## MONONUCLEAR AND DINUCLEAR TERTIARY PHOSPHINE MOLYBDENUM COMPLEXES. OXO-MOLYBDENUM(IV), DINUCLEAR M0<sub>2</sub>Cl<sub>4</sub>L<sub>4</sub> AND RELATED DERIVATIVES

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Abstract—Green and blue isomers of the oxo derivative  $MoOCl_2(PMe_3)_3$  have been obtained by an oxygen-atom abstraction reaction between  $MoCl_4(thf)_2$  and equimolar amounts of water in the presence of PMe<sub>3</sub>. Methathesis with KX(X = NCO, NCS) yields  $MoOX_2(PMe_3)_3$  and with  $NaS_2CNEt_2$ ,  $MoO(S_2CNEt_2)_2(PMe_3)$ . The latter complex readily loses PMe<sub>3</sub> to give  $MoO(S_2CNEt_2)_2$  from which it can be prepared by addition of the phosphine ligand.

Reaction of the blue purple complex,  $MoCl_3(thf)_3$  (I), with excess PMe<sub>3</sub> gives *mer*-MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> which loses PMe<sub>3</sub> on heating in toluene to afford  $[MoCl_3(PMe_3)_2]_2$ . Reduction of (I) with phosphines and zinc in tetrahydrofuran gives the dinuclear molybdenum(II) halide complexes  $Mo_2Cl_4L_4$  (L = PMe<sub>3</sub>, PEt<sub>3</sub>, PhMe<sub>2</sub>Ph, PEt<sub>2</sub>Ph; L<sub>2</sub> = dppm), while Znacetic acid reduction yields  $Mo_2(CO_2Me)_4$ . Interaction of the chlorocarbonyl species  $MoCl_2(CO)_2(PMe_3)_3$  with Tl(acac) affords  $Mo(acac)Cl(CO)(PMe_3)_3$  which has an unusually low C–O stretching frequency for a terminal carbonyl group (1755 cm<sup>-1</sup>).

Previous work from our laboratories has resulted<sup>1</sup> in the preparation of a variety of tertiary phosphine derivatives of group VI metals. More recently<sup>2</sup> we have reported the isolation and structural characterisation of the oxotungsten species WOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and related complexes. As an extension of this work we report the facile conversion of the molybdenum(IV) adduct MoCl<sub>4</sub>(thf)<sub>2</sub> to the oxo complex MoOCl<sub>2</sub>(PMe<sub>3</sub>), by oxygen abstraction from water in wet acetone or tetrahydrofuran in the presence of trimethylphosphine. We also report additional chemistry of MoCl<sub>3</sub>(thf)<sub>3</sub> (I), which relates to its reduction to dinuclear complexes containing the  $Mo_2^{4+}$  core. Although this unit may be generated by different procedures<sup>3-6</sup> and several methods are now available for preparing the molybdenum(II) halide complexes,<sup>7</sup>

 $Mo_2X_4L_4$  (L = phosphine), no simple high yield route has however been devised for reduction in non-aqueous media of higher oxidation state molybdenum halides without metal-metal bonds. The reactions leading to the complexes studied in this work are shown in the Scheme.

### **RESULTS AND DISCUSSION**

(a) Oxomolybdenum(IV) complexes

Several synthetic methods have been devised for the preparation of oxomolybdenum(IV) complexes. These include oxygen abstraction by phosphine from dioxomolybdenum(VI) complexes,<sup>8</sup> reaction of a high oxidation state molybdenum halide with alcohol in the presence of the appropriate ligand<sup>8,9</sup> and ligand addition or displacement reaction of oxomolybdenum(IV) complexes.<sup>8-11</sup> As an extension of our earlier work on oxotungsten(IV) complexes, we have now prepared the trimethylphosphine derivative MoOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> by the reaction of MoCl<sub>4</sub>(thf)<sub>2</sub> with equimolar amounts of water in the presence of an excess of

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(i) dppm; (ii) excess PMe<sub>3</sub> in thf; (iii) reflux toluene; (iv) NaCO<sub>2</sub>Me in thf; (v) Zn and MeCO<sub>2</sub>H; (vi) phosphine and Zn in thf; (vii) PEt<sub>2</sub>Ph and Zn in thf; (viii) dppm and Zn in thf, 12 hr, in CH<sub>2</sub>Cl<sub>2</sub>, 4 hr; (ix) see references 6 and 7; (x) H<sub>2</sub>O, PMe<sub>3</sub> in thf; (xi) KX (X = OCN, SCN) in thf; (xii) NaS<sub>2</sub>CNEt<sub>2</sub>, excess PMe<sub>3</sub>.

