Preparation of Trichlorotris(tetrahydrofuran)molybdenum(III) and its Use in the Preparation of Complexes of Molybdenum-(III) and -(0)

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The synthesis of trichlorotris(tetrahydrofuran)molybdenum(III) is described. This complex reacts with tertiary phosphines (PR_3, R = alkyl or aryl) to yield $[MoCl_3(PR_3)_3]$, $[MoCl_3(thf)(PR_3)_2]$, or $[MoCl_3(thf)_2(PR_3)]$ (thf = tetrahydrofuran) depending on the size of R. Some binuclear complexes have also been isolated. The complex $[MoCl_3(thf)_3]$ reacts with various phosphines and magnesium or sodium amalgam in the presence of nitrogen to form molybdenum(0) complexes including $[Mo(N_2)_2(PMe_2Ph)_4]$, $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$, $[Mo(PH_2Ph)_6]$, and $[Mo(Ph_2PCH_2PPh_2)_3]$.

In our development of the chemistry of molybdenum and tungsten halido-complexes with tertiary phosphine and arsine ligands we prepared[1,2] a series of derivatives in which the oxidation state of the metal was IV and reduced these to yield complexes of zero oxidation state such as $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$.[3] During these reductions, we prepared, incidentally, derivatives of tungsten(II) and molybdenum(II), but no derivatives in oxidation state III. This oxidation state is of particular interest because it may be active in biological nitrogen-fixing systems.[4] The present work was undertaken in order to characterise tertiary phosphine complexes of molybdenum(III) and to investigate the interactions of molybdenum in low oxidation states with unsaturated ligands such as olefins and dinitrogen.

RESULTS AND DISCUSSION

The complex $[MoCl_4(NCEt)_2]$, (I), is a useful starting material for the preparation of molybdenum(IV) derivatives,[1] but we could not reduce it cleanly to $[MoCl_3(NCR)_3]$ (R = alkyl). This substance is already known, having been prepared from $[Mo_2Cl_9]^{3-}$ and the alkyl cyanide.[5] Reduction of (I) using a tertiary phosphine (PR_3) and RCN yielded $[MoCl_3(NCR)(PR_3)_2]$, (II) [reaction series (1)]. Complexes (II) showed a weak band in the range 2 260—2 280 cm^{-1} in the i.r. spectrum,

$$[Mo_2Cl_{10}] \xrightarrow{RCN} \underset{(I)}{[MoCl_4(NCR)_2]} \xrightarrow{PR_3}$$

$$[MoCl_4(PR_3)_2] \xrightarrow{RCN} \underset{(II)}{[MoCl_3(NCR)(PR_3)_2]} \quad (1)$$

assignable to ν(C≡N). We were unable to replace the organic cyanide in (II) by tertiary phosphines and this approach to the problem was abandoned; representative complexes of type (II) are listed in Table 1.

Nevertheless we were able to convert (I) into $[MoCl_3(thf)_3]$, (III) (thf = tetrahydrofuran), by the reaction series (2), and this material provided an excellent source of other molybdenum(III) complexes. Complex

$$[Mo_2Cl_{10}] \xrightarrow{EtCN} \underset{(I)}{[MoCl_4(NCEt)_2]} \xrightarrow[25\,°C]{thf}$$

$$[MoCl_4(thf)_2] \xrightarrow[\substack{thf,\,0\,°C,\\ Zn}]{CH_2Cl_2} \underset{(III)}{[MoCl_3(thf)_3]} \quad (2)$$

(III) is an orange-pink, air-sensitive, solid with a magnetic moment in the solid state at 20 °C of 3.63 B.M.,† which is within the range found for Mo^{III}.[6] The far-i.r. spectrum (Nujol mull) has an intense broad band centred at *ca.* 325 cm^{-1} and a weaker band at 266 cm^{-1}, but these are not diagnostic of a given configuration because both metal–oxygen and metal–chlorine frequencies are expected in this region. The complex is slightly soluble in thf and the solutions are stable, though very sensitive to air. In other solvents loss of thf occurs, and, consequently, polymerisation. Thus, in benzene, $[MoCl_3(thf)_3]$ dissolves to give a red solution, which deposits a pinkish red, diamagnetic, solid during several hours. Its i.r. spectrum (4 000—400 cm^{-1}) is very similar to that of (III), and so the complex does not contain benzene. Below 400 cm^{-1} there are several changes, the principal peaks being at 352vs, 320(sh), 310s, and 252m cm^{-1}. The analysis is best represented

TABLE 1

Products of the reaction * of $[MoCl_3(thf)_3]$, (III), with tertiary phosphines, PR_3

PR_3	Value of *n* in $[MoCl_3(thf)_{3-n}(PR_3)_n]$
PPh_3	2
$P(CH_2CH_2CH{:}CH_2)Ph_2$	2
$P(CH_2CH{:}CH_2)Ph_2$	2
$PEtPh_2$	2, 1
$PMePh_2$	3, 2
$PBu^n{}_2Ph$	3
$PPr^n{}_2Ph$	3
PEt_2Ph	3, 1
PMe_2Ph	3

* In thf solution, using 3—5 equivalents of tertiary phosphine at room temperature.

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† 1 B.M. ≈ 9.27 × 10^{-24} A m^2, 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[2] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J.C.S. Dalton*, 1972, 1064.

[3] J. Chatt and A. G. Wedd, *J. Organometallic Chem.*, 1971, **27**, C15.

[4] R. J. P. Williams and A. D. Wentworth, *Proc. 1st Internat. Conf. Molybdenum*, 1973, Climax Molybdenum Co. Ltd., London, 1974.

[5] P. W. Smith and A. G. Wedd, *J. Chem. Soc.* (*A*), 1968, 1377.

[6] B. N. Figgis and J. Lewis, in 'Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.

