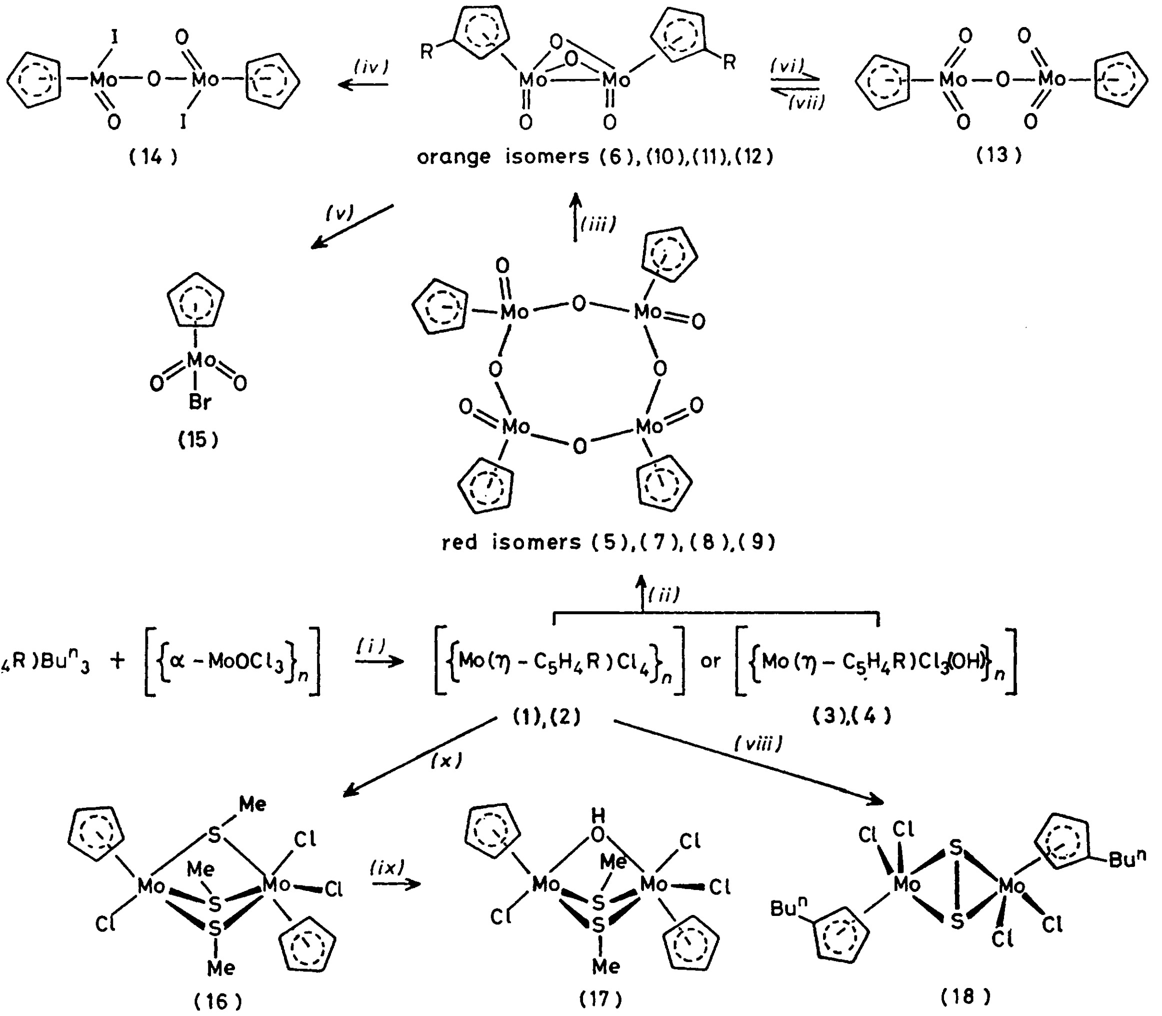
[a] Found (calc.) %. [b] Given as: chemical shift (τ), **rel. intensity**, *multiplicity* (*J* in Hz), assignment. *c* = Complex spectrum. [c] For assignment see the text. [d] O–H stretch at 3 400 cm^{-1}. [e] Mass spectrum shows a highest peak at *m/e* = 305 (P^+ – HCl, for ^{98}Mo). [f] In $CDCl_3$, sep. = separation. Mo=O stretch at 920s, Mo–O–Mo asym. stretch at 695 ms cm^{-1}. [g] Mass spectrum shows a highest peak at 474 ($\frac{1}{2}$ P^+). Mo=O stretch at 925s, Mo–O–Mo asym. stretch at 703ms cm^{-1}. [h] In C_6D_6. [i] Mass spectrum shows a highest peak at *m/e* = 502 ($\frac{1}{2}$ P^+). Mo–O stretch at 923s, asym. Mo–O–Mo stretch at 694ms cm^{-1}. [j] In CD_2Cl_2. [k] Mo=O stretch at 927s, Mo–O–Mo asym. stretch at 715ms cm^{-1}. [l] Mass spectrum shows a highest peak at *m/e* = 474, P^+. [m] Mo=O stretch at 938ms and asym. stretch of Mo–O–Mo at 720ms cm^{-1}. [n] Mass spectrum shows a highest peak at *m/e* = 501 (P^+ – I). Mo=O stretch at 939vs cm^{-1}. [o] Cl, 18.6 (18.7); S, 16.9 (16.9) %. [p] Characterised by *X*-ray crystal-structure determination only.

