

### 311. *Some Oxo- and Oxochloro-cyclopentadienylmolybdenum Complexes.*

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The preparation and properties of the oxo-complexes,  $[\text{C}_5\text{H}_5\text{MoO}_2]_2$  and  $[\text{C}_5\text{H}_5\text{MoO}_2]_2\text{O}$ , and of the oxochloro-complexes,  $\text{C}_5\text{H}_5\text{MoO}_2\text{Cl}$  and  $\text{C}_5\text{H}_5\text{MoOCl}_2$  are given. Their infrared spectra in the region 4000—280  $\text{cm}^{-1}$  are reported and discussed. Structures for the complexes are suggested.

THE complex  $[\text{C}_5\text{H}_5\text{TiCl}_2]_2\text{O}$  has been fully characterised<sup>1</sup> and its structure from X-ray data shows that it contains an unusual, linear Ti—O—Ti system in which the Ti—O distance, 1.78 Å, is anomalously short.<sup>2</sup> Other complexes in this class are the vanadium complexes,  $\text{C}_5\text{H}_5\text{VOX}_2$ , where X = Cl or Br,<sup>3</sup> and the tetrameric oxo-complex  $[\text{C}_5\text{H}_5\text{CrO}]_4$ .<sup>4</sup> Recently, we reported that the oxidation of the  $\pi$ -allyl complex,  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\pi\text{-C}_3\text{H}_5)$ , in the presence of hydrogen chloride gave small yields of the oxochloro-complex,  $\text{C}_5\text{H}_5\text{MoO}_2\text{Cl}$ .<sup>5</sup> Now a more detailed study of this reaction and of other methods of preparation of the complex is reported. These studies have shown that a number of stable oxo- and oxochloro-cyclopentadienylmolybdenum complexes can be prepared.

*Preparation and Properties.*—Oxidation under various conditions of complexes, such as  $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ ,  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ ,<sup>6</sup> and  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\pi\text{-C}_3\text{H}_5$ ,<sup>5</sup> affords a variety of oxo- and oxochloro-cyclopentadienylmolybdenum complexes, whose reactions are shown in the Chart; and whose preparations are described in the Experimental section; the formulation of all the complexes has been established by total analysis and molecular-weight determination. Tetraoxo- $\mu$ -oxodicyclopentadienyl-dimolybdenum (III) is the most readily prepared of the complexes. It forms pale yellow crystals, decomposing at 100—150°, which are stable in air for several weeks. The complex is slightly soluble in ether and benzene but more soluble in polar organic solvents, and may be recrystallised from hot

<sup>1</sup> Corradini and Allegra, *J. Amer. Chem. Soc.*, 1959, **81**, 5510.

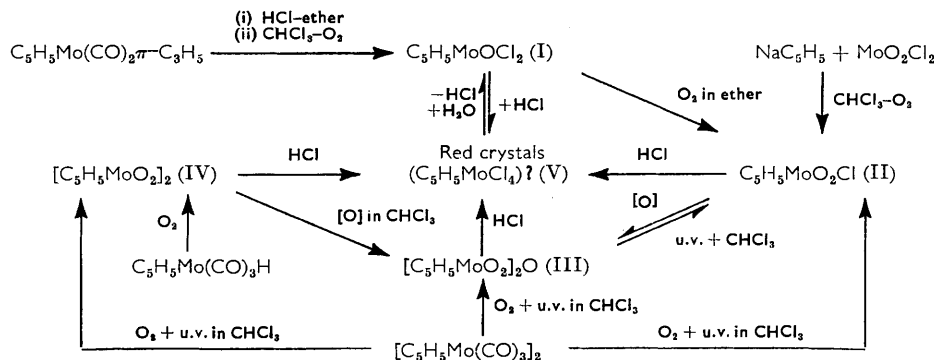
<sup>2</sup> Allegra, Porri, and Corradini, *Atti Accad. naz. Lincei., Rend. Classe Sci. fis. mat. nat.*, 1961, **30**, 44.