TABLE 2

Preparation and properties of the new molybdenum(III) complexes

Complex	M.p.[a] (θ_c/°C)	Colour	Stability [b]	Analysis [c] (%)				M[c]	λ[d]/S cm^2 mol^{-1}	Solid-state magnetic moment at 20 °C ($\mu_{eff.}$/B.M.)	I.r. spectra (Nujol) (400—250 cm^{-1})
				C	H	P	Cl				
$[MoCl_3(PMe_2Ph)_3]$	176—178	Yellow	u	46.4 (46.7)	5.35 (5.40)		16.8 (17.3)			3.72	315vs, 300s, 290 (sh), 277m
$[MoCl_3(PEt_2Ph)_3]$	135—137	Yellow	u	51.7 (51.4)	6.35 (6.45)	13.0 (13.2)	15.4 (15.7)		11 [e]		
$[MoCl_3(PPr^n_2Ph)_3]$	152—156	Yellow	m	55.0 (56.1)	7.60 (7.30)	12.4 (11.8)	12.7 (13.6)	460 (789)	2.4 [e]	3.83	318s, 294s, 275m
$[MoCl_3(PBu^n_2Ph)_3]$	121—124	Yellow	m	58.9 (58.0)	8.55 (8.00)			551 (869)	5.7 [e] 10 [i]	3.69	317s, 292s, 274m
$[MoCl_3(PMePh_2)_3]$ α form	161—162	Yellow	m	57.3 (58.3)	4.80 (4.90)		13.5 (13.3)			3.71	333 (sh), 318s, 292s, 274m
β form	152—155	Yellow	m	57.7 (58.3)	4.90 (4.90)		13.5 (13.3)			3.97	347vw 317s, 299s 273w
$[MoCl_3(py)_3]$	173—176	Yellow	s	40.7 (41.0)	3.45 (3.45)	9.4 (9.6)		478 (440)		3.87	320s, 310s, 276w, 251m
$[MoCl_3(thf)(PMePh_2)_2]$ α form	134—135	Yellow	s	54.6 (53.4)	5.20 (5.10)					3.51	320vs, 290w, 250vw
β form	137—138	Yellow	s	53.2 (53.4)	5.30 (5.10)	9.5 (9.2)	15.4 (15 8)	583 (675)	4 [e]	3.82	320vs, 282vw, 256vw
$[MoCl_3(thf)(PEtPh_2)_2]$	148—152	Yellow	s	54 8 (54.7)	5.50 (5.30)	9.3 (8.8)	15.3 (15.1)	195 (703) [g]	8 [f]	3.81	320vs, 290w, 267vw
$[MoCl_3(thf)\{P(CH_2CH{:}CH_2)Ph_2\}_2]$	123—128	Yellow	m	55.9 (56.2)	5.25 (5.25)			560 (727) [g]	20 [e]	3.80	320vs, 290 (sh)
$[MoCl_3(thf)\{P(CH_2CH_2CH{:}CH_2)Ph_2\}_2]$	125—127	Yellow	s	57.2 (57.3)	5.65 (5.60)	8.5 (8.2)	13.8 (14.1)		1.6 [e]	3.74	322vs, 286w, 268vw
$[MoCl_3(thf)(py)_2]$	155—157	Yellow	m	38.3 (38.7)	4.35 (4.15)	6.2 (6.45)	24.6 (24.6)	559 (433)	20 [e]	3.90	340 (sh) 318vs, 250vw
$[MoCl_3(NCEt)(PBu^n_2Ph)_2]$	98—100	Yellow	u	53.2 (53.1)	7.30 (7.25)	2.1 [h] (2.0)[h]			0	3.80	320vs, 308 (sh)
$[MoCl_3(NCMe)(PEtPh_2)_2]$	169—172	Yellow	u	53.8 (53.6)	5.1 (5.0)	2.1 (2.1) [h]		642 (701)			
$[MoCl_3(NCEt)(PEtPh_2)_2]$	142—146	Yellow	u	54.3 (54.3)	5.6 (5.4)	2.0 (2.0) [h]		641 (585)	0	3.80	325vs, 290 (sh)m, 245vw
$[MoCl_3(thf)_2(PEt_2Ph)]$	115—117	Yellow	m	42.7 (42.2)	6.35 (6.10)	6.4 (6.0)	21.0 (20.7)	510 (513)	0.9 [e]	3.71	323vs, 292s, 274s, 255 (sh)
$[MoCl_3(thf)_2(PEtPh_2)]$	130—134	Orange	m	47.2 (47.1)	5.80 (5.55)	5.8 (5.5)	18.9 (19.0)	530 (561)	0.2 [e]	4.29	330vs, 300s, 281s, 255m
$[MoCl_3(thf)_2(py)]$	203—205	Yellow	m	36.7 (36.7)	4.95 (4.95)	3.4 (3.3)				3.92	330 (sh), 312s, 268m

[a] With decomposition. [b] In the solid state in air: u = significant decomposition within hours; m = significant decomposition within days; and s = stable for several weeks. All the complexes were indefinitely stable under nitrogen. [c] Calculated values are given in parentheses. [d] 10^{-3}M Solutions. [e] In acetone. [f] In nitrobenzene. [g] Solutions changed colour rapidly during measurements: molecular weights determined by extrapolation to zero time. [h] Analyses for N. [i] In nitromethane.

by the formula $Mo_3Cl_9(thf)_5$, and the material undoubtedly contains halogen bridges.