Treatment of (6) in dichloromethane with one equivalent of iodine gave an instant deep rose solution from which dark green crystals could be isolated Analyses are consistent with the empirical formulation $C_{10}H_{10}I_2MoO_3$, (14). The i.r. spectrum showed the presence of both Mo=O and Mo–O–Mo bonding (Table). The mass spectrum showed a series of very weak bands at *m/e* = 501—495 for which an isotope pattern corresponding to Mo_2 was discernible: the envelope may be assigned to the ion $C_{10}H_{10}IMo_2O_3^+$. There were also bands due to mononuclear species at *m/e* = 433 and 322 corresponding to the ions $C_5H_5I_2MoO^+$ and $C_5H_5IMoO_2^+$ respectively.

The crystal structure of the compound (14) has been determined (see Scheme) and this together with the above data shows the compound to be $[\{Mo(\eta\text{-}C_5H_5)OI\}_2(\mu\text{-}O)]$, (14).[6]

Treatment of (5) in dichloromethane with one mol equivalent of dibromine gave an immediate reaction and the known bromo-compound $[Mo(\eta\text{-}C_5H_5)O_2Br]$, (15),[2] was formed in high yield.

Treatment of a suspension of $[Mo(\eta\text{-}C_5H_5)Cl_4]$ in diethyl ether with methanethiol gave a small yield of red-black crystals of stoicheiometry $C_{13}H_{19}Cl_3Mo_2S_3$, (16). The ^1H n.m.r. showed two single bands at τ 4.09 and 4.71 assignable to two different ($\eta\text{-}C_5H_5$) groups. There were also three singlets at τ 7.56, 7.59, and 7.75 assignable to three different MeS groups. The mass spectrum showed bands assignable to a binuclear dimolybdenum species but no parent ion peak was observed. The compound (16) is soluble in dichloromethane from which it may be recrystallised. When the recrystallisation was carried out in air then partial hydrolysis resulted giving crystals which an *X*-ray structure determination showed to be a 1 : 1 mixture of the compounds (16) and (17).[7] Hydrolysis of solutions of (16) gave very low yields of orange-black needles, (17). The crystal structure of these [7] showed close similarity to that of (16), as shown in the Scheme.



SCHEME (*i*) In Et_2O or CH_2Cl_2 at room temperature (r.t.); (1), R=H; (2), R=Me; (3), R=Pr^i, as the 0.5(1,2-$C_2H_4Cl_2$) solvate; (4), R=Bu^n, as the $0.5CH_2Cl_2$ solvate. (*ii*) H_2O and $COMe_2$, 5 min, *ca.* 70% yield. (*iii*) Toluene or CH_2Cl_2 at r.t. for 24 h, 80% yield. (*iv*) I_2 in CH_2Cl_2, R=H, 80% yield. (*v*) Br_2 in CH_2Cl_2, 20 min, R=H, 78% yield. (*vi*) Ag_2O in CH_2Cl_2 for 1.5 d at 55 °C, R=H, 79% yield. (*vii*) PPh_3, R=H, 60% yield. (*viii*) Chlorobenzene–light petroleum; HCl gas at 70 °C then H_2S for 5 min, R=Bu^n, *ca.* 50% yield. (*ix*) Extract with toluene–dichloromethane, add Et_2O and stand in air, ≈15% yield. (*x*) Et_2O then MeSH for 20 min, 2—20% yield

Treatment of a solution of [{Mo(η-$C_5H_4Bu^n$)(μ-O)O}$_2$] with hydrogen chloride and then with dihydrogen sulphide gave orange crystals [{Mo(η-$C_5H_4Bu^n$)Cl_2}$_2$(μ-S_2)], (18), whose molecular structure [8] is shown in the Scheme.