<sup>3</sup> Fischer, Vigoreux, and Kuzel, *Chem. Ber.*, 1960, **93**, 701.

<sup>4</sup> Fischer, Ulm, and Fritz, *Chem. Ber.*, 1960, **93**, 2167.

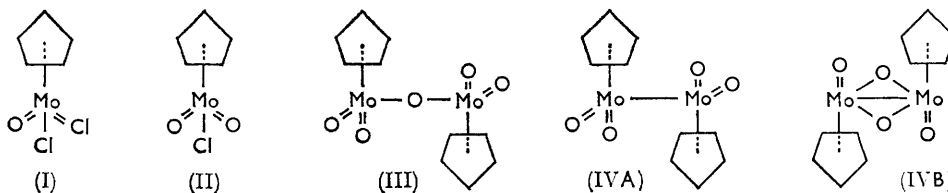
<sup>5</sup> Cousins and Green, *J.*, 1963, 889.

<sup>6</sup> Piper and Wilkinson, *J. Inorg. and Nuclear Chem.*, 1956, **3**, 104.



acetone. Solutions in chloroform slowly decompose forming the dioxo-chloride (II). Tetraoxodicyclopentadienyldimolybdenum (IV) can only be prepared in small yields as slightly volatile brown microcrystals, which sublime in vacuum with decomposition at *ca.* 200°. The complex (IV) is stable in air and to moisture and is slightly soluble in acetone and chloroform. Again, chloroform solutions slowly decompose and the tetraoxo- $\mu$ -complex (III) and the dioxo-chloride (II) are formed.

Oxodichlorocyclopentadienylmolybdenum (I) forms brown microcrystals which sublime *in vacuo* at *ca.* 50° with slight decomposition. The complex is unstable in air and decomposes (*ca.* 50% in 2 days) forming the dioxo-chloride (II) and unidentified material. The complex (I) is soluble in ether, acetone, and chloroform. Solutions in ether decompose quite rapidly (50% in 6 hr.), the dioxo-chloride (II) and unidentified material being formed. Purification of this complex was achieved by treating ether solutions of it with hydrogen chloride, when red crystals readily separated. This latter complex (V) is very unstable and readily hydrolyses in moist air to re-form the parent complex (I). Thus, the oxo-dichloride complex (I) can be separated from traces of its decomposition product, the dioxo-chloride (II).



The red complex (V) is also formed by reaction of hydrogen chloride or hydrochloric acid with the other oxo- and oxochloro-complexes (II—IV) as indicated in the Chart, but it has not yet been possible to characterise it fully. Preliminary analyses and infrared spectra indicate that it may be a chloro-complex, such as  $C_5H_5MoCl_4$ ; further studies are in progress.

The pure oxo-dichloride (I) is paramagnetic; the magnetic moment is 1.74 B.M. at 24.5°, which indicates one unpaired electron.<sup>7</sup> The electron spin resonance (e.s.r.) spectrum of the pure complex has been determined at -195° and shows a very broad band of low intensity (line width 2000 gauss), occurring slightly on the high field side of  $g = 2$ . The spectrum confirms the paramagnetism of the complex and indicates that there are orbitals of similar energy which may contain the unpaired electron. Since the complex  $C_5H_5MoOCl_2$  would not be expected to have high octahedral symmetry, the occurrence of metal orbitals of similar energy is presumably fortuitous. The dioxo-chloride  $C_5H_5MoO_2Cl$  forms volatile yellow crystals.<sup>5</sup> The complex is stable under nitrogen, but the pure crystals

<sup>7</sup> Lewis and Wilkins, "Modern Co-ordination Chemistry," Interscience, London, 1960, p. 400.

decompose slowly in air and solutions are oxidised quite rapidly, to form the pentoxide (III) and unidentified blue material.