Complexes of Molybdenum(III).—The complex $[MoCl_3(thf)_3]$, (III), reacts with donors L such as pyridine to form $[MoCl_3L_3]$. Where L = tertiary phosphine, however, the product depends critically on the phosphine and the reaction conditions. Even with pyridine, intermediates $[MoCl_3(thf)_2L]$ and $[MoCl_3(thf)L_2]$ can be isolated. Table 1 shows the products obtained from (III) and a tertiary phosphine under arbitrary standard conditions (thf solution, 3—5 mol of phosphine, and room temperature for 1 h). Complete substitution of thf by tertiary phosphine was only found with phosphines less sterically demanding than $PEtPh_2$, and with larger phosphines the reaction stopped at $[MoCl_3(thf)(PR_3)_2]$ (PR_3 = tertiary phosphine). With $PMePh_2$ itself, the bis(phosphine) derivative was isolated in two of the three possible isomeric forms, although our i.r. data do not allow unambiguous assignments. The complex $[MoCl_3(PMePh_2)_3]$ was isolated only after all solvent had been removed and then both *meridional* and *facial* isomers of $[MoCl_3(PMePh_2)_3]$ were obtained. The i.r. spectra of the two forms are different, but no assignment of structure is possible on the basis of metal–chlorine stretching frequencies. The complexes $[MoCl_3(thf)_{3-n}(PR_3)_n]$ (n = 1—3) each have characteristic i.r. spectra in the metal–chlorine stretching region, and although this region of the spectrum is complicated by metal–oxygen absorptions it can be used unequivocally to identify the degree of substitution (see Table 2).

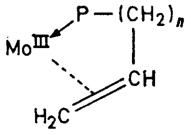
The phosphines PEt_2Ph and $PEtPh_2$ cause precipitation of products $[MoCl_3(thf)_2(PR_3)]$ from the reaction mixture and the more highly substituted products were obtained from the supernatant liquids. This we ascribe to an accidental insolubility because complexes of this type were not generally attainable with other phosphines. Indeed, the isolation of the three pyridine-containing derivatives would also appear to be a consequence of the general insolubility of pyridine complexes.

Reactions with a few other phosphines were investigated. Diphenylphosphine produced a small amount of $[MoCl_3(thf)_2(PPh_2H)]$, but the remaining product could not be characterised. We have not isolated pure products from the reaction of di(isopropyl)phenylphosphine, but the colour changes during the reaction resemble those observed during the reaction of triphenylphosphine and the two phosphines have similar steric requirements. The reaction of 1,2-bis(diphenylphosphino)ethane (dppe) produces a different kind of complex, the pink air- and light-sensitive $[MoCl_3(dppe)_2]$.

We believe that the degree of replacement of thf in these reactions is mainly controlled by steric factors. In a system $Mo{-}P(Ph_2){-}CH_2{-}CH_2{-}CH_2 \cdots$ the β-carbon atom, together with its protons, has most effect in blocking access to the metal ion. If the other groups on the phosphine are sufficiently large (*e.g.*, phenyl groups) the length of the alkyl chain has a decisive influence on the reactivity. This is consistent with the data in Table 1 where $PMePh_2$ is apparently the dividing point between the series $[MoCl_3(thf)_{3-n}(PR_3)_n]$ (n = 2 or 3).

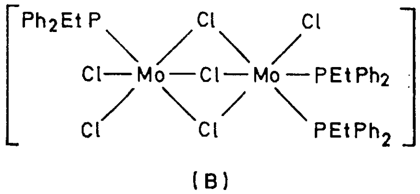
The complexes $[ReCl_2(N)(PR_3)_n]$ (n = 2 or 3) show a similar pattern with tertiary phosphines. Thus for $PMePh_2$, complexes with both n = 2 and 3 can be isolated, whereas for $PEtPh_2$ only the complex with n = 2 can be obtained, even under extreme conditions.[7] Similarly, the complexes $[ReCl_2(NO)(PR_3)_n]$ can be obtained with both n = 2 and 3 from $PMePh_2$, but from $PEtPh_2$ only the complex with n = 2 can be synthesised.[8] More indirect evidence for the β-hydrogen interaction in complexes like this has been obtained from the ^1H n.m.r. spectra of the paramagnetic complexes $[ReCl_3(PR_3)_3]$ [9] and $[WCl_4(PR_3)_2]$.[2] Where PR_3 contains alkyl groups the anomalous high-field chemical shifts of the alkyl protons are at a maximum for the β-methylene hydrogen atoms.

Our data also exclude the possibility that interactions of the type (A) occur in our complexes where the tertiary phosphines contain olefinic groups. Thus the i.r. spectra of $[MoCl_3(thf)(PR_3)_2]$ $[PR_3 = P(CH_2CH_2CH{:}CH_2)Ph_2$ or $P(CH_2CH{:}CH_2)Ph_2]$ showed bands near 1 640 cm^{-1} assignable to free ν(C=C), but none assignable to complexed olefin.



(A)

When the reaction of (III) and a tertiary phosphine is carried out under more extreme conditions, other products are obtained. The action of neat $PEtPh_2$ at 80 °C during 4 h yields a green diamagnetic material with analysis and molecular weight corresponding to the formula $[Mo_2Cl_6(PEtPh_2)_3]$. The structure of this complex is probably derived from the $[Mo_2Cl_9]^{3-}$ ion [10] which contains a triple halogen bridge, and a plausible structure is (B). We attempted to extend this reaction to other phosphines using the same reaction conditions. With PPr^nPh_2, PBu^nPh_2, and PEt_2Ph more or less



(B)

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[7] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 2288.

[8] R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1974, 1075.

[9] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

[10] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.* (*A*), 1969, 57.

impure materials with physical properties similar to those of $[Mo_2Cl_6(PEtPh_2)_3]$ were obtained, but the analyses were usually not good. The phosphines PMe_2Ph and $PMePh_2$ yielded only $[MoCl_3(PR_3)_3]$, and PEt_3 gave a complex, not further characterised, the analysis of which corresponded to the formula $MoCl_3(PEt_3)_2$.