Scheme. Some reactions of mer-[MoCl<sub>3</sub>(thf)<sub>3</sub>] and [MoCl<sub>4</sub>(thf)<sub>2</sub>].

PMe<sub>3</sub> according to the equation.

$$\begin{aligned} \text{MoCl}_4(\text{thf})_2 + \text{H}_2\text{O} + 5 \text{ PMe}_3 \xrightarrow{\text{thf}} \text{MoOCl}_2(\text{PMe}_3)_3 \\ &+ 2[\text{Me}_3\text{PH}]\text{Cl}. \end{aligned}$$

Interaction of MoCl<sub>4</sub>(thf)<sub>2</sub> with trimethylphosphine in slightly wet acetone or thf at 50°C for 5-6 hr yielded a green solution from which green crystals of the diamagnetic MoOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> were isolated. In some instances the reaction carried out under apparently identical conditions, gave a blue solution from which blue crystals of the same stoichiometry and spectral properties as the green complex were obtained. Although for other related  $MoOCl_2L_3$  complexes<sup>9</sup> the green isomers irreversibly convert to the blue complexes in warm organic solvents, green MoOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> seems to be the more stable of the two forms and we have been unable to ascertain the conditions under which the blue complex is generated. The IR spectrum of both isomers shows a strong absorption at 940  $cm^{-1}$  due to coordinated PMe<sub>3</sub> with a shoulder at *ca.* 960 cm<sup>-1</sup> possibly due to v(Mo=O). While for other MoOCl<sub>2</sub>L<sub>3</sub> complexes<sup>9</sup> the green isomers show v(Mo=O) at slightly lower values than the blue ones, the overlapping of the PMe<sub>3</sub> and M=O bands in MoOCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> makes difficult the precise determination of the Mo-O stretching frequency in the two isomers.

The <sup>1</sup>H NMR spectrum shows a pattern of five lines due to the  $PMe_3$  protons, from which the components of a virtually-coupled triplet centred at  $\delta$  1.55 and of a doublet at 1.45 ppm can be clearly distinguished. This is consistent with *mer*-PMe<sub>3</sub> groups and by analogy with other similar



complexes *cis* chloride ligands; the structure is probably as in (1).

Interaction of the complex with KNCO and KNCS yielded the corresponding blue crystalline metathesis products  $MoOX_2(PMe_3)_3$ , (X = NCO, NCS); green isomers were not observed. Although the NCS derivative gives a distinct IR absorption at *ca*. 955 cm<sup>-1</sup> due to v(Mo = O), for the cyanate derivative the presence of an oxo group could only be inferred from the asymmetry of the strong band at 940 cm<sup>-1</sup> and the presence of a small shoulder at 960 cm<sup>-1</sup>. Both complexes have two strong bands at 2210 and 2170 cm<sup>-1</sup> (NCO) and 2050 and 2020 cm<sup>-1</sup> (NCS) due to v(C-N) of the NCX ligands, thus confirming the structure type 1.