*Proton Magnetic Resonance Spectra.*—Other than the paramagnetic oxodichloro-complex, all the complexes (II—IV) show one band in their proton magnetic resonance (p.m.r.) spectra, which may be assigned to the hydrogen atoms of the  $\pi$ -cyclopentadienyl group. The sharpness of these bands indicates that the complexes are diamagnetic. The bands occur in the region  $\tau$  3.4—3.7, which when compared with the position of the analogous bands in the complexes  $C_5H_5Mo(CO)_3R$  ( $\tau \sim 5.0$ <sup>5,6</sup>) and  $[C_5H_5Mo(CO)_3C_3H_6]^+$  ( $\tau 4.0$ <sup>5</sup>) indicates a higher oxidation state of the metal in these complexes. Despite careful examination of the oxo-dichloride complex over a wide region, no spectrum assignable to the complex was found. The absence of a spectrum is consistent with the paramagnetism of the molecule.

*Infrared Spectra.*—The spectra of the complexes (I—IV) from 4000—250  $cm^{-1}$  are given in the Table. The spectra of some related complexes have also been determined for purposes of comparison. The complexes (I—IV) show bands which can be assigned to a  $\pi$ - $C_5H_5$ -Mo

Complex	Infrared spectra.			
	$[C_5H_5MoO_2]_2O$ *	$[C_5H_5MoO_2]_2$ †	$C_5H_5MoOCl_2$ †	$C_5H_5MoO_2Cl$ †
C—H stretch of $\pi$ - $C_5H_5$ .....	3100m	3090m	3098m 2920vw 1887vw 1798vw	3100m 2840vw 1887vw 1785vw
$\pi$ - $C_5H_5$ frequencies.....	1450m 1425m 1355m 1020m 1008m	1443m 1433m 1357m 1065w 1018m	1451m 1422m 1359w 1018m 1000m	1457m 1421m 1360w 1070w 1024m 1001m
Asymmetric Mo=O stretch ...	930s, sh 920s	925s 901m	949s	920s
Symmetric Mo=O stretch.....	898s 850m			887s
$\pi$ - $C_5H_5$ frequencies.....	835s, sh 820s	830s 820s	835s 826s	830s
Mo—O—Mo asymmetric stretch	770s 600w 431s 392s 348s	710m 600w 462s 396s 360s 300s	585w 386s 360s 338m 312m 307m, sh	600w 397s 376s 322m

\* Measured in mulls and  $CHCl_3$  and acetone solutions. † Measured as mulls in hexachlorobutadiene and Nujol. § Mo=O deformation frequencies, Mo—Cl stretches (where applicable) and  $\pi$ - $C_5H_5$ -Mo frequencies;  $MoO_2Cl_2$  shows bands in this region at 444s, 402m, 377s, 346s, and 287sh; similarly,  $C_5H_5Mo(CO)_3Cl$  shows bands in this region at 604w, 565s, 472s, 431m, 416s, 395m, 362m, and 285vs.

system and also to Mo=O frequencies.<sup>8,9</sup> The tetraoxo- $\mu$ -oxo-complex (III) shows bands in the region 820—950  $cm^{-1}$  which can be assigned to Mo=O symmetric and asymmetric stretches. There is also a band at 770  $cm^{-1}$  which, by analogy with the assignment of bands in this region in the spectra of  $TiOSO_4$  and  $MoO_3$  as the —Ti—O—Ti— and —Mo—O—Mo— asymmetric stretch,<sup>9</sup> can be assigned to the Mo—O—Mo asymmetric stretch. The spectrum of the complex  $[C_5H_5TiCl_2]_2O$  has not been described. However, the reported spectrum of  $C_5H_5TiCl_3$ ,<sup>10</sup> which was later noted as being incorrect,<sup>11</sup> contained a band at 770  $cm^{-1}$  which may have been due to the Ti—O—Ti asymmetric stretch of the hydrolysis product of

<sup>8</sup> Nakamoto, "Infrared spectra of inorganic and coordination compounds," Wiley and Sons, London, 1963.

