Arene–Molybdenum Chemistry: A Novel Redistribution Reaction of Alkenes on Molybdenum forming Cationic Diene Complexes and Alkanes

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The dimeric complexes $[(\pi\text{-}C_6H_6)Mo(R^1C_3H_3R^2)Cl]_2$, $R^1C_3H_3R^2 = C_3H_5$, MeC_3H_4, or MeC_3H_3Me, are formed from $(\pi\text{-}C_6H_6)_2Mo$ and $R^1C_3H_3R^2Cl$. They react with ethylaluminium dichloride in benzene giving violet solutions. With mono-olefins at 20° these give alkanes and, after hydrolysis and treatment with NH_4PF_6, cationic diene complexes of type $[(\pi\text{-}C_6H_6)Mo(\pi\text{-alkenyl})(diene)]^+PF_6^-$. Thus, propene undergoes oxidative dimerisation to the *trans,trans*-hexa-2,4-diene complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(\pi\text{-}C_6H_{10})]^+PF_6^-$ whereas *cis*-pent-2-ene yields the penta-1,3-diene complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+PF_6^-$ and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+PF_6^-$. The diene compounds may also be synthesised from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ with the corresponding conjugated dienes. A possible mechanism is presented for the disproportionation of the mono-olefins into diene complexes and alkanes. The violet solutions also act as catalysts for the dimerisation of ethylene to butenes at 20° and for co-dimerisation of ethylene and propene to pentenes.

THE factors controlling the role of transition metals in the activation of olefins and subsequent catalytic reactions such as dimerisation, oligomerisation, or metathesis are generally not well understood. Until recently relatively few studies using the heavier metals of Groups IV—VII have been made. The observation of olefin metathesis by systems containing molybdenum[1] together with our own interest in the organic chemistry of this metal[2] led us to look for further catalytic reactions of olefins using molybdenum. The 16-electron dimer $[(\pi\text{-}C_3H_5)NiCl]_2$ has been shown to be a precursor for a variety of olefin activation catalyses.[3] The 18-electron dimer $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$[4] clearly bears some simple similarities to the nickel compound. It has also been shown that this molybdenum dimer readily gives rise to highly electron-rich systems which react with molecular nitrogen.[5] We set out therefore to explore possible olefin activation and catalytic activity of the dimeric allyl molybdenum system. The work described below shows that this system is indeed active and *inter alia* causes oxidative dimerisation of propene giving a hexa-2,4-diene complex and the catalytic dimerisation of ethylene to butene. A brief report of this work has been made.[6]

(a) *Syntheses of the π-Allylic Dimers* $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$, $R^1C_3H_3R^2 = C_3H_5$, MeC_3H_4, MeC_3H_3Me, *or* EtC_3H_4.—Bis(benzene)molybdenum reacts, at 30° in benzene solution, with allyl chloride forming the dimeric complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$. Analogous reactions using *trans*-1-chlorobut-2-ene, *cis,trans*-2-chloropent-3-ene, and 3-chloropent-1-ene yield respectively the complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$, $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$, and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)Cl]_2$.

All are purple crystalline solids, sensitive to oxygen and sparingly soluble in organic solvents, insufficiently so for their n.m.r. spectra to be determined. They have been characterised by analysis and i.r. spectroscopy and by analogy with the π-allyl dimer $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ whose crystal structure has been determined.[7]

These complexes act as polymerisation catalysts for buta-1,3-diene and alkynes[2] but no interaction between them and mono-olefins has been observed. Thus the complex $[(\pi\text{-}C_6H_5Me)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ was heated in pure propene as solvent (in which it is slightly soluble) at 80° for 20 h. The starting dimer was recovered in high yield and no organic products other than propene were identified. Similarly the presence of excess of propene during the preparation of the dimeric complexes from $(\pi\text{-}C_6H_6)_2Mo$ did not significantly affect their formation.

(b) *Reaction of* $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ *with*

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[1] N. Calderon, *Accounts Chem. Res.*, 1972, **5**, 127.

[2] M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, and W. E. Silverthorn, *Chem. Comm.*, 1971, 1619.

[3] G. Lefebvre and Y. Chauvin, 'Aspects of Homogeneous Catalysis,' ed. R. Ugo, Manfredi, Milan, 1970, vol. 1, p. 108.

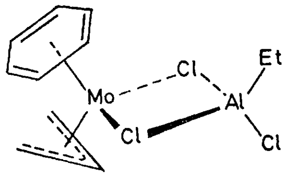
[4] M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.

[5] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

[6] M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, and W. E. Silverthorn, *Chem. Comm.*, 1972, 987.

[7] T. S. Cameron, C. K. Prout, and G. V. Rees, personal communication.

Ethylaluminium Dichloride.—The dimers $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ react instantly at 20° with benzene solutions of ethylaluminium dichloride giving reactive violet solutions. Although the violet species have not been fully characterised, the identity of the product of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ and $EtAlCl_2$ as $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl,AlEtCl_2$ (I) is suggested by the following



(I)

evidence: (i) the dimer complex is virtually insoluble in benzene alone and the minimum quantity of ethylaluminium dichloride necessary for complete solution corresponds to a Mo : Al ratio of 1 : 1; (ii) the n.m.r. spectrum of the violet solution obtained shows resonances due to the $\pi\text{-}C_6H_6$ and $\pi\text{-}C_3H_5$ groups together with resonances due to an ethyl group whose chemical shift values are similar to those of the ethyl group in the spectrum of ethylaluminium dichloride itself; the data is given in the Experimental section; (iii) addition of diethyl ether to a benzene solution of the violet species causes almost quantitative precipitation of the initial dimer complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ and (iv) of the four aluminium compounds $AlBr_3$, $EtAlCl_2$, Et_2AlCl, and Et_3Al, the first three react rapidly with $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ at 20° giving violet solutions whilst Et_3Al reacts only slowly and gives a red solution from which the initial dimer complex cannot be recovered. These data are most consistent with the presence of two chlorine bridges in the violet species and suggest that the ethyl group present in the violet complex from ethylaluminium dichloride fulfils no special role in relation to the molybdenum.