In contrast to the stability of the oxotungsten complexes  $WO(S_2CNR_2)_2(PMe_3)$  towards dissociation of the phosphine ligand, the molybdenum analogues readily lose PMe<sub>3</sub> in solution to give  $MoO(S_2CNR_2)_2$ . Thus the interaction of  $MoOCl_2(PMe_3)$  with anhydrous  $NaS_2CNEt_2$ yielded mainly the 5-coordinate oxo complex  $MoO(S_2CNEt_2)_2$ . Synthesis of the phosphine adduct  $MoO(S_2CNEt_2)_2PMe_3$  requires the presence of an excess of PMe<sub>3</sub> to solutions of  $MoO(S_2CNEt_2)_2$ ; it forms green crystals moderately stable to air that can be kept at room temperature for several days under nitrogen without apparent conversion to  $MoO(S_2CNEt_2)_2$ . The room temperature 'H NMR spectrum shows broad resonances for the methylene (3.6 ppm, q) and methyl (1.0 ppm, t,  ${}^{3}J_{\text{H-H}} = ca.$  7 Hz) dithiocarbamate protons, and a broad doublet at 1.3 ppm ( ${}^{2}J_{\text{P-H}} = ca.$  9 Hz) for the phosphine ligand.

# (b) Reactions of $MoCl_3(thf)_3$ and its reduction to the $Mo_2^{4+}$ core

In earlier work,<sup>1a</sup> we obtained the complex  $MoCl_3(PMe_3)(thf)_2$  by reaction of  $MoCl_3(thf)_3$  with one equivalent of PMe<sub>3</sub> while an excess gave  $MoCl_3(PMe_3)_3$ .<sup>1b</sup> The *tris* (phosphine) complex, prepared from blue-purple<sup>12,13</sup>  $MoCl_3(thf)_3$  is a yellow solid which slowly decomposes above 55°C under N<sub>2</sub>, finally melting at 160°C. The IR spectrum shows bands at 340 and 290 cm<sup>-1</sup> while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of a doublet and a triplet (ratio 2:1) characteristic of a *mer* configuration of phosphines. It may be noted that two forms of  $MoCl_3(PMe_2Ph)_3$  are obtained on reaction of orange  $MoCl_3(thf)_3$  with  $PMe_2Ph$ .<sup>12</sup>

On refluxing in toluene *mer*-MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> loses PMe<sub>3</sub> to form a diamagnetic red solid of stoichiometry [MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sub>n</sub>. This appears to be the chloro bridged dimeric species (**2a**, **b**) based on the molecular weight. By contrast, MoCl<sub>3</sub>(thf)<sub>3</sub> on refluxing with PEt<sub>3</sub> has been shown to give an uncharacterised species, MoCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>, while





PEt<sub>2</sub>Ph formed  $Mo_2Cl_6(PEt_2Ph)_3$  thought to be derived from the  $Mo_2Cl_9^{3-}$  core.<sup>12</sup>

The reaction of 1,2-diphenylphosphinomethane (dppm) with (I) gave a red purple solid which analysed as  $MoCl_3(dppm)$  and showed a magnetic moment of 1.79 BM consistent with magnetically dilute  $Mo^{III}$  centres suggesting the existence of weak Mo–Mo bonds. The complex has not been characterised further on account of its insolubility and inability to replace dppm with other phosphines. However, the IR spectrum is similar to that of  $Mo_2Cl_6(dppe)_2^{14}$  prepared from  $Mo_2Cl_6(MeCN)_3$  of which analogous complexes exhibit intermetallic bonding.<sup>15</sup>

During attempts to prepare MoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> we found that the reaction of (I) in thf with excess PMe<sub>3</sub> in the presence of granular zinc over long periods gave, after extraction of mer- $MoCl_3(PMe_3)_3$  small amounts of a blue complex. Repetition with zinc powder gave a green solution from which  $Mo_2Cl_4(PMe_3)_4$  identical to a sample prepared from (NH<sub>4</sub>)<sub>5</sub>Mo<sub>2</sub>Cl<sub>9</sub>·H<sub>2</sub>O was obtained. The dinuclear molybdenum(II) complex could similarly be prepared from mer-MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. Subsequent reactions with PEt<sub>3</sub>, PMe<sub>2</sub>Ph, PEt<sub>2</sub>Ph gave the respective  $Mo_2Cl_4L_4$  complexes, while dppm yielded Mo<sub>2</sub>Cl<sub>4</sub>(dppm)<sub>2</sub> (see Table 1). PPh<sub>3</sub> gave a yellow gum which failed to solidify.