<sup>9</sup> Nyholm, Lewis, and Barraclough, *J.*, 1959, 3552.

<sup>10</sup> Sloan and Barber, *J. Amer. Chem. Soc.*, 1959, **81**, 1364.

<sup>11</sup> Gorisch, *J. Amer. Chem. Soc.*, 1960, **82**, 4211.

$C_5H_5TiCl_3$ , namely the oxo-chloride  $[C_5H_5TiCl_2]_2O$ . In the spectrum of the complex (III) there is no band which can be assigned to a Mo-O-Mo symmetric stretch which is consistent with a linear or almost linear structure for the Mo-O-Mo group. The far-infrared spectra of complexes (I-IV), when compared with the spectra of other complexes containing Mo-Cl, Mo=O, and  $C_5H_5$ -Mo systems, are consistent with the suggested formulations. However, it is not possible to separate assignments, such as M=O deformation and Mo-Cl stretch, by inspection. Comparison of the spectra of the oxo-dichloride (I) and the dioxo-chloride (II) shows that in the former there is one band less in the region  $900\text{ cm.}^{-1}$  assignable to Mo=O stretches, and one band more in the region  $300\text{ cm.}^{-1}$ , assignable to Mo-Cl stretches. These changes are in agreement with the suggested formulations of the complexes (I) and (II).

In the spectrum of the tetraoxide (IV) the bands at  $901$  and  $925\text{ cm.}^{-1}$  may be assigned to symmetric and asymmetric Mo=O stretches; however the former band is much less intense than the latter. This anomaly is discussed below.

*Discussion.*—From the above evidence and by analogy with the structures of the  $\mu$ -oxo-chloride  $[C_5H_5TiCl_2]_2O$ , and  $C_5H_5TiCl_3$ ,<sup>2</sup> the structures (I)–(IV) are suggested for the complexes. There are two structures A and B shown for the tetraoxide (IV). Structure A is suggested on the grounds of analogy with the complex (III) and by the consideration that Mo-Mo bonds have been demonstrated in other complexes.<sup>12</sup> However, structure B provides a possible explanation of the infrared spectrum in that the bands at  $901$  and  $710\text{ cm.}^{-1}$  may be assigned to the Mo-O-Mo bridging system and the band at  $925\text{ cm.}^{-1}$  may be assigned to a Mo=O stretch. It is less satisfactory to assign the infrared spectrum in terms of structure A, in view of the marked difference in the intensity of the bands assignable to Mo=O symmetric and asymmetric stretches and the difficulty of accounting for the band at  $710\text{ cm.}^{-1}$ . Structures for complexes (III) and (IV) involving dicyclopentadienylmolybdenum systems are rejected on the grounds of the method of preparation and chemical reactions of the complexes (see Chart).

The preparation of the complexes (I)–(IV) sometimes by use of vigorous oxidising conditions, such as reaction in chloroform with pure oxygen under irradiation with ultraviolet light, demonstrates the stability of the cyclopentadienylmolybdenum system. As shown in the chart, complexes (I)–(IV) may in most cases be prepared from each other, and have similar chemistry. For example, complexes (II and III) which are formally in the 6-oxidation state are reduced by hydrogen chloride to the paramagnetic oxo-dichloride (I), which is in the 5-oxidation state. Thus, the relative stability of these complexes, both to oxidation and to hydrolysis, offers a system for the study of molybdenum-oxygen and -chlorine chemistry. There should be a considerable number of oxo- and oxohalogeno-cyclopentadienyl-complexes of the Groups IV–VII metals.

#### EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory, Lensfield Road, Cambridge. Preparations and purifications were performed under nitrogen or in a vacuum, unless otherwise stated. Long-column sublimations were done in a glass tube ( $60 \times 1.5\text{ cm.}$ ), which was sealed at one end and enclosed in a close-fitting copper tube. The bottom 5 cm. of the tube were immersed in an oil bath.