DISCUSSION

The structures proposed for the new compounds are shown in the Scheme. The structure originally proposed for (5) is incorrect.[1] The details for the crystal structures of the compounds (5), (14), (16), (17), and (18) are given elsewhere.[4,6-8]

The presence of the μ-disulphido-ligand in (18) is of note since this constituted the first example where two metal moieties are held together solely by a μ-S_2 unit without the presence of metal–metal bonding. The formation of a M(μ-S)$_2$M system by addition of two electrons to a M^+(μ-S_2)M^+ system may be seen as a method of electron storage which does not involve reduction of the metal centres.

In conclusion, so far we have been unable to cause the Mo=O system in these compounds to become reactive towards olefins. We have, however, shown the cyclopentadienyloxomolybdenum chemistry is quite extensive and it seems probable that parallel chemistry will be found for other transition metals, *e.g.* rhenium.

EXPERIMENTAL

All manipulations were carried out under dinitrogen or *in vacuo*. Glass vessels were dried by flaming under vacuum immediately before use. Solvents were dried and distilled before use. Infrared spectra were determined as mulls using a Perkin-Elmer 457 or 580 instrument and were calibrated with polystyrene film.

Hydrogen-1 n.m.r. spectra were measured using a Perkin-Elmer R12 or R14 instrument and were calibrated against either solvent peaks or internal $SiMe_4$.

E.s.r. spectra were determined using a Varian E-line spectrometer and were calibrated against 1,1-diphenyl-2-picrylhydrazyl as an external standard. Mass spectra were recorded on A.E.I. MS9 or V.G. Micromass 16F spectrometers.

The compound $Sn(\eta\text{-}C_5H_5)Bu^n{}_3$ was prepared in 300 g batches, *ca.* 85% yield. The compounds $Sn(\eta\text{-}C_5H_4R)\text{-}Bu^n{}_3$ ($R = Me, Pr^i$, or Bu^n) were prepared in the same manner as the unsubstituted analogue from $SnClBu^n{}_3$ and $Na[C_5H_4Me]$, $K[C_5H_4Pr^i]$, or $K[C_5H_4Bu^n]$ respectively. The alkali-metal salts of the alkylcyclopentadienides were prepared from the dienes C_5H_5R, which were prepared as described.[9,10] α-Molybdenum trichloride oxide was prepared as described.[11]

Tetrachloro-η-cyclopentadienylmolybdenum, (1).—A suspension of $[\{\alpha\text{-}MoOCl_3\}_n]$ (4.73 g, 21.7 mmol) in dry diethyl ether (500 cm^3) was treated with tri-n-butylcyclopentadienyltin (8.14 g, 22.9 mmol) in a dropwise manner. The mixture was stirred for 15 h, giving a deep yellow-brown solution and a dark solid. This mixture was filtered and the blue-black residue was extracted with diethyl ether. The diethyl ether solutions were combined and concentrated (to 300 cm^3) giving a few crystals of the intermediate $[Mo(\eta\text{-}C_5H_5)OCl_2]$ (i.r. spectrum).[1] The solution was then treated with hydrogen chloride gas for 10 min. Shining red microcrystals immediately deposited. These were collected, washed with dry diethyl ether and then light petroleum (b.p. 60—80 °C). They were finally dried *in vacuo*, 4.9 g, 75%.

Tetrachloro(η-methylcyclopentadienyl)molybdenum, (2).—The procedure was essentially identical to that for compound (1) using $[\{\alpha\text{-}MoOCl_3\}_n]$ (1.39 g, 6.37 mmol) and $Sn(\sigma\text{-}C_5H_4Me)Bu^n{}_3$ (2.45 g, 6.7 mmol) in diethyl ether (80 cm^3), yield 1.37 g.

Trichlorohydroxo(η-isopropylcyclopentadienyl)molybdenum, (3).—The procedure was essentially identical to that employed for (2) using $[\{\alpha\text{-}MoOCl_3\}_n]$ (2.14 g, 9.8 mmol) and $Sn(\sigma\text{-}C_5H_4Pr^i)Bu^n{}_3$ (4.13 g, 10.4 mmol) in diethyl ether (90 cm^3). A minor modification was that the filtrate from the reaction mixture was cooled to −30 °C giving red needles, yield 2.6 g, 81%. These were recrystallised from 1,2-dichloroethane saturated with hydrogen chloride giving red crystals of the 1,2-dichloroethane solvate.