Complex	Yield (%)	С	н	CŁ	P
Mo2 <sup>C#4(PMe3)4</sup>	63	22.8	5.8	22.3	20.2
		(22.4)	(5.7)	(22.1)	(19.9)
Mo2 <sup>C\$4(PEt3)</sup> 4	68	36.1	7.6	17.5	15.9
		(35.8)	(7.5)	(17.6)	(15.4)
Mo <sub>2</sub> CL <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>4</sub>	69	43.7	5.3	16.5	14.1
		(43.4)	(5.0)	(16.0)	(14.0)
Mo <sub>2</sub> CL <sub>4</sub> (PEt <sub>2</sub> Ph) <sub>4</sub>	64	47.8	6.1	13.9	12.1
		(48.1)	(6.1)	(14.2)	(12.4)
Mo <sub>2</sub> C\$ <sub>4</sub> (dppm) <sub>2</sub> ,3CH <sub>2</sub> C\$ <sub>2</sub>	82	46.5	3.8	26.3	9.3
		(46.9)	(3.7)	(26.1)	(9.1)

Table 1. Analytical data for Mo<sub>2</sub>Cl<sub>4</sub>P<sub>4</sub> complexes prepared from mer-MoCl<sub>3</sub>(thf)<sub>3</sub>

In light of these reactions it seemed possible that molybdenum(II) acetate could be prepared by the reductive procedure. Stirring a solution of (I) in acetic acid with zinc powder gave a green solution which darkened to yellow brown under reflux and after cooling deposited  $Mo_2(CO_2Me)_4$ . As yet the nature of the green intermediate formed during the reaction, or, alternatively, by reacting (I) with NaOAc in thf, has not been fully established. The poorly soluble material obtained from the latter reaction analysed closely to  $Mo_2(CO_2Me)_4Cl$  and showed an identical IR spectrum to  $Mo_2(OAc)_4$ . While an  $Mo^{II}$ — $Mo^{III}$  core could be proposed, the diamagnetism suggests a higher polymeric species.

The above reactions indicate that molybdenum(III) may be readily reduced to dinuclear molybdenum(II) under the appropriate conditions. Although large scale preparations have not been carried out the method would seem to offer a viable alternative route to the  $Mo_2^{4+}$  core considering the ease of preparing the starting material  $MoCl_3(thf)_3$ .<sup>13</sup>

As noted earlier<sup>16</sup> the complex trans-MoCl<sub>2</sub>  $(PMe_3)_4$  can be easily carbonylated to the sevencoordinate derivative MoCl<sub>2</sub>(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>. While the reaction of the latter complex with sulphur chelating ligands is always accompanied by the loss of one or two of the coordinated phosphines to afford  $Mo(S_2CNR_2)_2(CO)_n(PMe_3)_{3-n}^{16}$  (n = 1, 2), the interaction with Tl(acac) yields a complex of composition Mo(acac)Cl(CO)(PMe<sub>3</sub>)<sub>3</sub>. The IR spectrum shows two sharp bands at 1570 and 1515 cm<sup>-1</sup> due to vibrations derived from the acac group and a strong absorption at  $1755 \text{ cm}^{-1}$  that indicates the presence of a carbonyl ligand. The unusually low frequency of this band suggests strong  $\pi$ -back donation from the metal to the CO  $\pi^*$  orbitals. Although the band position lies in the bridging CO region the complex is monomeric by cryoscopic molecular weight determinations thus eliminating a dinuclear formulation; other related complexes<sup>16</sup> having terminal CO groups have v(C-O) in the range 1760–1735 cm<sup>-1</sup>. In accord with the above formulation, the <sup>1</sup>H NMR shows a sharp singlet at  $\delta$  2.1 ppm and a slightly broad singlet at  $\delta$  5.7 ppm for the acac methyl and methyne protons (6:1). The phosphine ligands give rise to a filled-in doublet almost a pseudo triplet and a doublet at 1.6 and 1.2 ppm, (18:9 respectively). The first arises from two equivalent PMe<sub>3</sub> molecules with intermediate coupling between the phosphorus nuclei and the second to a unique phosphine cis with respect to the others. Due to the structural complexity inherent to sevencoordination chemistry<sup>17</sup> an unique stereochemical assignment cannot be made with the present data.