*Oxodichlorocyclopentadienylmolybdenum.*—(i) From dicarbonyl- $\pi$ -allylcyclopentadienylmolybdenum. Dicarbonyl- $\pi$ -allylcyclopentadienylmolybdenum<sup>5</sup> (1 g.) in ether (30 ml.) was treated with a stream of dry hydrogen chloride and nitrogen for 1 hr. A red-brown precipitate was formed of which the infrared spectrum showed bands assignable to terminal carbonyl-stretching frequencies. The precipitate was washed with ether (20 ml.), dried, and dissolved in chloroform (50 ml.). The solution was set aside in air for 5 min., during which time carbon monoxide was evolved. Chloroform was removed *in vacuo*; and the black residue was extracted with ether and then treated with hydrogen chloride (10 min.). The red product was separated by decantation, washed with ether and petrol, and dried *in vacuo*. The dried crystals were exposed

<sup>12</sup> Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

to moist air for 20 min., hydrogen chloride was lost, and brown crystals (yield 25%) were obtained which were finally dried in a vacuum for 1 hr. at 35° [Found: C, 24.1; H, 2.6; Cl, 29.8; Mo, 38.8; O, 6.5%; *M*(cryoscopic in benzene), 256.  $C_5H_5Cl_2MoO$  requires C, 24.2; H, 2.0; Cl, 28.7; Mo, 38.7; O, 6.5%]; *M*, 248].

Slow sublimation of the compound (10 days at 35°/10<sup>-3</sup> mm.) gave large blue-black crystals, which appeared red by transmitted light. Solutions of the blue-black crystals were yellow and their infrared spectrum was the same as for the yellow-brown form. The complex formed mixed crystals with the dioxo-chloride (II).

(ii) *From the complex*  $[C_5H_5Mo(CO)_3]_2$ . The solution from experiment (A), described below, was evaporated under reduced pressure and the residue was extracted with ether (50 ml.). The resulting solution was separated and treated with hydrogen chloride affording deep red crystals of the complex (V) from which the oxo-dichloride (yield ca. 7%) was obtained as described above.

(iii) *From tetraoxo-μ-oxodicyclopentadienyldimolybdenum.* This complex (0.5 g.) was treated with concentrated hydrochloric acid (1 ml.). A red solution and a red precipitate were formed immediately. The precipitate was separated and washed with ether, giving the red complex (V) from which the oxo-dichloride (I) (yield 60%) was obtained, as described above.

(iv) *From tetraoxodicyclopentadienylmolybdenum.* The pure dry complex (IV) was treated with excess of hydrogen chloride, affording immediately the bright red colour of the complex (V). The oxo-dichloride (yield ca. 90%) was isolated as above.

(v) *From dioxochlorocyclopentadienylmolybdenum.* The oxo-dichloro-complex (I) was obtained in 90% yield from the complex (II) using method (IV) above.

*Reactions of the Binuclear Complex*  $[C_5H_5Mo(CO)_3]_2$ .—Depending on the conditions, the reaction of the complex  $[C_5H_5Mo(CO)_3]_2$ <sup>6</sup> in chloroform with oxygen affords all the oxo- and oxochloro-complexes (I)—(IV). The products of two reactions were studied: (A) Hexacarbonyldicyclopentadienyldimolybdenum<sup>6</sup> (5 g.) in chloroform (500 ml.) was exposed to air and light for ~3 hr., the solution changed from a deep red to blue-orange. From this solution the following products (with approximate yields) could be separately isolated:  $C_5H_5MoO_2Cl$  (15%);  $C_5H_5MoOCl_2$  (7%);  $C_5H_5Mo(CO)_3Cl$  (25%);  $[C_5H_5MoO_2]_2O$  (20%);  $[C_5H_5MoO_2]_2$  (8%);  $[C_5H_5Mo(CO)_3]_2$  (15%). The isolation of these complexes is described elsewhere in the text. (B) If the above chloroform solution was left in air for two days then the only cyclopentadienyl complexes that could be isolated were the tetraoxo-μ-oxo-complex (III) and the dioxo-chloride (II) in a 20 and 25% yield, respectively.

