Arene Molybdenum Chemistry: The Preparation of some Arene Molybdenum π-Allyl Derivatives and a Unique Diprotonation Reaction of Benzenetristertiaryphosphinemolybdenum Derivatives

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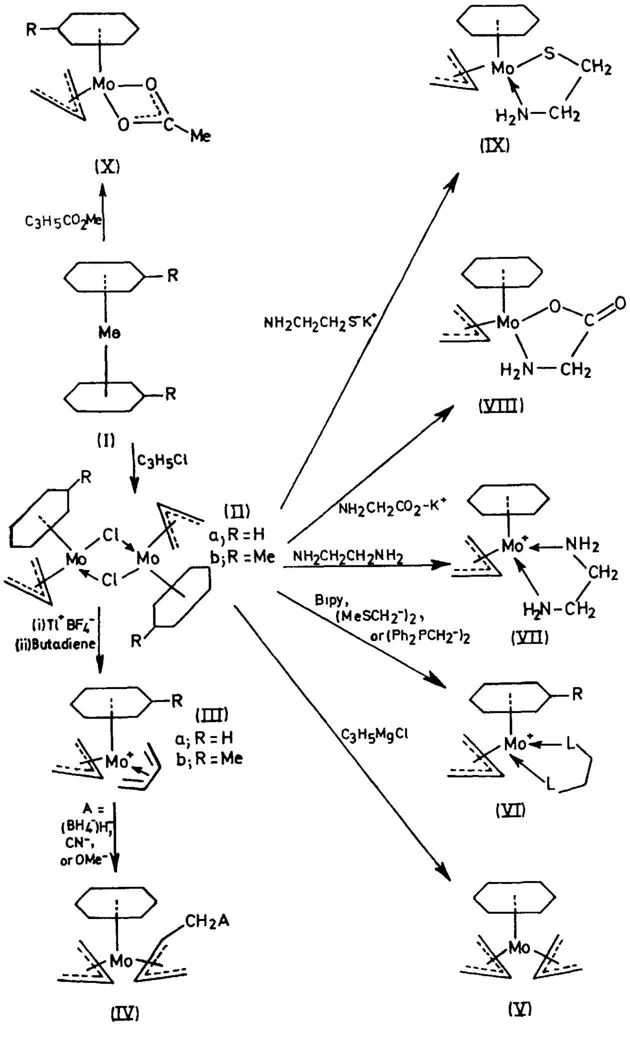
Summary New arene–molybdenum derivatives are described of stoicheiometry $PhRMo(\pi\text{-}C_3H_5)Y$ [$Y = \pi\text{-}C_3H_5$, $\pi\text{-}C_3H_4Me$, $\pi\text{-}C_3H_4(CH_2{\cdot}CN)$, $\pi\text{-}C_3H_4(CH_2{\cdot}OMe)$, $MeCO_2$, $NH_2{\cdot}CH_2{\cdot}CO_2$, or $NH_2{\cdot}CH_2{\cdot}CH_2S$; R = H or Me] and of stoicheiometry $[PhRMo(\pi\text{-}C_3H_5)L_2]^+PF_6^-$ (or BF_4^-) [L_2 = butadiene, $MeS{\cdot}CH_2{\cdot}CH_2{\cdot}SMe$, bipyridyl, ethylenediamine, or $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$]; the dication $[C_6H_6Mo(Me_2PhP)_3H_2]_2^{2+}$ formed by addition of two protons to the neutral compound $C_6H_6Mo(Me_2PhP)_3$.

TREATMENT of the compounds $(PhR)_2Mo$ (I; R = H or Me) (Scheme 1) with allyl chloride gives the binuclear derivatives $[PhRMo(\pi\text{-}C_3H_5)Cl]_2$ (IIa or b).[1] Here we describe further reactions of the arene–molybdenum–π-allyl system.

The dimeric compounds (IIa and b) in acetone react readily with butadiene in the presence of thallium tetrafluoroborate giving orange butadiene derivatives (IIIa and b). Compound (IIIa) reacts with nucleophilic anions such as H^- (from BH_4^-), CN^-, or OMe^- giving the substituted bis-π-allyl derivatives (IV). The parent bis-π-allyl compound (V) may be prepared from the binuclear compound (IIa) and allylmagnesium chloride.