Complexes of Molybdenum(II) *and Molybdenum*(0).—The reduction of (III) in the presence of a ditertiary phosphine in thf with zinc under argon or nitrogen yields complexes $[MoCl_2(diphosphine)_2]$. These complexes are all non-conductors in nitromethane, and have solid-state magnetic moments in the range 2.5—2.8 B.M. at 20 °C. With the unidentate phosphine PMe_2Ph, reduction does not occur and $[MoCl_3(PMe_2Ph)_3]$ was isolated. In the presence of magnesium or sodium amalgam, however, the systems may be further reduced to give molybdenum(0) complexes (Table 3). It is not clear why the product of reduction is dependent on the phosphine.

TABLE 3

Reduction of $[MoCl_3(thf)_3]$ under various conditions

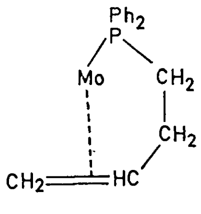
	Products		
Phosphine	Reductant: Zn(Ar or N_2)	Mg (or Na–Hg)	
		Ar	N_2
PMe_2Ph	$[MoCl_3(PMe_2Ph)_3]$	$[Mo(PMe_2Ph)_4]$	$[Mo(N_2)_2(PMe_2Ph)_4]$
PH_2Ph		$[Mo(PH_2Ph)_6]$	$[Mo(PH_2Ph)_6]$
$Ph_2PCH_2PPh_2$(dppm)	Not identified	$[Mo(dppm)_3]$	$[Mo(dppm)_3]$
$Ph_2PCH_2CH_2PPh_2$(dppe)	$[MoCl_2(dppe)_2]$	$[MoCl_2(dppe)_2]$	$[Mo(N_2)_2(dppe)_2]$
$Ph_2PCH{:}CHPPh_2$(dppen)	$[MoCl_2(dppen)_2]$		$[Mo(N_2)(dppen)_2]$
$Ph_2PCH_2CH_2CH_2PPh_2$(dppp)	$[MoCl_2(dppp)_2]$	$[MoCl_2(dppp)_2]$	$[MoCl_2(dppp)_2]$

Of the diphosphines, bis(diphenylphosphino)methane (dppm) does not form a dinitrogen complex and $[Mo(dppm)_3]$ was isolated from reactions under either nitrogen or argon. This complex is presumably analogous to the known $[Mo(dppe)_3]$ [11] which we could not prepare directly but were able to obtain *via* $[Mo(N_2)_2(dppe)_2]$ (see Experimental section). Finally, no complex of 1,3-bis(diphenylphosphino)propane (dppp) with metal in oxidation state lower than II was obtained, and the reason is obscure.

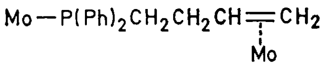
Complexes $[MoL_6]$ (Mo in oxidation state 0, L = phosphorus donor group) are not new. In addition to our new complexes $[Mo(dppm)_3]$ and $[Mo(PPhH_2)_6]$, $[Mo(Me_2PCH_2CH_2PMe_2)_3]$ and the chromium and tungsten analogues were obtained by Chatt and Watson by the reduction of an appropriate halide in the presence of the diphosphine,[12] and $[Mo(dppe)_3]$ and $[Mo\{o\text{-}C_6H_4(PEt_2)_2\}_3]$ were obtained from bis(benzene)molybdenum.[11]

The complex $[Mo(N_2)_2(dppen)_2]$ [dppen = 1,2-bis(diphenylphosphino)ethylene] apparently exists in two isomeric forms. It was first obtained as a deep orange, indefinitely stable, solid at −20 °C when free from solvent or at 20 °C in contact with thf, from which it can be recrystallised. At room temperature under N_2, or at 60 °C in high vacuum, or on washing in methanol, the colour changes to light orange. A solution of the deep orange complex in thf shows a strong absorption at 2 000 cm^{-1}, with a shoulder at 1 968 cm^{-1}. A fresh Nujol mull of the complex exhibits two strong absorptions, at 2 002 and 1 970 cm^{-1}. The latter band rapidly decreased in intensity, and after 15 min the spectrum was identical with that ascribed to the completely characterised *trans* isomer. No evolution of gas occurred during the conversion at 60 °C. The most plausible explanation is that the deep orange material is the *cis* isomer. Dinitrogen in *trans*-$[Mo(N_2)_2(dppen)_2]$ in warm thf exchanges rapidly (100% in a few minutes) with $^{15}N_2$. The isomerisation of the putative *cis* isomer *in vacuo* at 60 °C makes it unlikely that isomerisation occurs *via* an exchange process.

The reduction of $[MoCl_3(thf)_3]$ by sodium amalgam in the presence of $P(CH_2CH_2CH{:}CH_2)Ph_2$ (PR_3) in thf yields a complex which analyses for $Mo(PR_3)_3$, and is too insoluble for a molecular-weight determination. It has a medium-intensity band in its i.r. spectrum at 1 480 cm^{-1}, which we assign to ν(C=C) of the complexed olefin, and no bands assignable to free olefin. The complex reacts with carbon monoxide, pyridine, or iodine to give intractable products, all containing a band at 1 640 cm^{-1} presumably due to free olefin. Evidently the phosphine ligands in this complex are bonded to the metal through both the phosphorus lone pair and the electrons of the C=C double bond, and plausible modes of binding are shown in (C) and (D).



(C)



(D)

This complex is unusual because, apart from mixed carbonyl–olefin complexes, olefin complexes of Mo^0 are very rare.

The reduction of $[MoCl_3(thf)_3]$ in thf under argon by magnesium or sodium amalgam in the presence of an excess of dimethylphenylphosphine produces an exceedingly air-sensitive brown solution which is stable at 20 °C for at least 48 h. Passage of N_2 through the

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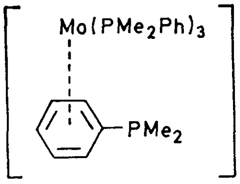
[11] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1962, 2545.

