Alkyl-arene and -cyclo-octadiene Complexes of Molybdenum(II) containing Tertiary Phosphines †

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Treatment of trichlorotris(tetrahydrofuran)molybdenum, $MoCl_3(C_4H_8O)_3$, with tertiary phosphines under certain conditions gives $MoCl_3(PR_3)(C_4H_8O)_2$ ($PR_3 = PMe_3$ or PMe_2Ph) which on alkylation with dimethylmagnesium in the presence of arenes yield the 18-electron methyl–arene complexes $Mo(CH_3)_2(\eta^6\text{-Ar})(PR_3)_2$ (Ar = benzene, toluene, or *o*- and *p*-xylene). The reaction in tetrahydrofuran affords the known dimers $Mo_2(CH_3)_4(PR_3)_4$. Action of CO on the benzene complex at 1 atm gives $Mo(CH_3)_2(\eta^6\text{-}C_6H_6)(CO)(PR_3)$ which when set aside under N_2 yields $Mo(\eta^6\text{-}C_6H_6)(PMe_2Ph)_3$ possibly *via* the acetone complex $Mo(Me_2CO)(\eta^6\text{-}C_6H_6)(PMe_2Ph)$. Reaction of $MoCl_3(PR_3)(C_4H_8O)_2$ with Me_2Mg and cyclo-octa-1,5-diene (cod) affords $Mo(CH_3)_2(cod)(PR_3)_2$ in low yields. The new compounds have been characterised by i.r. and ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy.

APART from studies on arene carbonyl complexes,[1-3] treatment of the bis-arene compounds $MoAr_2$ with allylic chlorides gives the dimers $\{Mo(\eta\text{-Ar})(\pi\text{-allyl})(\mu\text{-Cl})\}_2$ which have proved to be suitable starting materials for a number of reactions leading among others to hydrido- and dinitrogen-arene complexes.[4,5] Action of $(EtAlCl_2)_2$ on $Mo(arene)_2$ gives violet solutions which react with alkenes yielding cationic diene complexes of the type $[Mo(arene)(\pi\text{-allyl})(diene)]^+$ and alkanes.[6] Similar compounds were isolated with cyclic olefins.[7,8]

TABLE 1

Selected ^1H and ^{31}P n.m.r. data for the molybdenum alkyls

	^1H N.m.r.						
	Arene or olefin resonances		P–CH_3		Mo–CH_3		
Compound	τ	J_{PH}	τ	$J_{PH} + J_{PH'}$	τ	J_{PH}	^{31}P N.m.r. [c]
$MoMe_2(C_6H_6)(PMe_3)_2$	6.05t	1.5	8.7 [a]	6	10.75t	13.0	8.8
$MoMe_2(C_6H_5Me)(PMe_3)_2$	5.95 [b]		8.55 [a]	6	10.7t	13.0	9.5
$MoMe_2(o\text{-}C_6H_4Me_2)(PMe_3)_2$	6.08 [b]		8.75 [a]	6	10.76t	13.0	9.8
$MoMe_2(p\text{-}C_6H_4Me_2)(PMe_3)_2$	6.14t	1.8	8.67 [a]	6	10.67t	13.0	10.7
$MoMe_2(C_6H_6)(PMe_2Ph)_2$	6.13t	1.3	8.59 [a]	6	10.73t	13.0	19.0
$MoMe_2(C_6H_5Me)(PMe_2Ph)_2$	6.10 [b]		8.58 [a]	6	10.66t	13.0	19.7
$MoMe_2(o\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	6.05, 6.2 [b]		8.60 [a]	6	10.65t	12.6	19.3
$MoMe_2(p\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	6.18t	2.0	8.66 [a]	6	10.72t	13.0	22.1
$MoMe_2(C_6H_6)(CO)(PMe_2Ph)$	5.73s		8.54d	6.7 (J_{PH})	10.20d	10.7	
$MoMe_2(C_8H_{12})(PMe_3)_2$	7.35 [b]		8.47t	5.3	9.25t	8.3	16.1
$MoMe_2(C_8H_{12})(PMe_2Ph)_2$	7.5 [b]		8.15t	4.7	9.15t	7.7	27.3

[a] ' Filled-in ' doublet. [b] Broad multiplets. [c] Chemical shifts are to high frequency of external 85% H_3PO_4 (measured at 40.5 MHz).

