SOME ORGANIC CHEMISTRY OF MOLYBDENUM AND RELATED TOPICS

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ABSTRACT

General features of molybdenum chemistry are briefly surveyed and then three areas of molybdenum chemistry are presented in more detail. Evidence concerning the structure and bonding in bent bis π-cyclopentadienyl metal compounds is discussed. New reactions of bis π-cyclopentadienyl molybdenum (and tungsten) complexes are described: in particular the reactions of the dihydride $(\pi\text{-}C_5H_5)_2MoH_2$ leading to molybdenum aryl derivatives. Arene molybdenum chemistry has been explored and the arene–metal bond has been found to survive in a wide variety of chemical environments.

INTRODUCTION

The organometallic chemistry of molybdenum started in the mid-1950s and most of the early compounds were carbonyl derivatives. This was largely due to the availability of molybdenum hexacarbonyl together with its ease of handling. These carbonyl derivatives were usually prepared by thermal substitution:

$$nL + Mo(CO)_6 \rightarrow L_nMo(CO)_{6-n}$$

By this route molybdenum was bonded to arenes, azulenes, π-cyclopentadienyl and to many olefin ligands such as cycloheptatriene and bicycloheptadiene. Many of these compounds were important since they often provided the first examples of a particular organometal system at a time when it was by no means clear what were the limits of stability of organometal bonds.

Two other early compounds of interest were the bis π-cyclopentadienylmolybdenum dihydride and bis π-benzene molybdenum. Much of this early work was done in the laboratories of Fischer and Wilkinson[1].

The second phase of organomolybdenum chemistry largely concerned the development and study of arene molybdenum carbonyls, and, especially, of π-cyclopentadienyl molybdenum carbonyl chemistry. The $\pi\text{-}C_5H_5Mo(CO)_3X$ system has been shown to provide a wide range of derivatives where for example, X = alkyl[2], acyl[3], aryl[4], perfluoroalkyl[5], sulphinato[6], silyl[7], stannyl[8], germyl[9] and other metal ligands with aluminium[10], magnesium[11], palladium and platinum[12]. Also, the substitution properties of $\pi\text{-}C_5H_5Mo(CO)_3X$ by ligands such as nitrosyls[13], polypyrazolylborates[14], phosphines and phosphites have been studied[15]. Several molybdenum compounds containing 2 × 1e 'carbene' ligands have been described[16], and ligands which contribute three electrons to the molybdenum have been found in the compounds $\pi\text{-}C_5H_5Mo(CO)_2D$, D = π-allyl[17], benzyl[18],

CH_2SMe[19], $C_4H_3SCH_2$[20], Ph_2CNCPh_2[21] or 3π-cycloheptatrienyl[22] The Dewar benzene compound $Me_6C_6Mo(CO)_4$[23], and 4π-cyclobutadiene derivatives such as $[Ph_4C_4Mo(CO)_3Br]_2$[24], π-$C_5H_5Mo[p\text{-tolyl}C_4]Br$[25], $C_4H_4Mo(CO)_3(PPh_3)$[26] and π-$C_5H_5Mo(CO)(C_4Ph_4)H$[27] have been prepared more recently. The 7π-cycloheptatrienyl ligand is seen in compounds such as π-$C_7H_7Mo(CO)_2$-σ-C_6F_5[28], π-$C_7H_7Mo(CO)_3^+$[29] or π-C_5H_5Mo-π-C_7H_7[30].

The chemistry of a particular metal reflects the development of organo-transition metal chemistry as a whole and the changing pattern of interests. In the more recent years the interest in the use of organo-transition metal compounds as homogeneous catalysts for hydrocarbon reactions has focussed attention on the Group VIII metals which were thought to be likely to show greater activity. Molybdenum was considered a less attractive metal partly because the known organomolybdenum compounds were nearly always rather inert, 18 electron compounds with effective coordination numbers of six or more.

The occurrence of molybdenum in nitrogenase, xanthine oxidase and in the catalysis of olefin disproportionation[31] has, however, reawakened interest in both the organometallic and traditional inorganic chemistry of molybdenum.