[12] J. Chatt and H. R. Watson, *Proc. Chem. Soc.*, 1960, 243.

solution produces crystals of *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] and other unidentified dinitrogen-containing species. Passage of carbon monoxide yields a solution containing *trans*-[$Mo(CO)_2(PMe_2Ph)_4$], and further reaction then gives *mer*-[$Mo(CO)_3(PMe_2Ph)_3$]. Norbornadiene gives a crystalline solid which was not characterised. The brown solution apparently contains reactive solvated [$Mo(PMe_2Ph)_4$] as one of the components. On two occasions out of six, highly air-sensitive orange crystals of [$Mo(PMe_2Ph)_4$] were isolated. This substance is diamagnetic and has the structure (E).[13] This complex does not react with nitrogen in solution and it is probably a rearrangement product of the solvated [$Mo(PMe_2Ph)_4$] produced initially. Work is continuing to exploit the preparative possibilities of this reactive, reduced, solution.



(E)

EXPERIMENTAL

All reactions were carried out under an atmosphere of pure dry nitrogen except when stated otherwise, using solvents dried by standard procedures.

The i.r. spectra were recorded on Unicam SP 1200 and Perkin-Elmer 337E spectrometers (Nujol mulls, 400—4 000 cm^{-1}). Magnetic moments were measured on a Faraday balance calibrated against Hg[$Co(SCN)_4$] and conductivities on a Portland Electronics series 300 conductivity bridge using dry solvents. Melting points were recorded in sealed tubes at a pressure of *ca.* 0.1 mmHg and are uncorrected.

Trichlorotris(tetrahydrofuran)molybdenum(III), (III).—Tetrachlorobis(propionitrile)molybdenum(IV) (12.5 g) and tetrahydrofuran (80 cm^3) were stirred vigorously under nitrogen for 1 h. Yellow crystalline tetrachlorobis(tetrahydrofuran)molybdenum(IV) was filtered off and washed from the filter into a cooled (ice-salt) equivolume mixture of dichloromethane (50 cm^3) and thf (50 cm^3) containing granulated zinc (10 g). The suspension was stirred at 0 °C until the solution was bright blue and all the complex had been taken up and was then stored at 0 °C for 15 h during which time the solution became brown. The brown solution was filtered from the zinc, reduced in volume *in vacuo* to 25 cm^3, and crystallisation caused by the addition of thf (30 cm^3) and by refrigeration overnight. The *complex* was filtered off, washed with cold thf, and dried *in vacuo* (9.2 g, 70%). It was recrystallised from tetrahydrofuran–isopropyl alcohol as pink crystals (Found: C, 34 8; H, 6.0; Cl, 25.2. $C_{12}H_{24}Cl_3MoO_3$ requires C, 34.4; H, 5.8; Cl, 25.4%).

Trichlorobis(ethyldiphenylphosphine)(propionitrile)molybdenum(III), (II).—Propionitrile (10 cm^3) containing tetrachlorobis(ethyldiphenylphosphine)molybdenum(IV) (0.75 g) was heated under reflux for 20 min, the nitrile removed *in vacuo* to give an oil, and methanol (3 cm^3) added. Vigorous stirring caused the *complex* to precipitate as a powder which was recrystallised from benzene–methanol as yellow crystals (0.5 g, 60%). (*Acetonitrile)trichlorobis(ethyldiphenylphosphine)*- and *trichlorobis(di-n-butylphenylphosphine)(propionitrile)-molybdenum*(III) were prepared in a similar manner.

Trichloro(tetrahydrofuran)bis(triphenylphosphine)molybdenum(III).—A suspension of trichlorotris(tetrahydrofuran)molybdenum(III) (0.3 g) and triphenylphosphine (0.8 g, P : Mo = 3.8 : 1) in dry diethyl ether (30 cm^3) was heated under reflux for 15 h. The powdery pink solid was filtered from the colourless filtrate, washed several times with dry diethyl ether, and dried at a pressure of 1 mmHg (yield 75%).

Bis(but-3-enyldiphenylphosphine)trichloro(tetrahydrofuran)molybdenum(III).—But-3-enyldiphenylphosphine (3.19 g) was added to a suspension of (III) (1.55 g, P : Mo = 3.6 : 1) in dry thf (15 cm^3). The mixture was stirred at room temperature for 15 h, and a copious yellow precipitate was formed. The volume was reduced to 10 cm^3 and the product was filtered off, washed with thf (3 × 5 cm^3), and dried at a pressure of 1 mmHg (yield 74%).

Bis(allyldiphenylphosphine)trichloro(tetrahydrofuran)molybdenum(III).—Allyldiphenylphosphine (2.01 g) and (III) (0.55 g; P : Mo = 6.7 : 1) were stirred in dry thf (30 cm^3) for 1 h, to give a clear orange solution. The volume was reduced to 20 cm^3 and on addition of isopropyl alcohol a slightly oily solid began to precipitate. The product was recrystallised from tetrahydrofuran-isopropyl alcohol and dried at a pressure of 1 mmHg (yield *ca.* 50%).

Trichloro(ethyldiphenylphosphine)bis(tetrahydrofuran)molybdenum(III) *and Trichlorobis(ethyldiphenylphosphine)(tetrahydrofuran)molybdenum*(III).—Ethyldiphenylphosphine (1.78 g) was added to a suspension of (III) (0.79 g, P : Mo = 4.2 : 1) in thf (20 cm^3). The mixture was stirred at room temperature until all the solid had dissolved (*ca.* 1 h). Within another 10 min a yellow solid began to precipitate. The mixture was stored at 0 °C overnight and then filtered. The precipitate was washed with thf (2 × 3 cm^3) and diethyl ether (2 × 5 cm^3) and dried at a pressure of 1 mmHg. This product was identified as [$MoCl_3(thf)_2(PEtPh_2)$] (yield 33%). To the combined filtrate and washings another 50 cm^3 of diethyl ether were added, giving another yellow solid which was shown to be [$MoCl_3(thf)(PEtPh_2)_2$] (yield 41%). Another experiment using 0.48 g of (III) with a P : Mo ratio of 7 : 1 and stirring at room temperature overnight yielded only the bis(phosphine) complex.