*Dioxochlorocyclopentadienylmolybdenum.*—(i) *From the complex*  $[C_5H_5Mo(CO)_3]_2$ . The solution from experiment (B) was evaporated to dryness and the blue-black residue was extracted with ether (5 × 50 ml.). The extract was filtered, the solvent removed, and the yellow residue (yield ca. 25%) was sublimed in a long column at 35°/10<sup>-3</sup> mm. for 1 week (Found: C, 26.2; H, 2.2. Calc. for  $C_5H_5ClMoO_2$ : C, 26.2; H, 2.2%).

(ii) *From tetraoxo-μ-oxodicyclopentadienyldimolybdenum.* Complex (III) (1 g.) in chloroform (50 ml.), which was continuously purged with nitrogen, was irradiated with ultraviolet light (30 min.). The solvent was removed *in vacuo* and the residue was sublimed at 40°/10<sup>-3</sup> mm. The yellow sublimate was identified by its infrared spectrum as the dioxochloro-complex (II) (yield ca. 20%).

(iii) *From the reaction of sodium cyclopentadienide with molybdenum dioxide dichloride.* Pure molybdenum dioxide dichloride was prepared by passing a slow stream of dry oxygen over anhydrous molybdenum trichloride contained in a glass tube and heated to ca. 250°. The volatile  $MoO_2Cl_2$  readily sublimed and separated from the molybdenum trichloride and the less volatile molybdenum trioxide. A freshly prepared solution of sodium cyclopentadienide in tetrahydrofuran was slowly added to a stirred solution of molybdenum dioxide dichloride (5 g.) in tetrahydrofuran; the mixture became dark blue. The solvent was removed *in vacuo*, and the residue extracted with chloroform and left for 2 days. The solvent was removed, and the residue sublimed giving yellow crystals of the dioxo-chloro-complex (II) (yield ca. 2—20%).

*Tetraoxo-μ-oxodicyclopentadienyldimolybdenum.*—(i) *From the complex*  $[C_5H_5Mo(CO)_3]_2$ . The solution from experiment (B), described above, was evaporated to dryness, and the residue was extracted with ether (100 ml.) to remove most of the dioxo-chloride (II). The residue was then extracted with acetone (300 ml.) and the solution was concentrated; pale yellow crystals (yield ca. 25%) were precipitated, and further purified by recrystallisation (hot acetone).

(ii) *From the complex*  $[C_5H_5Mo(CO)_3]_2$  *by ultraviolet irradiation.* The complex  $[C_5H_5Mo(CO)_3]_2$

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(5 g.) in chloroform (200 ml.), through which was passing a slow stream of oxygen, was irradiated with ultraviolet light until the original dark red colour changed to greenish orange (*ca.* 45 min.). The solvent was removed *in vacuo* and the blue residue was extracted with an ether (95%)–chloroform (5%) mixture (3 × 80 ml.). The solution was filtered and concentrated slowly *in vacuo* affording pale yellow crystals. The mother-liquor, containing the dioxo-chloride (II) was decanted, and the crude crystals were washed with a little ether. Final purification by recrystallisation (hot acetone) gave large, flaky pale yellow crystals (yield *ca.* 40%) [Found: C, 30.0; H, 2.5; Mo, 47.7; O, 19.8%; *M* (by lowering of the vapour pressure of CH<sub>2</sub>Cl<sub>2</sub> solutions), 402. C<sub>10</sub>H<sub>10</sub>Mo<sub>2</sub>O<sub>8</sub> requires C, 29.9; H, 2.5; Mo, 47.7; O, 19.9%; *M*, 402].

Small yields of the tetraoxide (IV) were also formed in this reaction and were isolated as the most insoluble acetone fraction.