The type of structure proposed for the violet complexes thus contains two chlorine atoms bridging between a transition metal and aluminium and is not without precedent in organometallic chemistry. Indeed, an *X*-ray crystallographic determination of the structure of $(\pi\text{-}C_5H_5)_2TiCl_2AlEt_2$ [8] reveals the presence of chloride bridges between titanium and aluminium, and treatment of this complex with ether gives the analogous chloride dimer $[(\pi\text{-}C_5H_5)_2TiCl]_2$.[9]

(c) *Synthesis of Cationic Molybdenum Diene Complexes of Type* $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)(diene)]^+PF_6^-$ *from Conjugated Dienes.*—The violet solution formed from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ with ethylaluminium dichloride in benzene reacts with buta-1,3-diene at 5° yielding a red oil which precipitates from solution. Decomposition of the latter with ethanol at low temperature and subsequent extraction of the products into water and addition of ammonium hexafluorophosphate gives the complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)]^+PF_6^-$ in high yield.

TABLE 1

Analytical and n.m.r. data

Compound	Colour	Analytical data % Found (Reqd.) C	Analytical data % Found (Reqd.) H	^{1}H N.m.r. spectra [a]
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$	Purple	45·2(45·4)	5·0(5·0)	
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$	Purple	47·0(47·4)	5·7(5·4)	
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)Cl]_2$	Purple	46·5(47·4)	5·5(5·5)	
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)]PF_6$	Orange	37·4(37·7)	4·3(4·1)	4·37, **6**, *s*; 4·73, **2**, *c*; 4·83, **1**, *c*; 6·83, **2**, *d*(9·5); 6·95, **2**, *d*(7·5); 7·71, **2**, *d*(13·5); 8·45, **2**, *d*(10)
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_5H_8)]PF_6$	Orange	39·2(39·3)	4·2(4·5)	4·49, **6**, *s*; 4·84, **3**, *c*; 6·90, **1**, *d*(8·5); 6·94, **1**, *d*(9); 7·05, **1**, *d*(9); 7·65, **1**, *d*(14); 7·76, **1**, *c*; 7·83, **1**, *d*(14); 8·19, **3**, *d*(6); 8·56, **1**, *d*(12)
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]PF_6$	Orange	40·6(40·8)	4·8(4·8)	4·57, **6**, *s*; 4·74, **1**, *c*; 4·97, **2**, *d*(9·5); 6·99, **2**, *d*(8); 7·76, **2**, *d*(13); 7·90, **2**, *c*; 8·23, **6**, *d*(6)
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_5H_8)]PF_6$	Orange	40·7(40·8)	4·9(4·9) [b]	4·53, **6**, *s*; 4·61, **1**, *c*; 4·92, **2**, *c*; 6·81, **1**, *c*; 7·21, **1**, *d*(8·5); 7·35, **1**, *d*(9); 7·76, **1**, *c*; 8·03, **1**, *d*(13); 8·18, **3**, *d*(6); 8·41, **3**, *d*(6·5); 8·63, **1**, *d*(13) [b]
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_8H_{14})]PF_6$	Orange	44·4(44·7)	5·7(5·6)	
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]PF_6$	Orange	42·2(42·1)	5·1(5·1) [c]	4·55, **6**, *s*; 4·71, **2**, *c*; 5·07, **1**, *t*(12); 7·17, **1**, *c*; 7·31, **1**, *c*; 7·45, **1**, *d*(8·5); 7·77, **1**, *c*; 8·25, **3**, *d*(6); 8·29, **3**, *d*(6·5); 8·46, **3**, *d*(6·5); 8·66, **1**, *d*(11·5)
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]PF_6$	Orange	42·0(42·1)	4·9(5·1) [b]	4·52, **6**, *s*; 4·67, **1**, *c*; 4·92, **2**, *c*; 6·98, **1**, *c*; 7·18, **1**, *d*(7·5); 7·32, **1**, *d*(8); 7·75, **1**, *c*; 7·99, **1**, *d*(11·5); 8·08, **2**, *c*; 8·17 **3**, *d*(6); 8·59, **1**, *d*(12); 8·98, **3**, *t*(7·5) [b]
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_6H_{11})(C_6H_{10})]PF_6$	Orange	44·7(44·7)	5·8(5·6)	4·4—5·1, **9**, *complex band*; 6·9—9·1, **18**, *complex band*
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_8H_{15})(C_8H_{14})]PF_6$	Orange	48·8(48·9)	6·0(6·5)	4·4—5·1, **9**, *complex band*; 6·9—9·1, **26**, *complex band*

[a] Given as chemical shift (τ), relative intensity, multiplicity (*J* in Hz); in [$^2H_6$]dimethyl sulphoxide. [b] Data are given for one isomer only, prepared as described in Section D; the n.m.r. spectrum of the isomeric mixture, prepared according to Section C, exhibits the set of resonances given together with another set containing equal numbers of resonances of similar chemical shifts and multiplicities which are assigned to the second isomer. [c] Mo, 21·1, (21·0), P, 6·7, (6·8), F, 25·3, (25·0)%.

An analogous reaction of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ with *trans,trans*-hexa-2,4-diene in place of buta-1,3-diene yields $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$ and reactions of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ with penta-1,3-diene

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[8] G. Natta, P. Corradini, and I. W. Bassi, *J. Amer. Chem. Soc.*, 1958, **80**, 755.

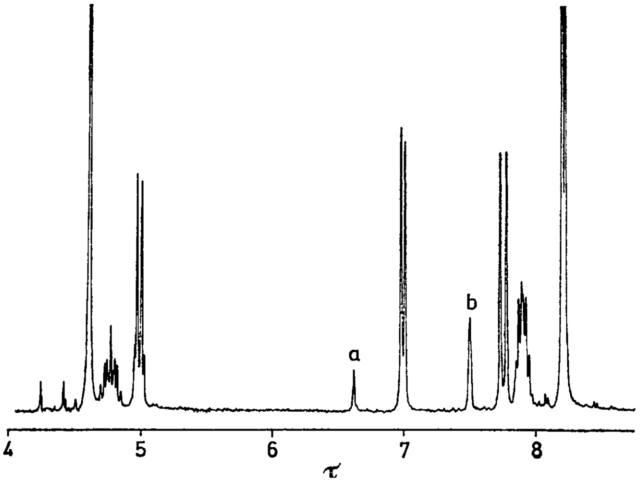
[9] D. S. Breslow and N. R. Newburg, *J. Amer. Chem. Soc.*, 1959, **81**, 81.

afford the series of complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)(C_5H_8)]^+PF_6^-$, $R^1C_3H_3R^2 = C_3H_5$, MeC_3H_4, MeC_3H_3Me, and EtC_3H_4.