### **EXPERIMENTAL**

Microanalyses were by Pascher (Bonn) and Imperial College microanalytical laboratories.

Spectrometers. IR Perkin–Elmer 577 and 597. Spectra (cm<sup>-1</sup>) in Nujol mulls. NMR Perkin– Elmer R-12A and R32 (<sup>1</sup>H 60 and 90 MHz), Varian XL100-12 (<sup>31</sup>P 40.5 MHz). <sup>1</sup>H NMR data in  $C_5H_6$  at 35°C unless otherwise specified. <sup>31</sup>P data references to external 85% H<sub>3</sub>PO<sub>4</sub>.

All operations were performed under oxygenfree nitrogen; solvents were dried over sodium or calcium hydride and distilled prior to use. Melting points were determined in sealed tubes under nitrogen and are uncorrected. MoCl<sub>3</sub>(thf)<sub>3</sub> was prepared according to the literature method<sup>13</sup> except that the reaction was prolonged to give the bluepurple isomer. MoCl<sub>4</sub>(thf)<sub>2</sub> and MoO(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> were also obtained as already reported.<sup>13,18</sup> For comparison the Mo<sub>2</sub>Cl<sub>4</sub>L<sub>4</sub> complexes (L = PMe<sub>3</sub>, PEt<sub>3</sub>, PMe<sub>2</sub>Ph, PEt<sub>2</sub>Ph) were prepared from (NH<sub>4</sub>)<sub>5</sub>Mo<sub>2</sub>Cl<sub>9</sub>.H<sub>2</sub>O.<sup>7b,c</sup> Petroleum used had b.p. 40-60°C.

Magnetic susceptibility measurements were made at ambient temperature on a Gouy balance constructed by Prof. D. F. Evans, F.R.S.

Oxodichlorotris (trimethylphosphine) molybdenum (IV) (Green isomer). Trimethylphosphine (1.3 cm<sup>3</sup>, ca. 13 mmol) and a few drops of oxygen-free water were added to a suspension of  $MoCl_4(thf)_2$  (1 g, ca. 2.6 mmol) in thf (40 cm<sup>3</sup>), and the mixture stirred at 50°C for 5–6 hr. (A large excess of water should be avoided otherwise considerable decomposition takes place.) The solution was filtered, evaporated and the residue extracted with EtOH (15 cm<sup>3</sup>). Centrifugation, partial removal of the solvent *in* vacuo and cooling at  $-25^{\circ}$ C afford the complex as green crystals in ca. 60% yield. [Found: C, 26.0; H, 6.6. C<sub>9</sub>H<sub>27</sub>OCl<sub>2</sub>P<sub>3</sub>Mo requires C, 26.3; H, 6.6%]. IR 1410s, 1295m, 1275s, 960sh, 940s, 850m,

840sh, 730s, 665m.

NMR <sup>1</sup>H:  $\delta$  1.45 (1) d (<sup>2</sup> $J_{P-H} = 8$  Hz); 1.55 (2) t (<sup>2</sup> $J_{P-H} = ca. 4$  Hz).

In some instances the above reaction carried out under apparently the same conditions, yielded a blue solution from which blue crystals of a complex analysing for MoOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and having IR and 'H NMR spectra identical to those of the green isomer were isolated. [Found: C, 26.2; H,  $6.7. C_9H_{27}OCl_2P_3Mo$  requires C, 26.3; H, 6.6%].

Oxobis(cyanato)tris(trimethylphosphine)molybdenum(IV). MoOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (0.41 g, ca. 1 mmol) and dry (100°C, 24 hr) KNCO (0.32 g, excess) were stirred at room temperature in thf (30 cm<sup>3</sup>) for 9–10 hr. The suspension was centrifuged and the solution evaporated. Crystallisation of the residue from EtOH (10 cm<sup>3</sup>) at -20°C overnight afforded blue crystals. Yield *ca.* 70%. [Found: C, 30.3; H,  $6.4. C_{11}H_{27}O_3O_3N_2P_3Mo$  requires C, 31.3; H, 6.4%].