For these reasons we set out to explore the organic molybdenum chemistry in new directions, and we chose two areas, namely, arene molybdenum systems and the bis π-cyclopentadienyl molybdenum system. As an integral part of the study of the latter system we became interested in the bonding and structure of bent bis π-cyclopentadienyl metal compounds of the type (π-$C_5H_5)_2MX_n$, where n may be 1, 2, or 3 with different metals. These compounds are known for the metals Ti, Zr, Hf, V, Nb, Ta, Mo, W, Re, Fe, Ru, and Os, and for each metal many different ligands X_n are found[1]. It follows that bent bis π-cyclopentadienyl metal derivatives provide a most extensive series of closely related compounds and so they provide an almost unparalleled opportunity for a comparative study of the chemistry of the different metals. This lecture considers three different aspects of molybdenum and related chemistry.

(1) Evidence concerning the structure and bonding in bent bis π-cyclopentadienyl metal systems is presented in terms of a simple M.O. description, and the nature of bis π-cyclopentadienyl metal dithiolates as ligands to transition metals is also discussed.

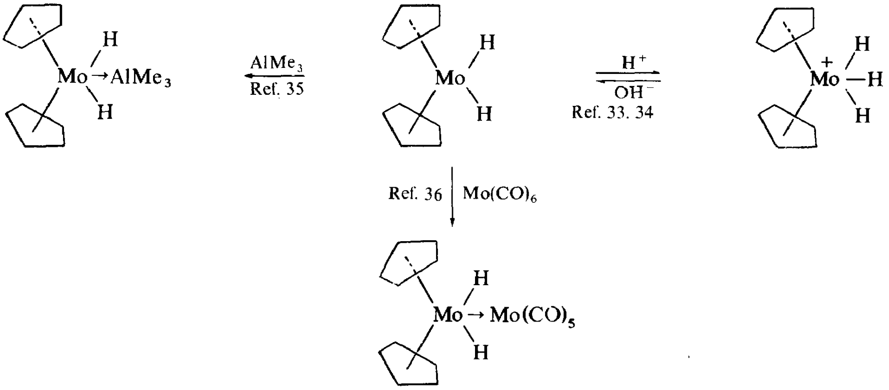
(2) Some chemistry of bis π-cyclopentadienyl molybdenum and tungsten derivatives is described, in particular, the homogeneous substitution of benzene by tungsten and the homogeneous oxidation of amines to aldehydes and ketones by molybdenum.

(3) Arene molybdenum chemistry has been explored and an extensive chemistry is revealed, including compounds of high reactivity.

1. BONDING AND STRUCTURE IN BENT BIS π-CYCLOPENTADIENYL METAL COMPOUNDS

The bonding in bent bis π-cyclopentadienyl complexes (π-$C_5H_5)_2MX_n$, n = 1, 2 or 3, has been discussed in terms of two models. The earliest model proposed by Balhausen and Dahl[32] involved three strongly directed orbitals ψ_0, ψ_1 and ψ_2, which were considered to be essentially non-bonding with respect to the bent bis π-cyclopentadienyl metal system; the orbitals are shown in *Figure 1*(*a*). This model was attractive in so far as it accounted for the basic, 'lone pair' properties of the dihydrides $(\pi\text{-}C_5H_5)_2MoH_2$, M = Mo or W, and the monohydride $(\pi\text{-}C_5H_5)_2ReH$. Examples of these properties are:

Figure 1. (*a*) Location of orbitals as proposed by Balhausen and Dahl.
(*b*) Location of orbitals as proposed by Alcock



The model also accounts for the existence of the trihydrides $(\pi\text{-}C_5H_5)_2MH_3$, M = Ta[34] or Nb[37].

However, Alcock determined the crystal structure of the rhenium compound $\pi\text{-}C_5H_5Re(C_5H_5Me)Me_2$[38] and found the Me–Re–Me angle to be 76° which would be too small to accommodate the lone pair which would be present in between the methyl groups if the Balhausen model were applicable. He therefore proposed a modified model which is shown in *Figure 1*(*b*). The essential difference between these models is the localization of the d^2, 'non-bonding' electrons in the ψ_0 orbital in one case and the ψ'_0 orbital in the other.

The crystal structures of a number of bis π-cyclopentadienyl metal compounds $(\pi\text{-}C_5H_5)_2MX_2$ have been determined and some selected data are given in *Table 1*. The Table shows that the X–M–X angle changes according to the number of metal electrons in the order $d^0 > d^1 > d^2$. This evidence strongly suggests that the essentially non-bonding d-electrons are located largely in an orbital of the location suggested by Alcock.