An alternative synthesis of the cation $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)]^+$, as its tetrafluoroborate salt, may be achieved under mild conditions by the reaction of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ with thallium(I) tetrafluoroborate in acetone solution under an atmosphere of buta-1,3-diene.[2]

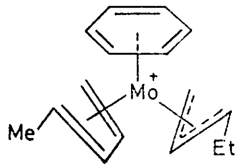
Some of the substituted diene compounds were also synthesised by analogous reactions, using the appropriate substituted allylic chloride dimer and the appropriate diene. The properties of complexes made by the two methods were found to be identical in all respects.

The compounds $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)(\text{diene})]^+PF_6^-$ are all orange air-stable crystalline solids, soluble in acetone and dimethyl sulphoxide and sparingly soluble in ethanol and ether. All have been characterised by analysis, n.m.r. at 270 MHz, and i.r. spectroscopy. The n.m.r. spectra are essentially first-order in all cases (Table 1). They indicate that only one isomer is present for most of the complexes and that when alkyl substituents are present either on the allylic or diene ligands, then the allylic ligand is in the *syn* conformation and the diene ligand in the *trans* conformation. For example, the n.m.r. spectrum of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$ (Figure) exhibits a resonance (τ 4·97) whose doublet structure arises from the coupling of hydrogen atoms bonded to C_3 and C_4 of the hexadiene ligand with those bonded to C_2 and C_5. The magnitude of coupling (9·5 Hz) suggests that the two sets of hydrogen atoms are *trans* to each other and hence the C_6H_{10} ligand is in the *trans,trans*-hexa-2,4-diene conformation. Likewise, the magnitude of coupling (12 Hz) of the triplet resonance (τ 5·07) occurring in the spectrum of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+PF_6^-$ suggests that the hydrogen atoms bonded to C_2 and C_4 of the $\pi\text{-}MeC_3H_3Me$ ligand are in a *trans* conformation in relation to the hydrogen atom bonded to C_3 and consequently the $\pi\text{-}MeC_3H_3Me$ ligand is assigned a *syn* conformation.

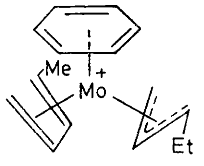


^1H N.m.r. spectrum at 270 MHz of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$ in $[^2H_6]$dimethyl sulphoxide; a, water resonance; b, solvent resonance

The n.m.r. spectra of the complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_5H_8)]^+PF_6^-$ and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+PF_6^-$, synthesised by both of the above methods, show that two species are present in each case because of the occurrence of two π-benzene resonances. The two forms are believed to be isomers which arise from the alkyl substituents on both the allylic and diene ligands being either on the same or opposite sides of the plane containing the molybdenum atom and bisecting the benzene, allylic, and diene groups (IIa, IIb).



(IIa)



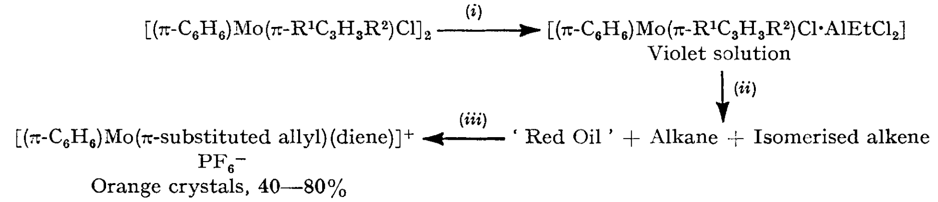
(IIb)

(d) *Synthesis of the Cationic Diene Complexes from Mono-olefins*.—The main part of this paper is concerned with the nature of products formed by interaction of the violet solutions with mono-olefins and with possible mechanisms for these reactions.

The general reaction is firstly described and then the results are presented in tabular form. Particular reactions are then discussed in more detail and finally the data obtained is used to suggest possible mechanisms for the reactions.

When the violet solutions obtained from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ with ethylaluminium dichloride are allowed to react with the mono-olefins propene, *cis*-but-2-ene, and *cis*-pent-2-ene at 20° (Scheme 1, Table 2), paraffin hydrocarbons are liberated and red oils are precipitated in each case. The oils may be decomposed with 95% ethanol at low temperature, extracted into water and the cations present precipitated with ammonium hexafluorophosphate. This yields cationic diene complexes of type $[(\pi\text{-}C_6H_6)Mo(\pi\text{-substituted allyl})(\text{diene})]^+PF_6^-$. Analytical, n.m.r., and i.r. data confirm that these complexes are identical to those prepared from conjugated dienes by the methods described above. The general reaction is represented by Scheme 1 and the organometallic products of particular reactions are shown in Table 2.

It is worth drawing attention to the following points from Scheme 1 and Table 2: (i) the principal alkane formed in each reaction contains the same number of carbon atoms as the alkene used and hence is presumably derived from it, (ii) likewise, each organometallic product contains an allylic group which is presumably derived from the alkene used because it also contains the same number of carbon atoms. In the case of reactions involving *cis*-pent-2-ene, both of the geometrical isomers of the pentenyl group, MeC_3H_3Me and EtC_3H_4, are observed in the organometallic products, (iii) each product also contains a conjugated diene group, which is penta-1,3-diene when either a C_5 olefin or C_5 allylic group is used.



SCHEME 1 Formation of cationic diene complexes and alkanes from reactions of the violet solutions with alkenes; (*i*) $EtAlCl_2$ in benzene, 20°; (*ii*) an excess of alkene, 20°; (*iii*) ethanol then NH_4PF_6

TABLE 2

Organometallic products of the reactions of the violet solutions from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2/EtAlCl_2$ with the alkenes propene, *cis*-but-2-ene, and *cis*-pent-2-ene [a]

	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$
Propene	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+$	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+$	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_5H_8)]^+$
cis-But-2-ene		$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_8H_{14})]^+$	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_5H_8)]^+$ [b]
cis-Pent-2-ene	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+$ + $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+$ [b]	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+$ + $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+$ [b]	$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+$ + $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+$ [b]

[a] Cations only are shown. [b] One isomer only.