IR 2210s, 2170s, 1415m, 1330m, 1300m, 1280m, 960sh, 940s, 850m, 725s; 665m, 615s, 580w.

NMR <sup>1</sup>H:  $\delta$  1.27 (1) d (<sup>2</sup> $J_{P-H} = 8$  Hz); 1.31 (2) t (<sup>2</sup> $J_{P-H} = ca. 4$  Hz).

A similar metathesis with KSCN gave small blue crystals of MoO(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> from EtOH at  $-25^{\circ}$ C in *ca.* 60% yield. [Found: C, 28.5; H, 5.8. C<sub>11</sub>H<sub>27</sub>OS<sub>2</sub>N<sub>2</sub>P<sub>3</sub>Mo requires C, 28.9; H, 5.9%].

IR 2050s, 2020s, 1405m, 1300m, 1280m, 1255w, 995s, 940s, 845m, 835m, 725s, 665w.

NMR: <sup>1</sup>H(CH<sub>2</sub>Cl<sub>2</sub>, 35°C):  $\delta$  1.65 (2) t (<sup>2</sup> $J_{P-H} = ca. 4$  Hz); 1.68 (1) d (<sup>2</sup> $J_{P-H} = 8$  Hz).

Oxobis(N, N-diethyldithiocarbamato)trimethylphosphine molybdenum(IV). To a stirred suspension of MoO(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> (O.4 g, ca. 1 mmol) in Et<sub>2</sub>O (15 cm<sup>3</sup>) an excess of PMe<sub>3</sub> (0.3 cm<sup>3</sup>, ca. 3 mmol) was added dropwise. The mixture was stirred for 10 min at room temperature then centrifuged and the resulting solution concentrated in vacuo; cooling at  $-25^{\circ}$ C overnight afforded green needles. Yield: ca. 50% [Found: C, 32.3; H, 5.9. C<sub>13</sub>H<sub>29</sub>OS<sub>4</sub>N<sub>2</sub>PMe requires C, 32.3, H, 5.9%].

IR 1480s, 1350s, 1295m, 1270s, 1205s, 1140s, 1090mm, 1070m, 1065sh, 1000m, 985sh, 945sh, 930s, 910sh, 840m, 775m, 665w.

NMR. <sup>1</sup>H:  $\delta$  1.0 (12) *bt* (<sup>3</sup>J<sub>H-H</sub>7 Hz); 1.6 (9) *bd* (<sup>2</sup>J<sub>P-H</sub> = 9 Hz); 3.6 (8) *bq*.

Chloro (2, 4-pentanedionato)carbonyltris (trimethylphosphine)molybdenum(II). A solution of  $MoCl_2(CO)_2(PMe_3)_3$  (0.5 g, ca. 1 mmol) in acetone or tetrahydrofuran (40 cm<sup>3</sup>) was treated with Tl (acac) (0.6 g, ca. 2 mmol) at 50–60°C overnight. The colour of the solution changed from yellow to red. The solvent was stripped under vacuum and the residue crystallised from petroleum at  $-25^{\circ}C$ to give red crystals which were collected and dried in vacuo. Yield, 0.2 g, 40%. This preparation is not reproducible and in four more attempts only one further crop of crystals could be obtained. [Found: C, 37.2; H, 6.9; Cl 7.0.  $C_{15}H_{34}O_3ClP_3Mo$  requires C, 37.0; H, 7.0; Cl 7.2%].

IR 1755s, 1570s, 1515s, 1420m, 1300m, 1280m, 1265m, 1200w, 1020w, 950s, 855w, 780w, 725m, 720m, 715m, 665m, 560m.

NMR. <sup>1</sup>H:  $\delta$  1.20 d (<sup>2</sup>J<sub>P-H</sub> = 8 Hz); 1.6 "filled-in" doublet (<sup>2</sup>J<sub>P-H</sub> = 10 Hz); 2.10 s; 5.7 s.

