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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 $\text{-}CH_2\cdot CH\text{-}(CH{:}CH_2)\text{-}$. 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.†

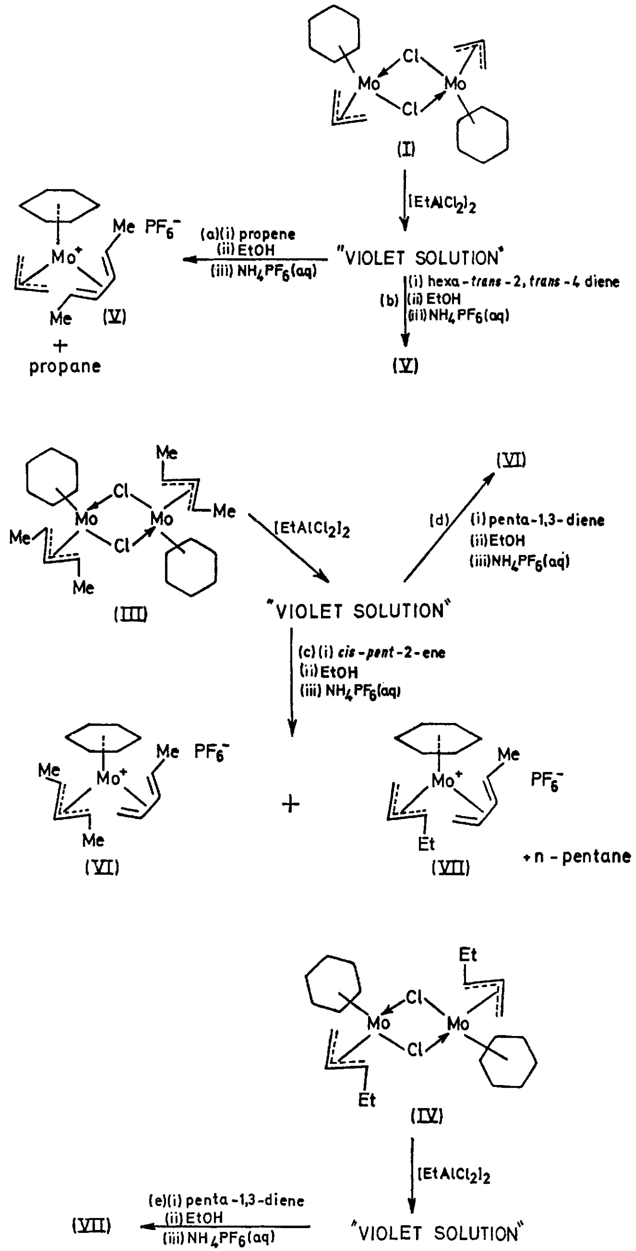
$(\pi\text{-}C_6H_6)_2Mo$, reacts with allyl chloride at 20° in benzene solution forming the dimeric complex $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)\text{-}Cl]_2$ (I, Scheme).[1] Analogous reactions of $(\pi\text{-}C_6H_6)_2Mo$ with *trans*-1-chlorobut-2-ene, *cis,trans*-2-chloropent-3-ene, and 3-chloropent-1-ene yield respectively the complexes $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_4Me)Cl]_2$ (II), $[(\pi C_6H_6)Mo(\pi\text{-}MeC_3H_3Me)\text{-}Cl]_2$ (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 $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)(C_4H_6)^+\text{-}PF_6^-$. 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 $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)\text{-}(C_6H_{10})^+PF_6^-$ (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,

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† 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.

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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]

(*Received*, 26*th June* 1972; *Com.* 1099.)

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

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

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