When an excess of *cis*-but-2-ene reacts with the violet solution formed from the π-allyl derivative $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ with ethylaluminium dichloride propene is produced and the *cis*-but-2-ene is isomerised, the isomers being present in approximately thermodynamic equilibrium proportions. The amount of alkanes in the vapour is negligible after this period.

Decomposition of the mixture with ethanol at low temperature gives a 60% yield of the π-crotyl dimer $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ but no diene complexes were isolated (Scheme 2).

The proportion of red oil to violet solution depends on the concentration of *cis*-but-2-ene; thus, addition of more olefin causes further deposition of red oil whereas partial removal of olefin by evacuation results in intensification of the violet colour of the mother-liquor. These changes occur rapidly, suggesting a rapidly-attained equilibrium.

This allyl–olefin exchange reaction, if assumed to be the initial step in all the mono-olefin reactions described, accounts for the observation that the allylic groups present in the diene complexes are derived from the alkene used. However it is also a complicating factor in elucidation of the reaction mechanisms and for this reason only those reactions will be discussed here in which the allylic group in the initial dimer complex contains the same number of carbon atoms as the alkene used.

The reaction of *cis*-pent-2-ene with the violet solution formed from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$ and ethylaluminium dichloride is rapid at 20°; the violet colour of the solution is discharged after 30 min, a red oil is formed, n-pentane is produced, and the excess of pentene is isomerised.

Hydrolysis of the red oil and addition of ammonium hexafluorophosphate yields the two isomeric complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)]^+PF_6^-$ (40% yield) and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+PF_6^-$ (20% yield), both of which are separable and have been isolated and purified. N.m.r. spectroscopy indicates that only one isomer of the ethyl–allyl complex has been produced and this is in contrast to the two forms of the compound which result when the synthesis from penta-1,3-diene is employed, using both of the methods described earlier.

Using a propene : Mo ratio of 10 : 1 and an Al : Mo ratio of 2 : 1 at 20°, the reaction of propene with the violet solution from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ is complete after 4 h, making it convenient to follow its course by g.l.c. Over this period the concentration of propane builds up at the expense of propene and simultaneously there is a deposition of red oil and a colour change of the mother-liquor to pale red after 4 h.

When the propene : Mo ratio is 4 : 1, the same changes are complete after 2 days at 20° and g.l.c. indicates that liberation of propane is approximately one mole per gram-atom of molybdenum.

The red oil yields the complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$ in 78% yield and its n.m.r. spectrum indicates that exclusively one species is present, namely, the *trans,trans*-hexa-2,4-diene complex. No other isomers of the compound were observed among the products.

The reaction between *cis*-but-2-ene and the violet solution from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ over 30 min leads to the deposition of some red oil but a pale violet solution remains and no n-butane is formed. Decomposition of the mixture gives back the starting dimer in high yield.

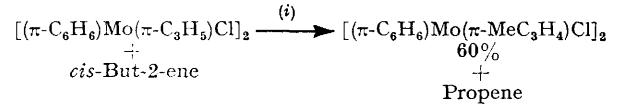
When the mixture is allowed to react until the violet colouration is discharged (5 days at 20° or 4 h at 60°), n-butane is produced and decomposition of the mixture as before yields an orange crystalline solid in 43% yield which analyses for $C_{18}H_{27}MoPF_6$. Its n.m.r. spectrum shows it to consist of at least four different species because of the four π-benzene resonances. Assuming that the different species are isomers each containing π-benzene and π-butenyl groups, the analytical data is consistent with a formulation $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_8H_{14})]^+PF_6^-$. The C_8H_{14} ligand could be an oxidative dimerisation product analogous to the *trans,-trans*-hexa-2,4-diene ligand in the propene reaction. However, in this case, straight- and branched-chain dimers such as octadienes and methylheptadienes may have been formed.

The violet solution from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ also reacts rapidly at 20° with larger straight-chain olefins such as hex-1-ene and oct-1-ene. The products are likewise red oils which on decomposition in a similar manner yield orange crystalline solids. Analytical and n.m.r. data for the products suggest the formulations $[(\pi\text{-}C_6H_6)Mo(\text{hexenyl})(\text{hexadiene})]^+PF_6^-$ and $[(\pi\text{-}C_6H_6)Mo(\text{octenyl})(\text{octadiene})]^+PF_6^-$ respectively. ^1H N.m.r. shows that each product contains a mixture of isomers.

Ethylene is catalytically dimerised to butene isomers at 20° by the violet solutions from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$. The number of cycles of dimerisation is low and some polymer is also obtained. The violet solution is converted to a red oil as before but decomposition of this with ethanol gave a solution from which no molybdenum diene complexes could be obtained.

When ethylene–propene (1 : 1) is employed, catalytic co-dimerisation to pentenes occurs as well as dimerisation of ethylene to butenes. Under similar conditions, g.l.c. studies show that the conversion of propene to hexenes is approximately stoicheiometric.

(e) *A Possible Mechanism for the Formation of Alkanes and Molybdenum Diene Complexes from Reactions of the Violet Solutions with Alkenes.*—Any mechanism for the reactions described in Section (d) must account for: (i) the allyl–olefin exchange reaction; (ii) the action of the violet solutions as olefin isomerisation catalysts;[6] (iii) the formation of approximately one mole of alkane per gram-atom of molybdenum; (iv) the oxidative dimerisation of propene *exclusively* to the *trans,trans*-hexa-2,4-diene derivative; (v) the apparent oxidative dimerisation of butene to a C_8 diene derivative rather than its oxidation to a buta-1,3-diene cation, and (vi) the formation of only one isomer of a diene complex in some cases when geometrical isomers are possible and appear to be obtained when the complex is synthesised from the corresponding diene. [Section (c)].