Trichloro (1,2 - diphenylphosphinomethane)dimolybdenum(III). Trichlorotris(tetrahydrofuran)molybdenum(III) and excess diphenylphosphinomethane were heated to the melting point of the diphosphine for 10 mins giving a purple solution. On cooling the solid was washed repeatedly with hot toluene leaving the complex as a purple solid. Yield ca. 100%. [Found: C, 50.9; H, 3.7; Cl, 18.7; P, 10.5.  $C_{50}H_{44}Cl_6P_4Mo_2$  requires C, 51.2; H, 3.8; Cl 18.1; P, 10.6%].  $\mu_{eff} = 1.79$  BM.

IR. 340m, 328s, 314s, 260w.

The complex dissolved very slighly in  $CH_2Cl_2$ but is insoluble in other solvents. Phosphine exchange does not occur on refluxing with  $PMe_2Ph$ or PEt<sub>3</sub> in thf or  $CH_2Cl_2$ .

mer - Trichlorotris (trimethylphosphine)molyb denum(III). This complex was prepared by a slight modification of the procedure already described.<sup>7b</sup> Details were as follows: trimethylphosphine (8 cm<sup>3</sup>, 72.7 mmol) was added to a suspension of MoCl<sub>3</sub>(thf)<sub>3</sub> (10 g, 23.9 mmol) in Et<sub>2</sub>O (450 cm<sup>3</sup>) and the mixture stirred for 24 hr. A grey solid was removed by filtration and the yellow-brown solution evaporated until crystallisation began. On cooling to  $-78^{\circ}$ C the complex was deposited as yellow crystals. Yield: 9.2 g, 89%; m.p. decomp. 55°C finally melting *ca*. 160°C. [Found: C, 25.3; H, 6.4; Cl 24.5; P, 21.2. C<sub>9</sub>H<sub>27</sub>Cl<sub>3</sub>P<sub>3</sub>Mo requires C, 25.1; H, 6.32; Cl, 24.7; P, 21.6%].

IR 330s, 280w.

NMR <sup>31</sup>P{<sup>1</sup>H}:  $\delta$  -63.25 (2), d, <sup>2</sup> $J_{P-P} = 24.5$  Hz; -69.3 (1) t, <sup>2</sup> $J_{P-P}$  24.5 Hz.

Di -  $\mu$  - chlorotetrachlorotetrakis(trimethylphos phine)dimolybdenum(III). mer-Trichlorotris(trimethylphosphine)molybdenum(III) (1.0 g) was refluxed in toluene (50 cm<sup>3</sup>) for 12 hr, the cooled solution filtered and the volume reduced to give a dark red solid which was collected and washed with cold Et<sub>2</sub>O. Yield: 0.68 g, 83%; m.p., decomp. > 85°C. [Found: C, 21.3; H, 5.2; Cl 29.3; P, 17.3. C<sub>12</sub>H<sub>36</sub>Cl<sub>6</sub>P<sub>4</sub>Mo<sub>2</sub> requires C, 20.4; H, 5.1; Cl 3.1; P, 17.5%. M, 652 (708)].

IR 324m, 268w.

Tetrachlorotetrakis(trimethylphosphine)dimolybdenum(II). Trimethylphosphine (1.0 cm<sup>3</sup>, 9 mmole) in thf (60 cm<sup>3</sup> was added to MoCl<sub>3</sub>(thf)<sub>3</sub> (1 g, 2.3 mmol) and zinc powder (0.6 g, 9.2 mmol; prewashed with thf) and the mixture stirred overnight. The solution was filtered, the solvent removed and the green gum washed with cold petroleum. After dissolving in benzene (50 cm<sup>3</sup>) and removing of a white solid, the solvent was stripped and the residue washed with cold methanol  $(2 \times 20 \text{ cm}^3)$ . The residual blue solid was dissolved in toluene (30 cm<sup>3</sup>), the volume reduced and the solution cooled at  $-30^{\circ}$ C to give the blue complex. Yield: 0.48 g, 63%, m.p., decomp. > 245°C. [Found: C, 22.8; H, 5.8; Cl 22.3; P, 20.2. C12H36Cl4P4M02 requires C, 22.4; H, 5.7; Cl 22.1; P, 19.9%. M, 625 (638)].

