Arene Molybdenum Chemistry: Oxidative Dimerisation of Propene to a Hexa-2,4-diene Derivative and Related Reactions

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Summary Arene molybdenum systems are shown to act as homogeneous catalysts for reactions of unsaturated hydrocarbons; thus $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ in the presence of $EtAlCl_2$, is shown to catalyse the conversion of mono-olefins into diene complexes and paraffins.

A BENZENE solution of $[(\pi\text{-}C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$[1] at 60° causes virtually quantitative polymerisation of buta-1,3-diene in 16 h (C_4H_6 : Mo = 400 : 1). The rubber-like product obtained was shown, by i.r. and n.m.r. spectroscopy, to be the 1,2-addition polymer of repeat unit $-CH_2\cdot CH(CH:CH_2)-$. The polymerisation reaction is solvent-dependent, no polymer being observed when methanol or THF was employed as solvent.

Solutions of $[(\pi\text{-}C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$ in benzene or acetone at 20° are catalysts for the conversion of propyne into polypropyne, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene. A THF solution of the same complex polymerises allene at 20°.

A red solution obtained after filtration of the reaction product of $[\pi\text{-}C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$ with thallium(I) tetrafluoroborate in acetone polymerises but-2-yne after 2 days at 20°. The product has the form of a white solid which is soluble in hydrocarbon solvents.†

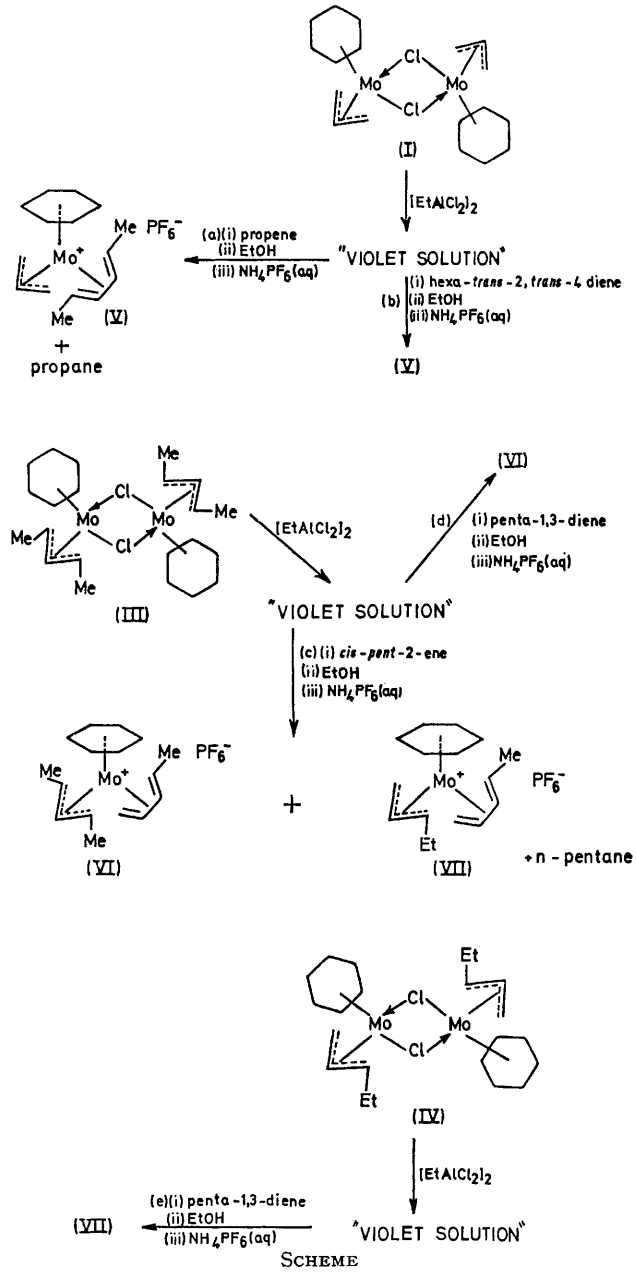
$(\pi\text{-}C_6H_6)_2Mo$, reacts with allyl chloride at 20° in benzene solution forming the dimeric complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (I, Scheme).[1] Analogous reactions of $(\pi\text{-}C_6H_6)_2Mo$ with *trans*-1-chlorobut-2-ene, *cis,trans*-2-chloropent-3-ene, and 3-chloropent-1-ene yield respectively the complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_4Me)Cl]_2$ (II), $[(\pi C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)Cl]_2$ (III), and $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_4Et)Cl]_2$ (IV).

All four compounds react with benzene solutions of $EtAlCl_2$ in the stoicheiometry Mo : Al 1 : 1 giving reactive violet solutions of unknown nature.

The solution obtained from (I) and $EtAlCl_2$ in benzene reacts with buta-1,3-diene at 0° yielding an insoluble red oil. Decomposition of the latter with 95% ethanol and addition of NH_4PF_6 gives the complex $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)^+PF_6^-$. The formation of this species from (I) by another route has already been demonstrated.[2]

Analogous reactions of (I) in the presence of hexa-*trans*-2, *trans*-4-diene and of (III) and (IV) in the presence of *cis*- and *trans*-penta-1,3-diene yield respectively $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_6H_{10})^+PF_6^-$ (V), $(\pi\text{-}C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)(C_5H_8)^+PF_6^-$ (VI), and $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_4Et)(C_5H_8)^+PF_6^-$ (VII).‡

The violet solutions of (I)—(IV) in $EtAlCl_2$–benzene react with mono-olefins at 20° (Mo : Al 1 : 2) forming paraffin hydrocarbons and insoluble red oils which, on decomposition with ethanol and addition of NH_4PF_6, yield cationic molybdenum diene complexes in 50—80% yield [Scheme, reactions (**a**) and (**c**)].



SCHEME

The complexes were characterised in each case by analysis, n.m.r. and i.r. spectroscopy and these properties,

† No polymer of but-2-yne has so far been reported and the structure of the white solid has not yet been elucidated.

‡ New compounds (V)—(VII) have all been characterised by analysis, n.m.r. 270 MHz, and i.r. The n.m.r. spectra are entirely consistent with the structures shown in the Scheme.

were found to be identical to those of the products formed from reactions of (I)—(IV) with conjugated dienes, [Scheme, reactions (**b**), (**d**), and (**e**)].

The solutions of (I) in $EtAlCl_2$–benzene are also isomerisation catalysts for mono-olefins; at 20°, using an olefin : Mo : Al ratio of 90 : 1 : 2, a 70% conversion of *cis*-pent-2-ene into the *cis,trans* equilibrium mixture was observed after 3 h and hept-1-ene was converted into internal isomers under similar conditions.

We believe that reaction (**c**) is the first example of redistribution of the double bond of a mono-olefin to give a conjugated diene ligand and a paraffin and that reaction (**a**) represents the first example of the conversion of propene into a hexa-2,4-diene group by a homogeneous system. A heterogeneous catalysed conversion of propene into hexa-1,5-diene has recently been reported.[3]

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[1] M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.
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[3] D. L. Trimm and L. A. Doerr, *J. Catalysis*, 1971, **23**, 49.