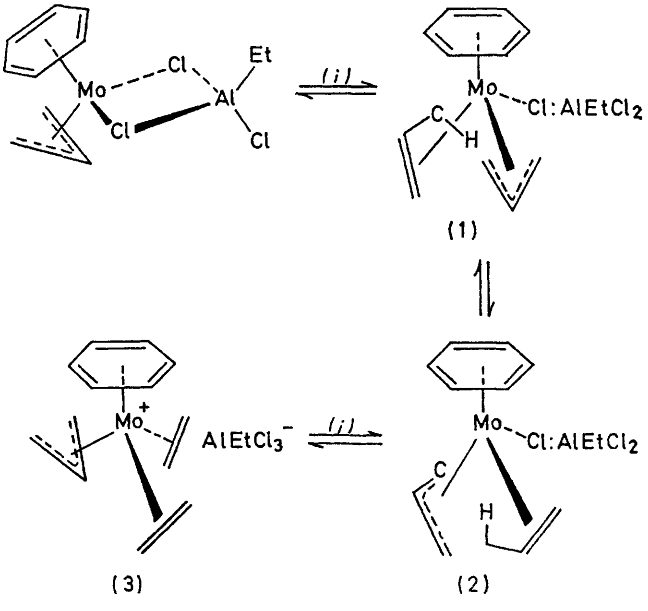
$$\begin{array}{c}[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2\\ +\\ cis\text{-But-2-ene}\end{array} \xrightarrow{(i)} \begin{array}{c}[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2\\ 60\%\\ +\\ \text{Propene}\end{array}$$

SCHEME 2 Formation of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ by allyl–olefin exchange; (*i*) $EtAlCl_2$ in benzene, 20°, 30 min, followed by ethanol

As a basis for a possible mechanism, it is assumed that the red oils produced just prior to hydrolysis and isolation of the diene cations as their hexafluorophosphate salts already consist of these cations (which are eventually isolated) together with tetrahedral chloroaluminate anions of type $EtAlCl_3^-$ or $Et_2Al_2Cl_5^-$ according to the concentration of $EtAlCl_2$ used.

Attempts to verify this by obtaining n.m.r. spectra of the oil in the propene reaction were foiled by partial solidification when solvent was removed. However since the alkane is released before addition of ethanol in all cases, the stoicheiometry of reaction suggests that dehydrogenation of the olefin has already occurred. Considerable amounts of ethane are evolved after addition of ethanol to the red oils, consistent with the latter containing the $EtAlCl_3^-$ and related anions.

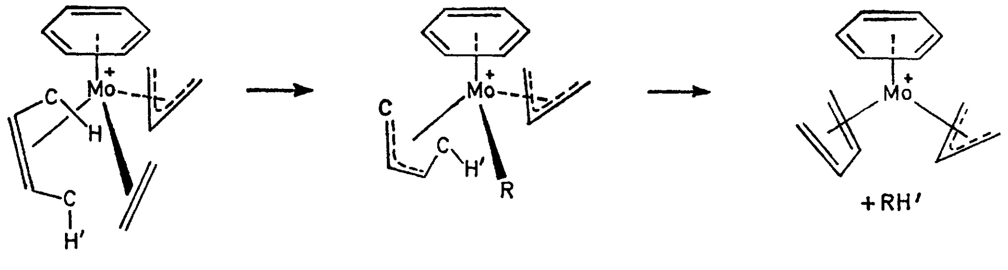
Accepting the structure proposed in Section (b) for the violet species obtained from the chloride dimers with ethylaluminium dichloride, the most likely roles for the aluminium group are first to decrease the electron density on the molybdenum relative to that in the dimers themselves, which do not react with mono-olefins under similar conditions. This would make initial co-ordination of olefin by the violet species more favourable. The second role would be to convert the bridging chlorine atoms into better leaving groups than chloride ion by co-ordination to one or more $EtAlCl_2$ molecules and subsequent removal as $EtAlCl_3^-$ or $Et_2Al_2Cl_5^-$ allowing co-ordination of a second olefin molecule (Scheme 3). Thus ethylaluminium dichloride acts as a chloride ion abstractor which, unlike thallium(I) tetrafluoroborate, operates in non-polar media.



SCHEME 3 A possible mechanism for the allyl–olefin exchange reaction; (*i*), ± olefin

Several of the observed facts may now be satisfactorily explained by postulating a sequence of hydrogen atom transfer reactions. Thus transfer of hydrogen between allylic and alkene groups in the intermediates shown (Scheme 3) accounts for the allyl–olefin exchange reaction and for the fact that the allylic groups in the organometallic products are derived from the alkene

(Table 2). Also, since alkene ligands in the intermediates could rapidly exchange with free alkene molecules, the hydrogen transfer also explains the role of the violet species as precursors for olefin isomerisation catalysts.[6] The hydrogen transfer may be envisaged to occur by several routes, for example, by a four-centre intermediate involving the metal, the two carbon atoms, and the hydrogen atom, or, an intermediate metal hydride may first be formed. Support for the conformation of the bis(olefin) cation intermediate [Scheme 3, (3)] has been obtained by isolation of the complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(\text{norbornadiene})]^+PF_6^-$ [10] whose n.m.r. spectrum indicates that the double bonds of the norbornadiene ligand are aligned with respect to the allyl group in a manner analogous to that shown in Scheme 3.



(3) (4) (5)

SCHEME 4 A possible mechanism for the formation of the diene complexes by alkane elimination

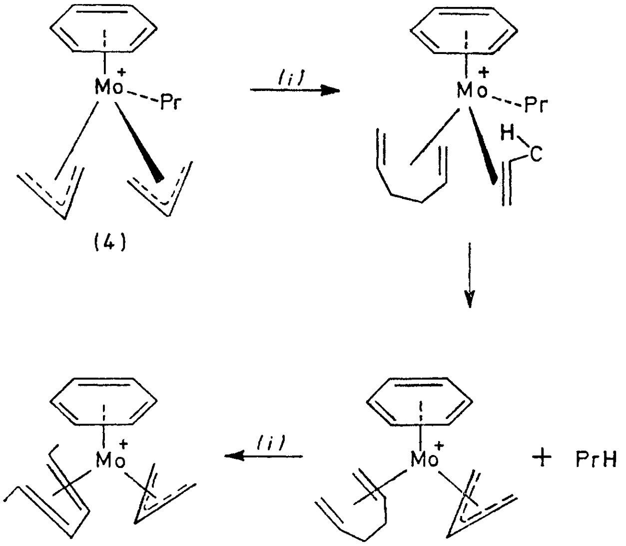
The liberation of alkane is presumed to be irreversible and it seems most reasonable that the species from which the alkane is removed contains the corresponding σ-alkyl group since simultaneous acquisition of two hydrogen atoms by a hydrocarbon group is less likely under these conditions. The desired products in some of the reactions may now be obtained by postulating further hydrogen transfer reactions *via* 18-electron intermediates (Scheme 4).