(iii) *From dioxochlorocyclopentadienylmolybdenum.* The latter complex (0.5 g.) was exposed for 1 week, during which the colour of the crystals changed from bright yellow to pale green-yellow. Slow sublimation of the products recovered starting product (II), and the involatile residue was recrystallised (acetone) affording pale yellow crystals of the tetraoxo- $\mu$ -oxo-complex (III) (yield 50%).

*Tetraoxidocyclopentadienylmolybdenum.*—(i) *From the complex* [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub>. The solution from experiment (A), described above, was evaporated in a vacuum and the residue was extracted with a 1 : 1 ether–acetone mixture. The remaining blue residue was then extracted with chloroform (50 ml.), the solution was filtered, and the solvent removed giving a brown scaly residue. The residue was finally recrystallised (hot acetone) (× 3) affording fine yellow-brown crystals (yield 8%) [Found: C, 31.0; H, 3.3; Mo, 49.0; O, 16.8%; *M* (by lowering of vapour pressure of CH<sub>2</sub>Cl<sub>2</sub> solutions), 406. C<sub>10</sub>H<sub>10</sub>Mo<sub>2</sub>O<sub>4</sub> requires C, 31.1; H, 2.6; Mo, 49.7; O, 16.7%; *M*, 386]. In chloroform solution, the compound (IV) slowly decomposes (2 days) forming the dioxo-chloride (II) and the tetraoxo- $\mu$ -oxo-complex (III) in good yields.

(ii) *From oxidation of tricarbonylhydridocyclopentadienylmolybdenum.* A solution of the above hydride, prepared by treating sodiotricarbonylcyclopentadienylmolybdenum (5 g.) in tetrahydrofuran (30 ml.) with glacial acetic acid (5 ml.) (see ref. 6), was treated with a stream of air for 30 min. The solvent was removed *in vacuo* and the residue was extracted with chloroform. The resulting solution was filtered and the solvent was removed *in vacuo*. The solid residue consisted of a mixture of the tetraoxo-complex (IV) and the complex [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub>. Separation was best achieved by extraction of the residue with chloroform, in which the tetraoxo-complex formed a suspension, whilst the complex [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub> remained at the bottom of the solution. The suspension was decanted and the tetraoxo-complex was filtered off. The crude tetraoxo-residue was extracted with carbon tetrachloride to remove traces of [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>]<sub>2</sub> and finally recrystallised from chloroform and then acetone, to give the complex (yield *ca.* 10%).

*Infrared Spectra.*—Measurements were made with a Perkin-Elmer model 21 spectrometer. The data and conditions of measurements are given in Table 1.

*Magnetic Susceptibility.*—Measurements were made with a standard Gouy balance relative to K<sub>3</sub>[Fe(CN)<sub>6</sub>] = 6.99 × 10<sup>-6</sup> at 20°. The susceptibility of the complex C<sub>5</sub>H<sub>5</sub>MoOCl<sub>2</sub> was also determined by using the method of Evans<sup>13</sup> and the results were in agreement with the value already quoted.

*Electron Spin Resonance Spectra.*—Measurements were made on a Varian 100 Kc. e.p.r. spectrometer operating at a microwave frequency of 9000 Mc./sec. with a Varian 6 in. magnet at -195°. Samples of the pure solid in a quartz tube were used.

*Proton Magnetic Resonance Spectra.*—Measurements were made on a Perkin-Elmer spectrometer at 40 Mc./sec. at room temperature. Samples were made up in deuteriochloroform and results are given relative to tetramethylsilane as an internal standard (Found: [C<sub>5</sub>H<sub>5</sub>MoO<sub>2</sub>]<sub>2</sub>O,  $\tau$  = 3.39. [C<sub>5</sub>H<sub>5</sub>MoO<sub>2</sub>]<sub>2</sub>,  $\tau$  = 3.68. C<sub>5</sub>H<sub>5</sub>MoO<sub>2</sub>Cl,  $\tau$  = 3.40).

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<sup>13</sup> Evans, J., 1959, 2003.