TABLE 2

Selected ^{13}C n.m.r. data for methyl–arene compounds

	Arene resonances (δ) [a]				P–Me					Mo–Me	
Compound	C(1)	C(2)	C(3)	C(4)	δ [a]	$\lvert J_{PC} + J_{P'C}\rvert$	J_{PC}	$J_{P'C}$	$\lvert J_{PP'}\rvert$	δ [a]	$\lvert J_{PC}\rvert$
$MoMe_2(C_6H_6)(PMe_3)_2$	88.9				20.7	17.7				−8.6	24.0
$MoMe_2(C_6H_5Me)(PMe_3)_2$	100.3	88.4	89.0	90.8	20.5	18.0				−8.2	23.3
$MoMe_2(o\text{-}C_6H_4Me_2)(PMe_3)_2$	89.6	98.6	91.3	88.7	20.2	17.8	±19	∓1.2	22	−7.5	22.8
$MoMe(p\text{-}C_6H_4Me_2)(PMe_3)_2$	103.7	88.3	88.3	103.7	20.4	17.6	±19	∓1.4	20	−7.5	23.0
$MoMe_2(C_6H_6)(PMe_2Ph)_2$	90.0				18.0	19.1				−7.0	22.5
$MoMe_2(C_6H_5CH_3)(PMe_2Ph)_2$	104.7	88.0	88.2	95.2	17.7	19.0	±20	∓1.0	20	−6.3	22.2
$MoMe_2(o\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	99.0	99.0	92.5	89.6	17.0	18.0	±19	∓1.0	22	−5.7	21.8
$MoMe_2(p\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	110.3	86.4	86.4	110.3	18.1	18.0				−4.6	22.0

[a] Measured in $[^2H_6]$benzene as solvent and internal reference (δ 128.7) and referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz.

Although there are dihydrido-arene complexes of molybdenum containing tertiary phosphines,[4] no alkyl analogues are known. We have studied the reactions of $MoCl_3(PR_3)(thf)_2$ (thf = tetrahydrofuran) with Me_2Mg in the presence of arenes that give the novel alkyl-arene

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† No reprints available.

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[6] M. L. H. Green and J. Knight, *J.C.S. Dalton*, 1974, 311.

[7] M. L. H. Green and J. Knight, *J.C.S. Dalton*, 1976, 213.

[8] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc.* (*A*), 1971, 2929.

complexes $MoMe_2(\eta^6\text{-}Ar)(PR_3)_2$ (Ar = benzene, toluene, or *o*- and *p*-xylene; $PR_3 = PMe_3$ or PMe_2Ph). We also report the formation under similar conditions of the cyclo-octadiene derivatives $MoMe_2(\eta\text{-}cod)(PR_3)_2$.

Spectroscopic data for new compounds are given in Tables 1 and 2, analytical data and molecular weights in Table 3.

TABLE 3

Analytical data and molecular weights of the molybdenum alkyls

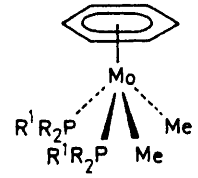
Compound	Analysis * (%) C	H	P	*M*
$MoMe_2(C_6H_6)(PMe_3)_2$	47.6 (47.2)	8.5 (8.4)	17.1 (17.4)	330 (356)
$MoMe_2(C_7H_8)(PMe_3)_2$	48.4 (48.6)	8.2 (8.6)		
$MoMe_2(p\text{-}C_6H_4Me_2)(PMe_3)_2$	50.0 (50.0)	8.9 (8.8)	16.2 (16.1)	
$MoMe_2(C_6H_6)(PMe_2Ph)_2$	61.5 (60.0)	7.5 (7.1)	12.5 (12.9)	450 (480)
$MoMe_2(C_6H_5CH_3)(PMe_2Ph)_2$	61.2 (60.7)	7.3 (7.3)	12.7 (12.5)	478 (494)
$MoMe_2(o\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	61.1 (61.4)	7.5 (7.5)	12.0 (12.2)	
$MoMe_2(p\text{-}C_6H_4Me_2)(PMe_2Ph)_2$	61.4 (61.4)	7.7 (7.5)	12.5 (12.2)	463 (508)
$MoMe_2(C_6H_6)(CO)(PMe_2Ph)$	55.8 (55.1)	6.2 (6.2)		
$MoMe_2(C_8H_{12})(PMe_3)_2$	49.1 (49.7)	8.4 (9.3)		
$MoMe_2(C_8H_{12})(PMe_2Ph)_2$	61.4 (61.2)	7.7 (7.8)	12.5 (12.2)	