In this way, the nature of the products formed in reactions not involving oxidative dimerisation is accounted for. When both allylic and diene ligands have alkyl substituents and there is a possibility of forming two geometrical isomers, this mechanism can also suggest why only one is formed. This is because in the highly crowded bis(allyl)alkyl intermediate [Scheme 4, (4)], the alkyl substituents will both be at the terminal carbon atoms of the allylic groups which are furthest from each other. The Scheme thus predicts that after the final hydrogen transfer the diene product will contain alkyl substituents which are on the same side of the plane bisecting the ligands and passing through the metal atom (IIa). Unfortunately this cannot be verified by n.m.r. since the spectra of both isomers are similar.

The presentation of a mechanism for the oxidative dimerisation reactions of propene and butene is more difficult. The reaction with ethylene does not yield a buta-1,3-diene complex and this difference of reaction of ethylene from those of propene and butene perhaps suggests an allylic coupling mechanism for the dimerisation step, this being clearly impossible in the case of ethylene. A possible mechanism for the formation of the hexadiene derivative is shown in Scheme 5, where coupling of the two allyl groups gives initially a hexa-1,5-diene derivative. Intramolecular coupling of two π-allyl groups forming hexa-1,5-diene is well known, for example, in nickel chemistry.[11]

Indeed, when the violet solution from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ is reacted with hexa-1,5-diene and the red oil obtained is decomposed as described above, some of the *trans,trans*-hexa-2,4-diene complex is obtained but other products are also formed which cannot be isolated in a pure condition.

If the allylic coupling mechanism (Scheme 5) is slow compared to the alkane elimination mechanism (Scheme 4) then when competition is possible between the two pathways, as in the case of the pentene reaction, the reaction would proceed *via* the alkane elimination mechanism exclusively.



SCHEME 5 A possible mechanism for the formation of the hexa-2,4-diene complex from propene by allylic coupling; (*i*), + propene

Another possible mechanism for the formation of the

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[10] M. L. H. Green and J. Knight, to be published.

[11] See, for example, G. Wilke and B. Bogdanovic, *Angew. Chem.*, 1961, **73**, 756.

hexadiene compound from propene is *via* an initial dimerisation of propene to hexenes. Hexenes have been observed by g.l.c. as products in this reaction and, when formed, would rapidly react with the violet species from $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$. In this case, hexene would not be present in an excess, being consumed as it was formed from dimerisation of the propene. The product would therefore be $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$.

Finally, the difference in reaction path of butene from that of pentene is even more difficult to explain. Although both olefins are capable of undergoing the alkane elimination step (Scheme 4), only pentene appears to follow this route. Butene, in contrast, appears to undergo a comparatively slow oxidative dimerisation to C_8 diene derivatives (Scheme 5). This difference may be rationalised by assuming that the bis(allyl) alkyl intermediate (4) may readily undergo elimination only when alkyl groups are present at both C_1 and C_3 of the allyl groups. The adjacent alkyl substituents would not only hinder allylic coupling but could also facilitate elimination by narrowing the angle between the allyl planes and consequently forcing the hydrogen nearer the alkyl group to which it transfers.

CONCLUSIONS

The olefin redistribution reactions described in this paper represent a novel type of activation of hydrocarbons by transition metal complexes. The oxidative dimerisation of propene to a hexadiene derivative, though not a catalyst for the reaction 3 propene $\longrightarrow$ hexadiene + propane, suggests that homogeneous catalysed reactions of this type are certainly possible. A heterogeneous catalysed oxidative dimerisation of propene to hexa-1,5-diene has recently been reported.[12]

The catalytic dimerisation of ethylene to butenes and co-dimerisation of ethylene and propene to pentenes calls to mind the chemistry of $[(\pi\text{-}C_3H_5)NiCl]_2$ and its tertiary phosphine adducts, which in the presence of alkylaluminium halides, are highly efficient catalysts for the dimerisation of propene.[3] It is possible that the mechanisms of dimerisation are similar in both cases, though the operation of the molybdenum system as an efficient dimerisation catalyst is probably prevented by the stable complex formation described. The isolation of any complexes formed from mono-olefins with the nickel system has not been reported. This difference of reactivity may be caused not only by differences in electronic configuration but also by the fact that in the molybdenum system the presence of the π-benzene ligand will require that other hydrocarbon groups around the metal atom are closer together than they would be in the nickel system, thus facilitating direct hydrogen transfer reactions. Also, nearly all arene molybdenum systems isolated or postulated here are 18-electron species whereas in nickel chemistry the conversion between 16- and 18-electron species is more facile.

EXPERIMENTAL

Operations were carried out under dry nitrogen. N.m.r. spectra were recorded on a Bruker 270 MHz spectrometer and i.r. spectra on a Perkin-Elmer 457 spectrometer. G.l.c. analyses were made using a Pye 104 chromatograph on five foot glass columns containing 10% potassium chloride on alumina. Analyses were performed at the Inorganic Chemistry Laboratory, Oxford and by Messrs. Bernhardt. Bis(benzene)molybdenum was prepared according to the method of Fischer and Stahl.[13] Ethylaluminium dichloride was used as a solution in AnalaR benzene (dried by refluxing over and distillation from finely powdered calcium hydride) which was made up from $EtAlCl_2$ (commercial, 85 g) and benzene (354 g). Reactions involving ethylaluminium dichloride were performed using carefully dried apparatus. *cis,trans*-2-Chloropent-3-ene and 3-chloropent-1-ene were prepared from *cis,trans*-pent-3-en-2-ol and pent-1-en-3-ol respectively by reaction at 20° with thionyl chloride without solvent. The products were twice distilled from anhydrous sodium carbonate giving colourless liquids (b.p. 96·5—99° and 98—107° respectively). 3-Chloropent-1-ene, although likely to contain 1-chloropent-2-ene formed by allylic rearrangement, was used without further purification since both compounds would react with $(\pi\text{-}C_6H_6)_2Mo$ forming the same product.