Trichlorotris (diethylphenylphosphine) molybdenum(III) and tetrachlorotetrakis (diethylphenylphosphine) dimolybdenum(II). Diethylphenylphosphine  $(2 \text{ cm}^3)$  in thf (60 cm<sup>3</sup>) was added to MoCl<sub>3</sub>(thf)<sub>3</sub> (1 g, 2.3 mmol) and zinc powder (0.6 g, 9.2 mmol). After stirring for 4 hr the mixture was filtered and the solution evaporated. The green gum was washed with petroleum  $(4 \times 10 \text{ cm}^3)$  to remove excess phosphine, then with methanol  $(2 \times 10 \text{ cm}^3)$  and the residue recrystallised from toluene/MeOH (1:1) to give MoCl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>3</sub> as a yellow crystalline solid. Yield: 0.72 g, 43%, m.p., 116°C. [Found: C, 51.4; H, 6.5; Cl 15.1; P, 13.3. C<sub>30</sub>H<sub>45</sub>Cl<sub>3</sub>P<sub>3</sub>Mo requires C, 51.4; H, 6.5; Cl 15.2; P, 13.3% *M*, 480 (700)].

The methanol extracts from above were reduced in volume and cooled at  $-30^{\circ}$ C to give tetrachlorotetrakis(diethylphenylphosphine)dimolybdenum(II) as a blue powder which was washed with cold methanol (2 × 5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.44 g, 37%. [Found: C, 47.8; H, 6.1; Cl, 13.9; P, 12.1. C<sub>40</sub>H<sub>60</sub>Cl<sub>4</sub>P<sub>4</sub>Mo<sub>2</sub> requires C, 47.9; H, 6.0; Cl, 14.2; P, 12.7%].

Repetition of the reaction with stirring for 24 hr gave a blue solution which was filtered from the solid and the solvent removed. The gum remaining was washed with petroleum  $(2 \times 20 \text{ cm}^2)$  and cold methanol  $(2 \times 10 \text{ cm}^3)$  to give the dimolybdenum complex (0.68 g, 5.7%) as a blue solid, identical in properties with a sample prepared from  $(NH_4)_5Mo_2Cl_9.H_2O$ .

Tetra-acetato)dimolybdenum(II). Degassed glacial acetic acid (50 cm<sup>3</sup>) was added to  $MoCl_3(thf)_3$ (1 g, 2.4 mmole) and zinc powder (0.8 g, 12.2 mmol) and the mixture stirred under reflux until a homogeneous solution was obtained. On cooling tetra(acetato)dimolybdenum(II) precipitated as yellow crystals which were collected and dried. Yield: 0.42 g, 41%.

The solvent was removed from the filtrate and the residue washed with cold thf  $(5 \text{ cm}^3)$  and diethyl ether  $(2 \times 10 \text{ cm}^3)$  to give a green solid which could not be obtained pure.

A similar product analysing as  $Mo_2(O_2CMe)_4Cl$ was obtained as follows: Tetrahydrofuran (50 cm<sup>3</sup>) was added to MoCl<sub>3</sub>(thf)<sub>3</sub> (0.92 g, 2.2 mmol) and sodium acetate (0.54 g, 6.6 mmol) and the solution refluxed for 4 hr and allowed to stand overnight. After filtering the solution and reducing the solvent volume, the complex precipitated as a green solid which was collected, washed with cold thf (5 cm<sup>3</sup>) followed by Et<sub>2</sub>O (2 × 10 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.36 g, decomp. > 110°C. [Found: C, 20.1; H, 2.9; Cl, 8.3; O, 27.4. C<sub>8</sub>H<sub>12</sub>O<sub>8</sub>ClMo<sub>2</sub> requires C, 20.7; H, 2.6; Cl, 7.7; O, 27.6%]. The diamagnetic complex is slightly soluble in thf; the IR spectrum is identical with that of  $Mo_2(CO_2Me)_4$ . Acknowledgement—We thank the Spanish C.A.I.C.Y.T. (E.C.) and the S.E.R.C. (A.J.N.) for support.

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