* Calculated values are given in parentheses.

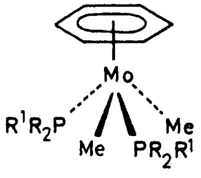
RESULTS AND DISCUSSION

Arene Complexes.—Interaction of $MoCl_3(thf)_3$ with PMe_3 under certain conditions (see Experimental section) gives a yellow-brown solid identified as $MoCl_3(PMe_3)(thf)_2$. This compound is stable in air for short periods of time but decomposes after longer exposure. It is soluble in aromatic hydrocarbons, dichloromethane, and tetrahydrofuran, but loss of tetrahydrofuran and consequently polymerisation occurs rapidly even in tetrahydrofuran solution, and a red, diamagnetic, slightly oily solid whose analysis is close to that for $Mo_2Cl_6(PMe_3)_2$ can be isolated. Similar behaviour has been observed for $MoCl_3(thf)_3$, and analogous dimeric complexes with other phosphines have been reported.[9]

When the dark solution obtained a few minutes after dissolution of $MoCl_3(PMe_3)(thf)_2$ in toluene, or after 1—2 h in tetrahydrofuran is treated with Me_2Mg, the dimer $Mo_2(CH_3)_4(PMe_3)_4$ is formed.[10] However, addition of solid, freshly prepared $MoCl_3(PMe_3)(thf)_2$ to a 2 : 1 mixture of benzene : tetrahydrofuran containing an excess of Me_2Mg gives a dark suspension, from which a red-purple solid, identified as $Mo(CH_3)_2(\eta^6\text{-}C_6H_6)(PMe_3)_2$, on the basis of analytical and spectroscopic data (Tables 1—3), can be obtained. Similar compounds are prepared using toluene and *o*- and *p*-xylene as solvents. $MoCl_3(PMe_2Ph)(thf)_2$ behaves similarly giving the red complexes $Mo(CH_3)_2(\eta^6\text{-}Ar)(PMe_2Ph)_2$. All the complexes are unstable to oxygen, decomposing immediately on exposure to air both in solution and in the solid state. They are all volatile, especially the trimethylphosphine derivatives which sublime at temperatures of 30—50 °C (10^{-2} mmHg). For the dimethylphenylphosphine complexes higher temperatures (80—100 °C) are required and extensive decomposition usually takes place. Molecular-weight determinations for some of the arenes indicate the compounds to be monomeric. On the basis of the similarities in their physical and spectroscopic properties, the remaining have also been assumed to be monomeric. None of the complexes gave a molecular ion when studied by mass spectroscopy, but the characteristic pattern for the corresponding arene was observed in every case.



(1)



(2)

The ^1H n.m.r. spectra of the alkyl-arene complexes are very similar. For the benzene and *p*-xylene complexes, the arene protons appear as a 1 : 2 : 1 triplet (J_{PH} *ca.* 1.5 Hz) centred at *ca.* τ 6, while the toluene and *o*-xylene derivatives give somewhat broad resonances, doubtless due to the presence of non-equivalent protons and to further coupling to the phosphorus nuclei. Each of the complexes exhibits a ' filled-in ' doublet for the methyl phosphine resonance. This situation has been described as intermediate coupling between the phosphorus nuclei [11] and in principle seems to suggest *cis*-stereochemistry for the phosphine (1). However, the alkyl resonance appears in every case as a well defined 1 : 2 : 1 triplet, only one coupling constant between the ^{31}P and ^1H nuclei being observed in the temperature range −80 to +80 °C in the instances in which variable-temperature n.m.r. studies were carried out. Furthermore, for the PMe_2Ph complexes only one methylphosphine resonance was observed indicating that the two phosphine methyl groups are equivalent, and that therefore the phosphines are ***trans*** (2). For a *cis*-structure there would be no plane of symmetry along the molybdenum phosphine axis, and the diastereotopic phosphine methyl groups would give rise to two distinct sets of doublets.[11,12] These conclusions are supported by *X*-ray crystal structure determinations [13] on $MoMe_2(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2$ and $MoMe_2(\eta^6\text{-}C_6H_5Me)(PMe_2Ph)_2$ which show *trans*-phosphines. The values of the P–Mo–P angle, 100.58 and 100.17° respectively, may account for the low magnitude of $J_{PP'}$ for these com-