The dimers (IIa and b) readily undergo bridge-cleavage reactions with neutral ligands such as bipyridyl, 2,5-dithiahexane, 1,2-bis(diphenylphosphino)ethane, or ethylenediamine giving the cationic derivatives (VI) or (VII) respectively.

With the potassium salts of glycine or cystamine, the dimer (IIa) forms the neutral complexes (VIII) and (IX) respectively.



SCHEME 1

The acetato-complex $C_6H_6Mo(\pi\text{-}C_3H_5)O_2CMe$ (X; R = H), which is structurally related to the compounds (VIII) and (IX), is readily formed by addition of allyl acetate to bisbenzenemolybdenum; it is soluble in light petroleum and is monomeric in benzene.

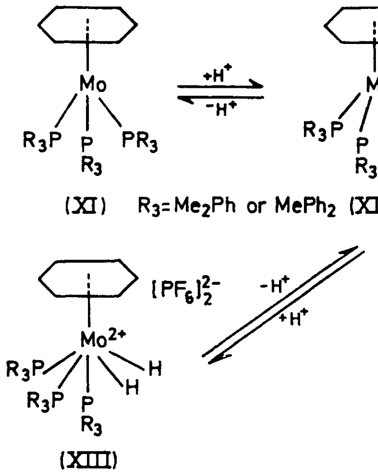
All the new compounds (III)—(X) are shown in Scheme 1 and have been characterised by analysis and i.r., ^1H n.m.r., and, in some cases, mass spectra.

The chemistry of the arene–molybdenum system is thus very extensive, so other transition metals may have similar arene–metal chemistry.

We have also found that bisbenzenemolybdenum reacts readily with tertiary phosphines forming the monobenzene derivatives $C_6H_6Mo(R_3P)_3$ (XI; $R_3 = Me_2Ph$ or $MePh_2$), which are basic and readily protonated forming the monohydride cations $[C_6H_6Mo(R_3P)_3H]^+$ (XII).[2]

N.m.r. studies on this system have shown that solutions of the complexes (XI; $R_3 = Me_2Ph$) or (XII; $R_3 = MePh_2$) in trifluoroacetic acid contain a new molybdenumhydride derivative, since the magnitudes of the chemical shift, τ 12·3, and of the splitting constant, $J(^{31}P\text{–}H)$ 43·5 Hz, are very different from those of the hydride (XII; $R_3 = Me_2Ph$) in solvents such as acetone or dichloromethane [τ 10·3, $J(^{31}P\text{–}H)$ 72·1 Hz]. Integration of the spectrum of (XII; $R_3 = Me_2Ph$) in trifluoroacetic acid shows a ratio of *ca.* 3 : 1 for the benzene : molybdenum hydrogen atoms. Also, the ^{31}P n.m.r. spectrum shows the phosphorus resonance to be a broad triplet. In $[^2H_1]$trifluoroacetic acid, benzene proton resonance of compound (XI; $R_3 = Me_2Ph$) appears as a broad quartet, $J(^{31}P\text{–}H)$ 1·8 Hz. Addition of hexafluorophosphoric acid (65%) to a solution of the complex (XI; $R_3 = Me_2Ph$) in trifluoroacetic acid gives yellow crystals which give analytical data in good agreement with the stoicheiometry $[C_6H_6Mo(Me_2PhP)_3H_2]^{2+}[PF_6^-]_2$ (XIII); the i.r. spectrum shows a band assignable to ν_{Mo-H} at 1880 cm^{-1}, 30 cm^{-1} lower than ν_{Mo-H} of the hydride $[C_6H_6Mo(Me_2PhP)_3H]^+PF_6^-$.

Therefore, we propose that the cation (XIII, $R_3 = Me_2Ph$) has the structure shown in Scheme 2. Since the three ^{31}P nuclei are equivalent in the ^1H n.m.r. spectrum compound (XIII; $R_3 = Me_2Ph$) is presumably a fluxional molecule, as is the compound (XII).



SCHEME 2

Analogous results to those given above have been found for the compounds (XI—XIII where $R_3 = MePh_2$).

We are unable to find any report of the diprotonation of any neutral molecule where the protons become attached to the same atom in the molecule. The diprotonation of compound (XI) shows that it is very electron rich and also that the positive charge may be effectively delocalised.

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[1] M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.
[2] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc.* (*A*), 1971, 2929.