The μ-Chloro-(π-allyl)(benzene)molybdenum Dimer.—To a solution of $(\pi\text{-}C_6H_6)_2Mo$ (4·0 g, 16 mmol) in benzene (350 ml) at 30° was added allyl chloride (1·5 ml, 19 mmol) and the solution allowed to stand until the colour was deep purple (10 min). The solution was then cooled to 5° and the product crystallised out leaving a paler purple mother-liquor which was discarded. The product was washed with 95% ethanol and then with diethyl ether and dried under vacuum [yield 3·4 g (85%)].

The 1,3-dimethylallyl analogue $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3\text{-}Me)Cl]_2$ was prepared in a similar manner using *cis,trans*-2-chloropent-3-ene in place of allyl chloride. The crude product was recrystallised from tetrahydrofuran–ethanol, *ca.* 80%.

The μ-Chloro-(π-1-methylallyl)(benzene)molybdenum Dimer.—A mixture of $(\pi\text{-}C_6H_6)_2Mo$ (1·2 g, 5 mmol) and benzene (25 ml) was treated with *trans*-1-chlorobut-2-ene (1 ml, 10 mmol) and stirred at 20° for 15 min giving a clear deep purple solution. Light petroleum (b.p. 100—120°, 20 ml) was added with stirring and the solution was filtered and reduced to low volume. Small purple crystals (0·95 g, 80%) were deposited. The crude product was recrystallised from tetrahydrofuran–ethanol.

The 1-ethylallyl analogue $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)Cl]_2$ was prepared in a similar manner using 3-chloropent-1-ene distillate instead of *trans*-1-chlorobut-2-ene, *ca.* 65%.

The π-toluene complex $[(\pi\text{-}C_6H_5Me)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ was similarly made from $(\pi\text{-}C_6H_5Me)_2Mo$ with *trans*-1-chlorobut-2-ene using light petroleum as solvent; it was characterised by analysis and i.r. spectroscopy.

Reaction of the Compounds $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}R^1C_3H_3R^2)Cl]_2$ *with Ethylaluminium Dichloride in Benzene.*—The dimer $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·50 g, 1 mmol) was treated with ethylaluminium dichloride solution in benzene (1·8 ml, 1 mmol) and a clear deep violet solution was formed. The n.m.r. spectrum of a portion of the solution exhibited the following resonances in addition to that of the solvent: 5·65, **1**, *c*, C_3H_5; 5·9, **6**, *s*, C_6H_6; 7·4, **4**, *d*(8), C_3H_5; 8·83, **3**, *t*(7), Me; 9·65, **2**, *q*(7), CH_2. The solutions were recombined and cooled to 5°. Dry diethyl ether (2 ml) was added

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[12] D. L. Trimm and L. A. Doerr, *J. Catalysis*, 1971, **23**, 49.

[13] E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, 1960, **93**, 2065.

dropwise with stirring producing a purple crystalline precipitate and a pale red solution. The solid was filtered, washed with ethanol and ether and dried (0·46 g, 92%). It was identified by i.r. spectroscopy as the starting material, $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$.

A 1 : 1 Mo : Al ratio was also found to be sufficient for the complete solution of the other dimer complexes.

Preparation of (π-*Alkenyl*)(*benzene*)*molybdenum*(*diene*) *Hexafluorophosphate*.—*Method A*. The synthesis of (π-allyl)(benzene)molybdenum (buta-1,3-diene) hexafluorophosphate is given as a typical example. The compound $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·47 g, 1 mmol, finely powdered) and thallium(I) tetrafluoroborate (0·90 g, 3 mmol) were suspended in AnalaR acetone (100 ml) and excess of buta-1,3-diene vapour (purified by passage through molecular sieves) was passed into the solution. The mixture was then stirred vigorously at 20° for 15 h and an orange solution was formed, together with a white precipitate. The filtered solution was added to an equal volume of ethanol and the combined solution reduced to low volume. Orange crystals (0·50 g, 90%) of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)]^+BF_4^-$ were deposited, which were washed with diethyl ether and dried.

$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)]^+PF_6^-$ was made by dissolving the corresponding tetrafluoroborate salt in water and precipitating the crude product with an aqueous solution of ammonium hexafluorophosphate. The yellow precipitate, after filtration and drying, was recrystallised from acetone–ethanol giving the pure complex as orange crystals.

Other complexes of type $[(\pi\text{-}C_6H_6)Mo(\pi\text{-alkenyl})(\text{diene})]^+$-$PF_6^-$ were made analogously in similar yield, using the corresponding alkenyl dimer and the corresponding conjugated diene, the latter being added as a two-fold excess of liquid.

Method B. The preparation of the hexadiene complex by this route is given as a typical example; other compounds of this type are made in a similar manner using the corresponding dimer and conjugated diene.

$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·67 g, 1·3 mmol) was placed in a dry vessel and was treated at 0° with $EtAlCl_2$ solution in benzene (2·0 ml, 2·7 mmol). The complex dissolved on shaking giving a deep violet solution. *trans,trans*-Hexa-2,4-diene (commercial, 0·5 ml, 4 mmol) was added dropwise to the solution at 5° and a red oil was rapidly formed, which separated from a pale red mother-liquor. The oil was washed with dry light petroleum (b.p. 30—40°, 50 ml) and then frozen at −100°. Ethanol (95%, 10 ml) was added and the mixture shaken vigorously until the temperature had risen to 20°. Ethanol was then removed from the orange-red solution and the residual viscous product was extracted into water (30 ml). The aqueous solution was filtered and to it was added a solution of NH_4PF_6 (0·5 g) in water (3 ml) producing a yellow precipitate. This was filtered off, washed with water, and dried. The solid was dissolved in acetone (20 ml) and the solution filtered into an equal volume of ethanol. The solution was reduced to low volume and yellow-orange crystals of the product separated. The pure complex was obtained after a further recrystallisation from acetone–ethanol (yield 0·97 g, 83%).