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[10] R. A. Andersen, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J.C.S. Chem. Comm.*, 1977, 283; R. A. Andersen, R. A. Jones, and G. Wilkinson, *J.C.S. Dalton*, 1978, 446.

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[12] J. R. Shapley and J. A. Osborn, *Accounts Chem. Res.*, 1973, **6**, 305.

[13] J. L. Atwood, personal communication.

plexes (see later) and hence for the appearance of the phosphine methyl resonances as 'filled-in' doublets. Low values of $J_{PP'}$ are also common in bis(phosphine) complexes in which the phosphorus atoms are bonded to a metal with tetrahedral configuration.[14]

^{31}P n.m.r. spectroscopy does not provide much information about the structure of these complexes, since, as expected, a single resonance is observed in every case.

$^{13}C\{^1H\}$ n.m.r. data for the arene complexes are given in Table 2. Assignments of the C(1) and C(4) carbons for the monosubstituted arenes and of C(1) and C(2) or C(1) and C(4) for the *o*- and *p*-disubstituted arenes is simplified by the absence of nuclear Overhauser effect for the quaternary carbon atoms.[15] Assignment of the other carbon atom resonances follows previous studies on similar complexes.[1,2,16] The large upfield shift of the aromatic carbons on complexation is a general feature in complexes of this type and has been explained in terms of a build-up of negative charge on the arene ligand due to interaction with the metal, or of a rehybridisation of the aromatic carbons leading to a more saturated character [1,2] (*ca.* 25% from being olefinic towards being saturated). Consistent with both rationalisations is the increase in aromatic C–C bond lengths to *ca.* 1.40 Å in $(C_6H_6)Cr(CO)_3$ [1.41 Å,[13] in $Mo(CH_3)_2(C_6H_6)(PMe_2Ph)_2$].

The methylphosphine carbon resonances are particularly informative. It was originally thought that the same requirements holding for observation of doublets *vs.* triplets in ^1H n.m.r. would apply to $^{13}C\{^1H\}$ n.m.r.[17] This assumption was later shown to be incorrect as the spin system for the ^{13}C nuclei in bis-phosphine complexes should not be $X_3AA'X'_3$ but rather AA'X or ABX.[18] For the complexes prepared in this work, the methyl phosphine resonances appear in most cases as quintets, although in some instances the outer lines were too weak to be clearly distinguished. As the intensities of the lines need to be used for the computation of the coupling constants $J_{PP'}$, J_{PC}, and $J_{P'C}$, only when a clear quintet was observed, a full analysis was attempted.[19] However, since the methyl-arene resonances appear also in this region and in some cases the quintets were slightly distorted, the results shown in Table 2 should be considered only approximate. The value of *ca.* 20 Hz found for $J_{PP'}$ is consistent with the appearance of the methyl–phosphine proton resonances as 'filled-in' doublets, and is probably determined by the low magnitude of the P–Mo–P angle.

The methyl alkyl resonance appears in every case as a well defined 1 : 2 : 1 triplet (J_{PC} *ca.* 23 Hz), also supporting the *trans* square-pyramid structure proposed for these complexes.