(η-n-Butylcyclopentadienyl)trichlorohydroxomolybdenum, (4).—This was prepared as described for (3) using $[\{\alpha\text{-}MoOCl_3\}_n]$ (2.18 g, 10 mmol) and $Sn(\sigma\text{-}C_5H_4Bu^n)Bu^n{}_3$ (4.3 g, 10.5 mmol) in diethyl ether (90 cm^3). The compound was recrystallised from dichloromethane saturated with hydrogen chloride giving the solvate, yield 2.21 g, 65%.

Tetrakis[(η-n-butylcyclopentadienyl)dioxomolybdenum], the Red Isomer, (9).—The compound $[Mo(\eta\text{-}C_5H_4Bu^n)Cl_3(OH)]$ (0.73 g, 2.12 mmol) in acetone (20 cm^3) was treated with water (30 cm^3), with shaking. Fine deep red microcrystals separated within a few min. The acetone was removed from the mixture under reduced pressure and the aqueous solution was filtered. The red crystals were washed with water (3 × 10 cm^3) and dried *in vacuo*, *ca.* 0.46 g, 87%. Alternatively, after precipitation of the red crystals the mixture was extracted with a light petroleum–dichloromethane mixture (9 : 1). The organic layer was separated, concentrated, and cooled to −30 °C. Large crystals separated which were washed with light petroleum and dried *in vacuo*, 0.46 g, 87%. Examination of the mother-liquors showed them to contain the compound $[\{Mo(\eta\text{-}C_5H_4Bu^n)(\mu\text{-}O)O\}_2]$, as described above.

Tetrakis[(η-isopropylcyclopentadienyl)dioxomolybdenum], the Red Isomer, (8).—This was prepared in a similar manner to the n-butyl analogue starting from $[Mo(\eta\text{-}C_5H_4Pr^i)\text{-}Cl_3(OH)]$ (0.22 g, 0.70 mmol) in acetone (6 cm^3) as red microcrystals, 0.11 g, 69%.

Tetrakis[(η-methylcyclopentadienyl)dioxomolybdenum], the Red Isomer, (7).—This was prepared as described for (9) starting from $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$, in *ca.* 70% yield.

Bis[(η-alkylcyclopentadienyl)-μ-oxo-oxomolybdenum], (6), (10), (11), (12).—Typical experiments are described.

(a) Compound (1) (3.35 g, 11.06 mmol) was treated with water (70 cm^3) and the mixture was shaken vigorously. The initially deep red solid gradually turned yellow-brown. After 1.5 days, with intermediate agitation, the whole of the solid was yellow-brown. The aqueous layer was decanted and the solid was washed with water and dried *in vacuo*, yield 1.2 g, 56%.

The product was moderately soluble in hot acetone or dichloromethane, from which it could be recrystallised to give pure crystals of (6). The compounds appear to be indefinitely stable in air.

(b) *Bis[(η-n-butylcyclopentadienyl)-μ-oxo-oxomolybdenum], the orange isomer*, (12). The red isomer $[\{Mo(\eta\text{-}C_5H_4Bu^n)\text{-}O_2\}_4]$ (0.3 g) was dissolved in toluene or dichloromethane (100 cm^3). After 12 h, the solution had become orange. It was then concentrated under reduced pressure and the concentrate was cooled to −30 °C for 12 h. Orange-golden crystals separated; they were collected, washed with cold light petroleum (b.p. 40—60 °C throughout, unless otherwise stated), and dried *in vacuo*. Yield, *ca.* 80%.

(c) *Bis[(η-isopropylcyclopentadienyl)-μ-oxo-oxomolybdenum], the orange isomer*, (11). This was prepared in a manner identical to that described for the n-butyl analogue, starting from the red isomer $[\{Mo(\eta\text{-}C_5H_4Pr^i)O\}_4]$, yield *ca.* 70%. The compound $[\{Mo(\eta\text{-}C_5H_4Me)(\mu\text{-}O)O\}_2]$, (10), is similarly prepared starting from the compound (7) in 70% yield.