Trichlorobis(methyldiphenylphosphine)(tetrahydrofuran)molybdenum(III) *and Trichlorotris(methyldiphenylphosphine)molybdenum*(III).—These two complexes can be isolated from the same reaction mixture depending on the conditions. A further complication is that both complexes can be obtained in two isomeric forms. Methyldiphenylphosphine (1.36 g) and (III) (0.82 g, P : Mo = 3.5 : 1) in thf (10 cm^3) were stirred overnight at room temperature and then filtered to remove a small quantity of solid by-product. The filtrate was evaporated to dryness and the residue solidified by washing with diethyl ether (4 × 20 cm^3), which also removed any excess of phosphine. The yellow powder produced (yield 74%) was principally the isomer designated α-[$MoCl_3(thf)(PMePh_2)_2$]. The product was not pure, however, as the elemental analyses indicated

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the presence of some of the tris(phosphine) complex. Recrystallisation of the compound from tetrahydrofuran–hexane yielded a second isomeric form (designated β), distinguished from the α form by its i.r. spectrum.

Isomer β could also be obtained directly from the reaction solution. The reactants [$PMePh_2$ (2.66 g) and (III) (1.05 g, P : Mo = 5.3 : 1)] were dissolved in thf (30 cm^3) and allowed to stand at room temperature for 70 h. A small quantity of orange crystals separated from the solution which was reduced in volume to 15 cm^3 and stored at 4 °C. The yellow product was filtered off, washed with diethyl ether (20 cm^3), and dried at a pressure of 15 mmHg (yield 31%). The filtrate was evaporated to an oily residue which soon solidified. The solid was stirred in diethyl ether (20 cm^3) for 15 d, then filtered and washed with diethyl ether (5 × 15 cm^3), and finally dried at a pressure of 1 mmHg. This product was identified as an impure sample of α-[$MoCl_3(PMePh_2)_3$] (yield 43%), the impurity being one of the bis(phosphine) isomers described above. Recrystallisation of the impure α isomer by dissolving in methylene chloride, adding diethyl ether, and refrigerating for 1—2 d gave the β isomer, which was clearly distinguished by its i.r. spectrum.

Trichlorotris(tertiary phosphine)molybdenum(III) (*Tertiary Phosphine = Di-n-butylphenylphosphine, Di-n-propylphenylphosphine, and Dimethylphenylphosphine*).—A similar procedure was used for each of these complexes. The phosphines were added to the suspensions of (III) (P : Mo *ca.* 3—4 : 1) in dry thf (*ca.* 10 cm^3). The solid starting material dissolved within 1 h giving a yellow-orange solution. After stirring for at least another hour, the solutions were filtered and then treated with isopropyl alcohol (10—20 cm^3). Concentration and cooling of the mixtures gave crystalline precipitates which were yellow and analytically pure for di-n-butyl- and di-n-propylphenylphosphine. In the case of PMe_2Ph a much cleaner product was obtained when metallic zinc was present in the reaction mixture.

Trichlorobis(diethylphenylphosphine)(tetrahydrofuran)-molybdenum(III) *and Trichlorotris(diethylphenylphosphine)-molybdenum*(III).—Diethylphenylphosphine (1.9 g) was added to a suspension of (III) (0.48 g, P : Mo = 10 : 1) in thf (10 cm^3). After 45 min the reactants had completely dissolved to give a clear orange solution. Within another 15 min a yellow solid began to precipitate. The volume of the solution was reduced to 10 cm^3 and diethyl ether (40 cm^3) was added. After holding at 4 °C for *ca.* 2 h the mixture was filtered. The yellow solid was washed with diethyl ether and dried at a pressure of 1 mmHg. This product was characterised as [$MoCl_3(thf)_2(PEt_2Ph)$] (yield *ca.* 50%). The filtrate was evaporated to *ca.* 5 cm^3 and treated with hexane (40 cm^3) to precipitate [$MoCl_3(PEt_2Ph)_3$]. The yellow product was recrystallised from dichloromethane–hexane to give the pure greenish yellow complex (yield *ca.* 20%).

Bis[1,2-*bis(diphenylphosphino)ethane*]*trichloromolybdenum*(III).—Tetrahydrofuran (30 cm^3) was distilled *in vacuo* from lithium tetrahydridoaluminate on to (III) (0.5 g) and 1,2-bis(diphenylphosphino)ethane (1.5 g). Dry argon was admitted to the system and the solution shaken overnight. The *complex* was precipitated on distilling diethyl ether (20 cm^3) from sodium wire into the solution under high vacuum. The precipitate was filtered off, washed with dry tetrahydrofuran–diethyl ether and diethyl ether, and dried *in vacuo* (Found: C, 62.2; H, 4.9; Cl, 11.0; P, 12.6; Mo, 10.1. $C_{52}H_{48}Cl_3MoP_4$ requires C, 62.5; H, 4.8; Cl, 10.6; P, 12.4; Mo, 9.6%). When oxygen and/or moisture were present in the system, absorptions associated with P–H, P=O, and Mo–O vibrations appeared in the 2 400, 11—1 200, and 900—1 000 cm^{-1} regions of the i.r. spectrum. Extreme care must be taken to exclude oxygen and moisture. Attempts to recrystallise the complex gave impure products.