Reaction of $Mo(CH_3)_3(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2$ *with* CO. Although the low yields obtained in the preparation of the methyl–arene complexes (see Experimental section) precluded a thorough investigation of their chemistry, attempts were made to study their chemical properties. No interaction was observed with H_2 and C_2H_4 at room temperature and atmospheric pressure over a period of 5—6 h, and extensive decomposition occurred on warming at 60 °C. However, on bubbling CO through a benzene solution of $Mo(CH_3)_2(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2$, carbon monoxide absorption takes place in a smooth, irreversible reaction with substitution of one phosphine group by CO. After being stirred at room temperature for *ca.* 1 h, the ^1H n.m.r. of the reaction mixture shows a singlet at *ca.* τ 5.7 and three doublets approximately centred at τ 8.5 (J_{PH} 6.7 Hz), 8.8 (J_{PH} 3.7 Hz, free phosphine), and 10.2 (J_{PH} 10.7 Hz). Following work-up, moderately air-stable red-orange crystals of $MoMe_2(\eta^6\text{-}C_6H_6)(CO)(PMe_2Ph)$ were isolated. Similar reactions took place with other arenes, but no attempts were made to isolate the products. On further bubbling of CO through the mixture some changes in the ^1H n.m.r. spectrum were observed. Thus, after *ca.* 5 h, new resonances appeared at τ 7.75 and 8.3, which as the reaction progressed grew in intensity at the expense of the doublet at τ 10.2. The singlet at τ 5.7 diminished also in intensity and two new resonances could be observed, the first, probably a triplet partially superimposed on the high-field region of the singlet at 5.7, only the two higher-field lines being observed, the second a quartet at *ca.* τ 6.15 (J_{PH} 2 Hz). Moreover, a somewhat broad resonance appeared in between the doublet at τ 8.5 while this doublet and the one at τ 8.8 corresponding to free phosphine became less intense. After bubbling of CO for 24 h the same features were observed and substantial amounts of the compound $MoMe_2(\eta^6\text{-}C_6H_6)(CO)(PMe_2Ph)$ were still present in solution. Some decomposition occurred as evidenced by the presence of a black, insoluble finely divided solid. The same changes in the ^1H n.m.r. were observed when the solution resulting from bubbling of CO for *ca.* 1½ h was stirred under nitrogen. After two days a yellow-brown solution and a black solid were obtained, occasional removal of solvent *in vacuo* considerably accelerating the course of the reaction. From the resulting solution orange crystals identified as $Mo(\eta^6\text{-}C_6H_6)(PMe_2Ph)_3$ (see Experimental section) were isolated. Clearly partial decomposition is required at some stage to account for the formation of the latter complex. A mechanism taking into account the above considerations is proposed in the Scheme. Dissociation of phosphine followed by attack of CO on the resulting 16-electron species gives $MoMe_2(\eta^6\text{-}C_6H_6)(CO)(PMe_2Ph)$ (3) which was isolated and characterised by microanalysis and i.r. and ^1H n.m.r. spectroscopy. Attack of

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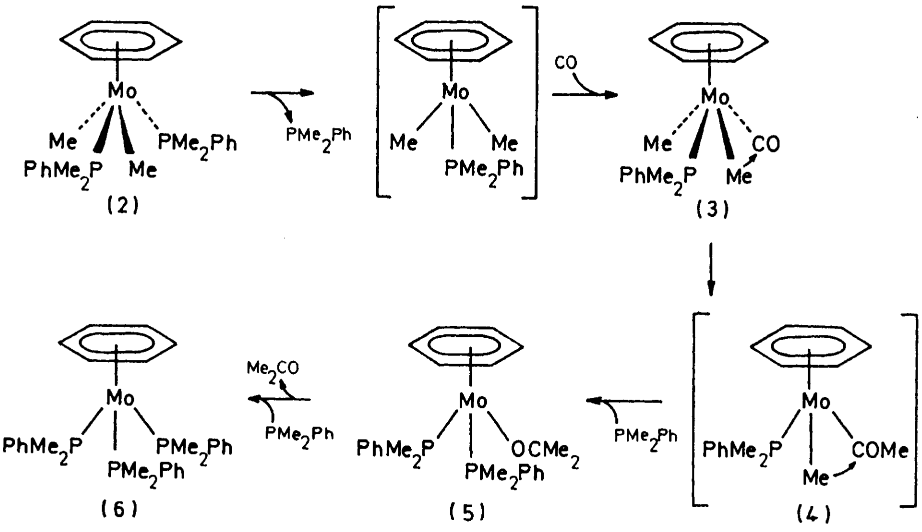
[18] D. E. Axelson and C. E. Holloway, *J.C.S. Chem. Comm.*, 1973, 455.