μ-Oxo-bis[(η-cyclopentadienyl)dioxomolybdenum], (13).—The compound $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}O)O\}_2]$ (0.375 g, 0.90 mmol) in hot dichloromethane (150 cm^3) was treated with silver(I) oxide (2.27 g, 9 mmol) and the mixture was stirred for 1.5 days at 55 °C. The initial deep orange solution became a pale yellow. The solution was filtered and the filtrate was concentrated under reduced pressure giving yellow crystals (from *ca.* 10 cm^3 of mother-liquor). The crystals were collected, washed with light petroleum, and dried *in vacuo*. The i.r. spectrum showed the absence of the starting material. The product was recrystallised from benzene–light petroleum (b.p. 100—120 °C) as pale yellow plates. Yield, 0.25 g, 79%.

μ-Oxo-bis[(η-cyclopentadienyl)iodo-oxomolybdenum], (14).—A solution of $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}O)O\}_2]$ (0.118 g, 0.31 mmol) in dichloromethane (60 cm^3) was treated with iodine (0.78 g, 0.31 mmol). The solution changed from orange to rose-red. After 45 min the solution was filtered and the solvent removed under reduced pressure giving an emerald green solid. This was extracted with toluene. The extract was concentrated under reduced pressure giving emerald green crystals which were collected, washed with light petroleum, and dried *in vacuo*. Yield, 0.157 g, 80%.

Bromo(η-cyclopentadienyl)dioxomolybdenum, (15).—The compound $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}O)O\}_2]$ (1.35 g, 3.50 mmol) in dichloromethane (250 cm^3) was treated in a dropwise manner with bromine (0.56 g, 3.5 mmol) in dichloromethane (21.8 cm^3). The initially orange solution became yellow and a small quantity of dark blue solid deposited. The solution was filtered and the solvent was removed from the filtrate under reduced pressure. The resulting yellow-brown solid was extracted with benzene and the extract was treated with cyclohexane and dioxygen for 12 h. Addition of light petroleum (b.p. 100—120 °C) and concentration of the mixture under reduced pressure gave bright yellow crystals of the pure compound, *ca.* 1.5 g, 78%.

Trichlorobis(η-*cyclopentadienyl*)-*tris*(μ-*methanethiolato*)-*dimolybdenum*, (16).—The compound [$\{Mo(\eta\text{-}C_5H_5)Cl_4\}_n$] (1.56 g, 5.15 mmol) was suspended in diethyl ether (250 cm^3) and treated with a rapid stream of methanethiol for 20 min. The solid red suspension turned brown, and the mixture was warmed to 35 °C. The resulting deep red-orange solution was filtered and the filtrate was concentrated to *ca.* $\frac{1}{3}$ volume under reduced pressure. The solution was allowed to stand overnight giving deep red-orange crystals. These were separated, washed with light petroleum (40—60 °C), and dried *in vacuo*. The compound could be recrystallised from a dry toluene–dichloromethane–diethyl ether solution as deep orange-red crystals which appeared almost black by reflected light. The yield varied between 0.02 and 0.20 g, 2 and 20%.

Preparation of Trichlorobis(η-*cyclopentadienyl*)-(μ-*hydroxo*)-*bis*(μ-*methanethiolato*)-*dimolybdenum*, (17).—The crude product from the preparation of the compound [$Cl_2(\eta\text{-}C_5H_5)Mo(\mu\text{-}SMe)_3Mo(\eta\text{-}C_5H_5)Cl$] (16) was extracted with a mixture of toluene–dichloromethane. Diethyl ether was added and the resulting deep orange extract was filtered and then allowed to evaporate in air giving large orange-red needles together with some dark material. The crystals were separated by hand and washed with toluene–light petroleum (1 : 1), then with light petroleum (b.p. 40—60 °C), and finally dried *in vacuo*, yield 15%. The crystals were suitable for study by *X*-ray diffraction. One crystal was 8 mm in length.

μ-*Disulphido-bis*[(η-*n-butylcyclopentadienyl*)*dichloromolybdenum*], (18).—The compound [$\{Mo(\eta\text{-}C_5H_4Bu^n)(\mu\text{-}O)O\}_2$] (0.02 g, 0.04 mmol) in chlorobenzene–light petroleum (1 : 2; 30 cm^3) was saturated with hydrogen chloride. Gentle warming redissolved the shimmering pink precipitate. Dihydrogen sulphide was passed into the solution at 70 °C for 5 min. The solution was allowed to cool and was kept at room temperature for 3 d. Long, deep orange-black crystals separated which were washed with light petroleum and dried *in vacuo*, yield 0.01 g, *ca.* 50%.

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