Binuclear Molybdenum(III) *Phosphine Complexes*.—(a) *From ethyldiphenylphosphine*. Ethyldiphenylphosphine (1.84 g, P : Mo = 12 : 1) and (III) (0.33 g) were stirred in thf (5 cm^3) for 20 min giving an orange solution of [$MoCl_3(thf)(PEtPh_2)_2$]. The solvent was evaporated at a pressure of 15 mmHg. The yellow residue was heated *in vacuo* (90—100 °C, 0.01 mmHg) for *ca.* 3 h. The resulting green oil was cooled and washed with diethyl ether (2 × 20 cm^3) giving a green powder. This was washed with thf (2 × 10 cm^3) leaving an insoluble grey-green solid (Found: C, 48.2; H, 4.55%; *M*, 950. $C_{42}H_{45}Cl_6Mo_2P_3$ requires C, 48.2; H, 4.35%; *M*, 1 050), molar conductivity 0.7 S cm^2 mol^{-1} (in dichloroethylene).

(b) *From diethylphenylphosphine*. Diethylphenylphosphine (1.0 g) was added to (III) (0.5 g) (P : Mo = 8 : 1) in thf (10 cm^3) and the mixture stirred for 20 min, yielding an orange-red solution. The solvent was removed at a pressure of 1 mmHg, and the residue heated (100 °C, 0.1 mmHg) for 4 h. The resulting dark green solid was washed with diethyl ether (2 × 20 cm^3) and dried at a pressure of 1 mmHg (Found: C, 40.3; H, 5.10. $C_{30}H_{30}Cl_6Mo_2O_3$ requires C, 39.9; H, 5.00%).

(c) Analogous solids were obtained using PBu^nPh_2 and PPr^nPh_2. On the other hand $PMePh_2$ and PMe_2Ph yielded only [$MoCl_3(PR_3)_3$].

Bis[1,2-*bis(diphenylphosphino)ethane*]*dichloromolybdenum*(II).—1,2-Bis(diphenylphosphino)ethane (2.0 g), (III) (1.0 g), and granulated zinc (1.0 g) were stirred vigorously in thf (60 cm^3) at 40 °C for 4 h and then at room temperature overnight. The finely divided yellow crystalline complex was washed with thf and dried *in vacuo* (2 g, 80%). Recrystallisation was effected from benzene–isopropyl alcohol (Found: C, 64.7, 64.8; H, 5.3, 5.2; Cl, 7.5; Mo, 10.2. $C_{52}H_{48}Cl_2MoP_4$ requires C, 64.8; H, 5.0; Cl, 7.4; Mo, 10.0%).

The following complexes were prepared in a similar manner: *bis*[1,3-*bis(diphenylphosphino)propane*]*dichloromolybdenum*(II) (Found: C, 65.4; H, 5.3; Cl, 7.0; Mo, 9.8. $C_{54}H_{52}Cl_2MoP_4$ requires C, 65.4; H, 5.3; Cl, 7.15; Mo, 9.7%); *dichlorobis*[o-*phenylenebis(dimethylarsine)*]*molybdenum*(II), very air-sensitive (Found: C, 34.4; H, 4.4. $C_{20}H_{32}As_4Cl_2Mo$ requires C, 34.5; H, 4.4%); *bis*[1,2-*bis(dimethylphosphino)ethane*]*dichloromolybdenum*(II), recrystallised from tetrahydrofuran–isopropyl alcohol in very poor yield (Found: C, 30.9; H, 7.3; Cl, 14.8. $C_{12}H_{32}Cl_2MoP_4$ requires C, 30.85; H, 6.9; Cl, 15.2%); and *dichlorobis*[cis-1,2-*bis(diphenylphosphino)ethane*]*molybdenum*(II), not completely pure (Found: C, 66.3, 65.5; H, 5.4, 5.7. $C_{52}H_{44}Cl_2MoP_4$ requires C, 65.1; H, 4.6%).

Tris(but-3-enyldiphenylphosphine)molybdenum(0).—Sodium amalgam (17 g, 1%) was washed with benzene and thf and then placed in a flask fitted with a small side tube containing (III) (0.54 g). The amalgam was covered with dry thf (*ca.* 20 cm^3), and, after addition of the phosphine (1.6 g), (III) was added to the solution from the side tube. The mixture was stirred at room temperature for 2.5 h giving a dark brown solution. In order to remove the finely divided suspension of mercury the solution was filtered through Kieselguhr. The filtrate was held at 0 °C for 3 d, giving a yellow crystalline precipitate which was filtered, washed with thf (2 × 5 cm^3), and dried at a pressure of 1 mmHg (yield *ca.* 20%). Higher yields (*ca.* 40%) could be obtained by reducing the volume of filtrate before cooling (Found: C, 70.1; H, 6.2; P, 11.3. $C_{48}H_{51}MoP_3$ requires C, 70.6; H, 6.30; P, 11.4%).

cis-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethylene*]*bis*(*dinitrogen*)*molybdenum*(0).— Trichlorotris(tetrahydrofuran)molybdenum(III) (1.0 g), 1,2-bis(diphenylphosphino)ethylene (3 g), and magnesium turnings (1 g) were stirred vigorously at 50 °C in thf (40 cm^3) overnight. The resulting red-orange precipitate was filtered off, washed from the magnesium with thf (250 cm^3), and the solution kept at −20 °C overnight. The deep orange crystalline complex was washed with thf, dried *in vacuo* for 2 min at room temperature and for 2 h at −78 °C, and stored at −20 °C (0.6 g). Physical measurements are difficult to carry out as the complex decomposes spontaneously when heated or in contact with other chemicals. When heated in a sealed tube at a pressure of *ca.* 0.1 mmHg the orange-red crystals lost colour and became orange at *ca.* 50 °C. They began to powder and break up at *ca.* 110 °C, then darkened progressively, and finally liquified at 160—165 °C. This product, probably the *cis* isomer, is too unstable for analysis and changes spontaneously under nitrogen to trans-*bis*[1,2-*bis*(*diphenylphosphino*)*ethylene*]*bis*(*dinitrogen*)*molybdenum*(0), a light orange material. This change occurs when it is stored at room temperature overnight, heated gently in high vacuum, or washed with methanol (Found: C, 66.4; H, 4.6; N, 6.0. $C_{52}H_{44}MoN_4P_4$ requires C, 66.2; H, 4.7; N, 5.9%).