[19] D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 727 and references therein.

one of the methyl groups on the co-ordinated CO to yield the unstable acyl-alkyl complex (4), and migration of the remaining methyl group as in the Scheme, followed by attack of phosphine, might account for the formation of the acetone complex $Mo(Me_2CO)(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2$ (5). The resonance at τ 7.75 can tentatively be assigned to the co-ordinated acetone methyl protons and the triplet at *ca.* τ 5.8 to the arene protons. Isolation of the acetone complex proved difficult since it irreversibly loses acetone to give $Mo(\eta^6\text{-}C_6H_6)(PMe_2Ph)_3$ [8] (6). The singlet at τ 8.3 can be attributed to free acetone by comparison with the spectrum of pure acetone in a benzene solution at approximately the same concentration. Acetone was also detected by g.l.c.



SCHEME

Cyclo-octadiene Complexes.—No reaction was observed when $MoCl_3(PR_3)(thf)_2$ was treated with Me_2Mg in the presence of C_2H_4, cycloheptatriene, and cyclo-octatetraene. With cyclo-octa-1,5-diene (cod), green crystalline products tentatively formulated as $Mo(CH_3)_2(\eta^4\text{-cod})(PR_3)_2$ ($PR_3 = PMe_3$ or PMe_2Ph) were isolated in low yields (*ca.* 10%). Similar compounds were formed in the presence of norbornadiene, but rapid polymerisation of the olefin in the reaction conditions precluded isolation of the products.

I.r. spectra of the cyclo-octadiene complexes clearly show the absence of unco-ordinated C=C, but unambiguous assignment of the complexed C=C stretching frequency is difficult due to the presence of other absorptions in this region. ^1H n.m.r. spectra are not very informative. While two sets of resonances, namely olefinic and aliphatic, are usually observed in cyclo-octadiene complexes of transition metals, in the complexes prepared in this work only a broad resonance has been found in the temperature range −80 to +60 °C (extensive decomposition occurs at higher temperatures). The methyl phosphine resonance appears in each case as a 1 : 2 : 1 virtually coupled triplet ($J_{PH} + J_{PH'}$ *ca.* 5 Hz), and for the molybdenum-bonded methyls, a 1 : 2 : 1 triplet (J_{PH} 8 Hz) is also observed in the temperature range studied. Integration of the three sets of resonances corresponds very closely to a formulation $MoMe_2(C_8H_{12})(PR_3)_2$, with the chemical shifts of the cod olefinic and aliphatic protons being coincidentally equivalent. On the basis of the available information, a structure with *trans*-phosphines and *cis*-methyl groups seems reasonable. An *X*-ray crystal-structure determination on $MoMe_2(C_8H_{12})(PMe_2Ph)_2$ is in progress.

EXPERIMENTAL

Microanalyses were by Imperial College, Butterworth Microanalytical Consultancy Limited, Middlesex, and Pascher, Bonn, Microanalytical laboratories.

Molecular weights were measured cryoscopically in benzene under N_2 atmosphere. Spectroscopic instruments: i.r. Perkin-Elmer models 457 and 257; ^1H n.m.r. Perkin-Elmer R12A, ^{13}C and ^{31}P n.m.r., Varian XL100-12.

Me_2Mg was prepared from MeMgCl and dioxan, and $MoCl_3(thf)_3$ as previously described.[9] Benzene and toluene were dried over sodium and distilled under N_2; *o*- and *p*-xylene were used as purchased after distillation under N_2. Olefins were dried over anhydrous Na_2SO_4 and distilled under N_2. The light petroleum used had b.p. 40—60 °C. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk-tube techniques.