Method C. (π-*Allyl*)(*benzene*)*molybdenum*(*hexa*-2,4-*diene*) *hexafluorophosphate*. $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (1·60 g, 3·2 mmol) was treated with $EtAlCl_2$ solution (6·9 ml, 9·3 mmol) in a large dry Schlenk tube. The solid reacted and a clear violet solution was formed. The vessel and contents were cooled to −196° and the system evacuated. Pure dry propene (1·08 g, 25·7 mmol), contained in a separate vessel at atmospheric pressure, was then condensed onto the frozen solution and the vessel was sealed and allowed to warm slowly to 20°. Some red oil formed as soon as the frozen solution melted. The mixture was allowed to stand at 20° for 2 days during which period the violet colour of the mother-liquor was slowly discharged. Vapour samples above the mixture were then analysed by g.l.c. and the relative amount of propane : propene was found to be 1·2 : 1, giving an estimate of 1·1 mol of propane liberated per gram-atom of molybdenum. The oil was washed (2 × 100 ml) with light petroleum (b.p. 30—40°) and then cooled to −100°. Ethanol (40 ml) was added and the mixture was shaken vigorously until the temperature had reached 20°. Ethanol was removed and the residue was extracted into water (40 ml) giving an orange-red solution. This was filtered and a solution containing ammonium hexafluorophosphate (1·5 g) in water (10 ml) was added producing a yellow precipitate. The solid was filtered, washed with water, and dried. Recrystallisation from acetone–ethanol as before yielded yellow-orange crystals of $[(\pi\text{-}C_6H_6)$-$Mo(\pi\text{-}C_3H_5)(C_6H_{10})]^+PF_6^-$ (2·15 g, 78%). N.m.r. spectroscopy revealed that the product was exclusively the *trans,-trans*-hexa-2,4-diene complex and no other isomers were observed.

(π-1-*Methylallyl*)(*benzene*)*molybdenum*(*octadiene*) *Hexafluorophosphate*.—The complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ (0·89 g, 1·7 mmol) was treated with $EtAlCl_2$ solution (6·0 ml, 8·1 mmol) and the resulting violet solution was transferred to a 15 ml ampoule ready for sealing. The ampoule was then cooled to −196°, evacuated, and pure *cis*-but-2-ene (2·5 ml, 35 mmol) was condensed into it. The ampoule, after sealing under vacuum, was allowed to stand at 20° for 5 days and a red oil was produced in a pale red solution. Hydrolysis and precipitation with NH_4PF_6 in the manner described above gave $(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)(C_8H_{14})^+PF_6^-$ as yellow-orange crystals (0·70 g, 43%). A considerable amount of water-insoluble material was also formed after hydrolysis but this was not investigated further.

The Other Diene Complexes.—A procedure similar to the one already described was adopted. The starting materials required for the preparation of the compounds are given in Table 2. The violet solutions were allowed to react with the alkenes for 30 min at 20° in each case. Subsequent hydrolysis and precipitation with NH_4PF_6 gave the products in 40—80% yield.

The two isomeric complexes, $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)$-$(C_5H_8)]^+PF_6^-$ and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)]^+PF_6^-$, which are formed as a mixture from reaction with *cis*-pent-2-ene were separated in a pure condition as follows: the mixture (1 g) was extracted (10 × 0·5 ml) with acetone. The first three extracts were combined and recrystallised twice from acetone–ethanol giving pure $(\pi\text{-}C_6H_6)Mo(\pi\text{-}EtC_3H_4)(C_5H_8)^+PF_6^-$ (0·1 g). The solid which remained undissolved after the acetone extractions was given two further recrystallisations from acetone–ethanol affording pure $(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)^+PF_6^-$ (0·2 g). This method was not successful for the separation of mixtures formed from reactions with higher alkenes because of the high solubility of all components in acetone.

Formation of the μ-*Chloro*-(π-1-*methylallyl*)(*benzene*)*molybdenum Dimer by Allyl–Olefin Exchange*.—$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·70 g, 1·4 mmol) was treated with $EtAlCl_2$ solution (5 ml, 6·8 mmol) at 5° and the violet solution obtained was exposed to excess *cis*-but-2-ene vapour and allowed to stand at 20° for 30 min. A red oil and pale purple solution were formed and a g.l.c. analysis of the vapour above the mixture indicated that propene and isomerised butenes had been produced. Decomposition of the mixture with ethanol after 30 min as before yielded a purple precipitate in an orange-red solution and this was filtered and dried. Recrystallisation from benzene–light petroleum (b.p. 100—120°) gave $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_4)Cl]_2$ (0·45 g. 60%). The aqueous extract gave virtually no yellow precipitate after addition of ammonium hexafluorophosphate.

Dimerisation of Ethylene and Co-dimerisation of Ethylene and Propene.—The violet solution formed by mixing $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·49 g, 1 mmol) with $EtAlCl_2$ solution (3·0 ml, 4·1 mmol) was transferred to an ampoule ready for sealing and this was then cooled to −196°, evacuated and Grade X ethylene (1·5 ml, 40 mmol) condensed in. After sealing under vacuum, the ampoule was maintained at 20° for 14 h. A red oil was formed in a colourless mother-liquor and small amounts of polymer were also observed. The vapours above the mixture were analysed by g.l.c. and found to contain butenes in approximately the thermodynamic equilibrium proportions. The number of cycles of dimerisation was estimated to be *ca.* 15. Addition of cold ethanol to the residue gave a red material but this was not soluble in water and neither the starting dimer nor any other complexes could be isolated from it.

Ethylene dimerisation was likewise achieved using $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$ under similar conditions and reaction of $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ with a 1 : 1 ethylene : propene mixture under the same conditions caused catalytic co-dimerisation (*ca.* 5 cycles) to isomerised pentenes as well as dimerisation of ethylene to isomerised butenes (10 cycles). Small amounts of hexenes were also produced.

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