cis-*Tetrakis*(*dimethylphenylphosphine*)*bis*(*dinitrogen*)*molybdenum*(0).—Magnesium turnings (2.0 g) and (III) (*ca.* 3.2 g) were placed in a flask together with dry thf (50 cm^3). Dimethylphenylphosphine (4 g) was then added. The mixture was stirred vigorously for 60 h, giving a red-brown solution. The magnesium was removed by filtration and the thf was removed at a pressure of 1 mmHg. The residue was extracted with diethyl ether (50 cm^3) and the ether solution evaporated to dryness to give a red-brown sticky solid. The solid was further extracted with pentane (50 cm^3) leaving a yellow powder. This was stirred with oxygen-free water (50 cm^3) for 4 h. The suspension was filtered, and the solid was washed with methanol (6 × 5 cm^3) and dried at a pressure of 1 mmHg. It was crystallised from tetrahydrofuran–methanol (1 : 1) as bright yellow crystals (yield *ca.* 50%) (Found: C, 54.3; H, 6.05; N, 7.9; P, 17.4. $C_{32}H_{44}MoN_4P_4$ requires C, 54.6; H, 6.30; N, 8.0; P, 17.6%). This material has bands in its i.r. spectrum assignable to $\nu(N_2)$ at 2 014 and 1 932 cm^{-1} (Nujol) and at 2 015 and 1 945 cm^{-1} (thf).

Tris[*bis*(*diphenylphosphino*)*methane*]*molybdenum*(0).—Bis(diphenylphosphino)methane (3.0 g), (III) (1.0 g), and magnesium turnings (0.5 g) were stirred vigorously in thf (60 cm^3) at 40 °C for 5 h and then at room temperature overnight. The resulting red-brown solution was reduced to half its volume and held at −20 °C for 15 h. The *complex* was filtered off, washed with tetrahydrofuran–isopropyl alcohol, isopropyl alcohol, and diethyl ether, and dried at a pressure of 15 mmHg, producing deep purple crystals (1.9 g, 60%) (Found: C, 71.9; H, 5.5; Mo, 8.0. $C_{75}H_{66}MoP_6$ requires C, 72.1; H, 5.3; Mo, 7.7%).

Tris[1,2-*bis*(*diphenylphosphino*)*ethane*]*molybdenum*(0).—*trans*-Bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)molybdenum(0) (0.75 g) and 1,2-bis(diphenylphosphino)ethane (0.6 g) were heated in benzene (40 cm^3) under reflux under argon for 4 h. The deep red solution was reduced in volume to 10 cm^3 and left to stand at 0 °C for 15 h. The orange-red crystalline complex was filtered off, washed with benzene–isopropyl alcohol and isopropyl alcohol, and dried *in vacuo* (0.9 g, 65%) (Found: C, 73.1; H, 5.8; Mo, 7.7. $C_{78}H_{72}MoP_6$ requires C, 72.6; H, 5.6; Mo, 7.4%).

The Reaction of $[MoCl_3(thf)_3]$, PMe_2Ph, *and* Na–Hg (*or* Mg) *in thf under Argon*: ' $[Mo(PMe_2Ph)_4]$.'—Tetrahydrofuran (50 cm^3) was dried over lithium tetrahydridoaluminate, degassed, and distilled under high vacuum on to (III) (1.0 g), sodium amalgam (2%, 15 g, an excess), and dimethylphenylphosphine (2 g, *i.e.* Mo : P *ca.* 1 : 6). Argon was admitted to the reaction vessel and the mixture stirred vigorously overnight. The dark orange solution was reduced to an oil, taken up with benzene (40 cm^3), filtered from the solid oxidation products, and stirred with water (30 cm^3) for 5 h. The benzene layer was syringed away from the emulsion. The emulsion was washed with benzene (2 × 15 cm^3) and the washings added to the total solution which was dried overnight over sodium sulphate. The solution was filtered from the sodium sulphate, reduced to 5 cm^3, and held at 0 °C for 15 h. The solution was taken down to the oil and hexane (20 cm^3) was added, yielding a considerable quantity of dark non-crystalline material under a bright orange mother liquor. This was filtered off and the dark material discarded. The filtrate was reduced to 5 cm^3 and held at 0 °C for 15 h. Large, orange-red, diamagnetic crystals formed (yield 0.3 g). The complex is very air-sensitive. This preparation is not reliable and in five more attempts one further crop (50 mg) was obtained [Found: C, 59.4; H, 6.9; P, 19.1; Mo, 15.1%; *M* (ebullioscopic, benzene), 563. $C_{32}H_{44}MoP_4$ requires C, 59.3; H, 6.85; P, 19.1; Mo, 14.8%; *M*, 649].

Hexakis(*phenylphosphine*)*molybdenum*(0).— Trichlorotris(tetrahydrofuran)molybdenum(III) (1.0 g), phenylphosphine (1.7 g), and sodium amalgam (2%, 15 g) were stirred vigorously in thf (30 cm^3) overnight. The yellow-brown solution was syringed from the reaction vessel, reduced to 5 cm^3, and taken up in benzene (40 cm^3). The benzene solution was washed with water, dried over sodium sulphate, reduced to 10 cm^3, and heated under reflux when methanol (25 cm^3) was slowly added. The *complex* separated overnight at 0 °C as light-sensitive yellow needles and was filtered, washed with benzene–methanol and methanol, and dried at a pressure of 15 mmHg (Found: C, 57.7; H, 5.8; P, 24.5; Mo, 12.9. $C_{36}H_{42}MoP_6$ requires C, 57.2; H, 5.6; P, 24.6; Mo, 12.7%). An absorption of weak to medium intensity at 2 100—2 300 cm^{-1} in the i.r. spectrum was attributed to the P–H stretching vibration.

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