Trichlorobis(tetrahydrofuran)(trimethylphosphine)molybdenum(III).—(*a*) $MoCl_3(thf)_3$ (0.21 g, *ca.* 0.5 mmol) and PMe_3 (1.5 mmol) were stirred in diethyl ether (60 ml) for 30 min. The resulting yellow-brown solid was filtered off, washed with ether (2 × 5 ml), and dried *in vacuo* for 5—10 min (yield 75%). Although this solid was sufficiently pure to be used in subsequent reactions, further purification could be achieved by rapid crystallisation at low temperature (*ca.* −30 °C) from dichloromethane–methanol (Found: C, 30.7; H, 6.0; Cl, 24.1; P, 7.3. Calc. for $C_{11}H_{25}Cl_3MoO_2P$: C, 31.2; H, 5.5; Cl, 25.2; P, 7.3), $\nu_{max.}$ (KBr disc) 2 970, 2 940, 2 900, 2 870, 1 480, 1 450, 1 420, 1 345, 1 285, 1 250, 1 175, 1 040, 1 010, 960, 920, 850, 740, 680, 570, 320, and 290 cm^{-1}.

(*b*) This procedure is essentially identical to that of Chatt *et al.* for similar complexes.[9] To a suspension of $MoCl_3$-

(thf)$_3$ (0.84 g, *ca.* 2 mmol) in tetrahydrofuran (25 ml), a large excess of PMe$_3$ (*ca.* 16 mmol) was added. The mixture was stirred at room temperature until all the solid had been taken into solution, and then the solvent was removed under reduced pressure until the final volume was *ca.* 5 ml. Cooling at -50 °C and addition of diethyl ether (50 ml) to the mixture caused a yellow-brown solid to precipitate. The compound was filtered off, washed with ether at room temperature (2×5 ml), and dried *in vacuo* for 5—10 min (yield 70—75%).

Trichloro(dimethylphenylphosphine)bis(tetrahydrofuran)-molybdenum(III).—This compound was prepared as in (*b*) above using MoCl$_3$(thf)$_3$ (1.68 g), PMe$_2$Ph (4 ml) and tetrahydrofuran (35 ml). Following precipitation with ether, the solid was thoroughly washed with light petroleum to remove excess of PMe$_2$Ph and dried *in vacuo* (yield 70—75%), $\nu_{max.}$ (KBr disc) 3 050, 2 980, 2 960, 2 890, 1 480, 1 450, 1 435, 1 340, 1 290, 1 245, 1 190, 1 010, 915, 895, 885, 850, 760, 745, 730, 695, 510, 460, 420, 325, and 295 cm^{-1}.

Both MoCl$_3$(PR$_3$)(thf)$_2$ complexes are unstable and decompose slowly even under N$_2$ and at 0 °C. The trimethylphosphine compound is particularly unstable and should be used immediately after being prepared.

Reaction of MoCl$_3$(PMe$_3$)(thf)$_2$ *with* Me$_2$Mg *in Tetrahydrofuran.*—MoCl$_3$(PMe$_3$)(thf)$_2$ (0.3 g) was stirred at room temperature in dry, deoxygenated tetrahydrofuran (25 ml) for *ca.* 3 h after which PMe$_3$ (0.1 ml) and an excess of Me$_2$Mg were added; the mixture was then stirred at room temperature overnight. Removal of the solvent under reduced pressure, extraction with light petroleum (50 ml), and filtration afforded a blue solution from which blue crystals were obtained on cooling of the solution at -25 °C. The compound was identified (i.r. and n.m.r. spectra) as the dimer Mo$_2$Me$_3$(PMe$_3$)$_4$ [10] (yield 60%).

Dimethyl(η^6-arene)bis(tertiary phosphine)molybdenum(II) *Complexes.*—All the arene complexes were prepared by similar procedures. Yields were between 15 and 25% although in some instances, especially when using freshly prepared reagents, the reactions were cleaner and yields of up to 30% (theoretical yield 50%) were obtained. Attempts to increase the yields by modifying the reaction conditions, the order of addition of the reactants, and the alkylating reagents (Me$_3$Al and MeMgI) failed. Addition of free phosphine did not improve the yields but made isolation of the complexes more difficult as other undesirable products were also formed. No improvements were observed by performing the reactions in the presence of Al–AlCl$_3$ or Zn powder. A typical preparation is the following:

MoCl$_3$(PR$_3$)(thf)$_2$ (*ca.* 1.5 mmol) was added to a 2 : 1 mixture of arene–tetrahydrofuran containing an excess of Me$_2$Mg (*ca.* 6 mequiv) and the resulting dark brown suspension was stirred at room temperature for 20—30 min. The solvent was then removed under reduced pressure and the residue extracted with light petroleum (60—80 ml). Filtration was difficult and several centrifugations and/or filtrations might be needed at this point before a completely clear solution were obtained. The solvent was again evaporated under reduced pressure and the residue dried under high vacuum to remove traces of solvent. Addition of light petroleum (50 ml) and filtration if necessary afforded red-purple (trimethylphosphine derivatives) or dark red (dimethyl phenyl complexes) solutions of the arenes. The MoMe$_2$(η^6-arene)(PMe$_2$Ph)$_2$ compounds were readily crystallised from these solutions on concentration and cooling at -25 °C (arene = benzene or toluene) or at -78 °C (arene = *o*- and *p*-xylene). For MoMe$_2$(η^6-Ar)(PMe$_3$)$_2$ complexes, crystallisation was only achieved by concentration to 2—3 ml and cooling at -78 °C. Rapid stirring might also be necessary to induce crystallisation. All the compounds are highly crystalline solids with the exceptions of MoMe$_2$(η^6-toluene)(PMe$_3$)$_2$ which is slightly oily at room temperature although crystalline at lower temperatures, and MoMe$_2$(η^6-*o*-xylene)(PMe$_3$)$_2$ which is a liquid at room temperature.

η-Benzene(carbonyl)dimethyl(dimethylphosphine)molybdenum(II).—Carbon monoxide was bubbled at room temperature with stirring through a solution of Mo(CH$_3$)$_2$(η^6-C$_6$H$_6$)(PMe$_2$Ph)$_2$ (60 mg) in benzene (5 ml) for 1 h. The solvent was then removed *in vacuo* and the dissociated phosphine distilled off by prolonged pumping at 25 °C and 10^{-3} mmHg. The residue was redissolved in light petroleum (30 ml) and filtered quickly. Concentration to *ca.* 10—15 ml and cooling at -25 °C afforded orange crystals of MoMe$_2$(η^6-C$_6$H$_6$)(CO)(PMe$_2$Ph) in 70% yield, ν(C≡O) 1 920 cm^{-1} (light petroleum solution). When a benzene solution of this complex was stirred under N$_2$ some changes in the ^{1}H n.m.r. spectrum were observed (see text). After removal of the solvent under reduced pressure and extraction with light petroleum an orange solution was obtained from which orange crystals precipitated on cooling at -25 °C. The compound was identified as Mo(η^6-C$_6$H$_6$)(PMe$_2$Ph)$_3$ on the basis of ^{1}H n.m.r. and analytical data; τ (benzene solution) 6.15 (quartet, J_{PH} 2 Hz) and 8.7br (multiplet) (Found: C, 61.1; H, 6.5; P, 15.8. Calc. for C$_{30}$H$_{39}$MoP$_3$: C, 61.2; H, 6.6; P, 15.8%).

Cyclo-octadiene(dimethyl)bis(phosphine)molybdenum(II).—To a 3 : 1 mixture of tetrahydrofuran–cyclo-octa-1,5-diene (20 ml), Me$_2$Mg (6 ml, 0.35M-solution) and MoCl$_3$(PR$_3$)(thf)$_2$ (*ca.* 1 mmol) were successively added in this order. The mixture was stirred at room temperature for 15—20 min and the solvent removed under reduced pressure. Extraction with light petroleum afforded a green-blue solution. Again several filtrations or centrifugations might be needed before a clear solution were obtained. The more soluble trimethylphosphine derivative required concentration to *ca.* 3—5 ml and cooling at -78 °C with rapid stirring, while for the dimethylphenylphosphine complex, green crystals were obtained on concentration to 5—10 ml and cooling at -25 °C. In the latter case, small amounts of red crystals, somewhat less petroleum-soluble than the green ones, were observed after the first crystallisation. The ^{1}H Fourier transform n.m.r. spectrum of the red crystals was identical to that of the green compound. The red material is probably an isomeric form that is slowly converted into the green species, but the lack of spectroscopic data precluded us from proposing a structure for this compound.

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