Table 1. Some distances and angles in compounds $(\pi\text{-}C_5H_5)_2MX_2$[42]

Compound	d^x	$<$X–M–X	$<$M–X, pm	Ref.
$(\pi\text{-}C_5H_5)_2MoCl_2$	d^2	81.6°	247	39
$[(\pi\text{-}C_5H_5)_2ReBr_2]^+BF_4^-$	d^2	82.0° (0.1)	256	40
$(\pi\text{-}C_5H_5)_2V(SMe)_2$	d^1	94°		41
$[(\pi\text{-}C_5H_5)_2MoCl_2]^+BF_4^-$	d^1	87.9° (0.1)	238	40
$(\pi\text{-}C_5H_5)_2NbCl_2$	d^1	85.7°	247	40
$(\pi\text{-}C_5H_5)_2ZrCl_2$	d^0	97.1°	244	39
$(\pi\text{-}C_5H_5)_2ZrF_2$	d^0	96.2°	198	43
$(\pi\text{-}C_5H_5)_2ZrI_2$	d^0	96.2°	283	43
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2$	d^0	99°	—	41

The relationship between the above two models (*Figure 1*) can be seen in terms of a simplified molecular orbital picture in the following manner.

The photoelectron spectra of $(\pi\text{-}C_5H_5)_2MoH_2$ and $(\pi\text{-}C_5H_5)_2MoMe_2$ suggest that the energy of the electrons associated with the bonding of the bis π-cyclopentadienyl molybdenum system is only slightly changed from that in ferrocene[44]. Therefore it seems reasonable to generate the M.O. diagram for bent bis π-cyclopentadienyl metal systems by 'bending' the ferrocene system. This is shown in *Figure 2* for the upper M.O. levels where

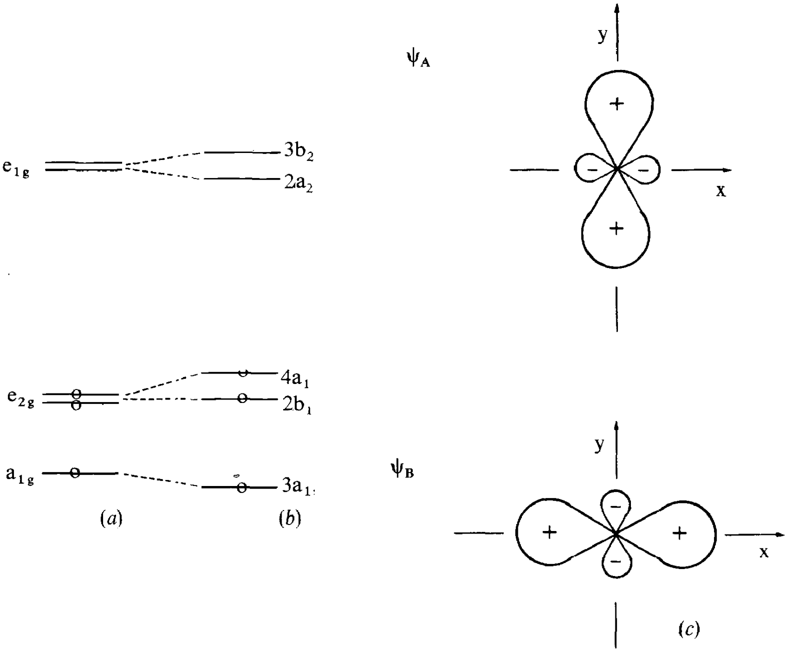


Figure 2. (*a*) The highest filled and lowest empty M.O.'s in ferrocene.
(*b*) The proposed M.O.'s in a bent $(\pi\text{-}C_5H_5)_2M$ system.
(*c*) Representation of the proposed hybrid orbitals ψ_A and ψ_B formed from the metal $d_{x^2-y^2}$ and d_{z^2} metal orbitals: section through the xy plane

the highest filled, 'non-bonding' orbitals in ferrocene, the e_{2g} and a_{1g} orbitals, become the $3a_1$, $2b_1$ and $4a_1$ orbitals in the bent $(\pi\text{-}C_5H_5)_2M$ system. Assuming that these orbitals are largely located on the metal then they can be said to arise primarily from the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} metal orbitals. Whilst the $2b_1$ orbital may be regarded as being essentially d_{xy} in character the $4a_1$ and $3a_1$ would be mixed and it can be envisaged that they might give rise to the two new orbitals for example, ψ_A and ψ_B shown in *Figure 2*. The ψ_A orbital resembles the ψ'_0 orbital of the Alcock model and the ψ_B orbital resembles the ψ_0 orbital of the Balhausen model, in their localization.

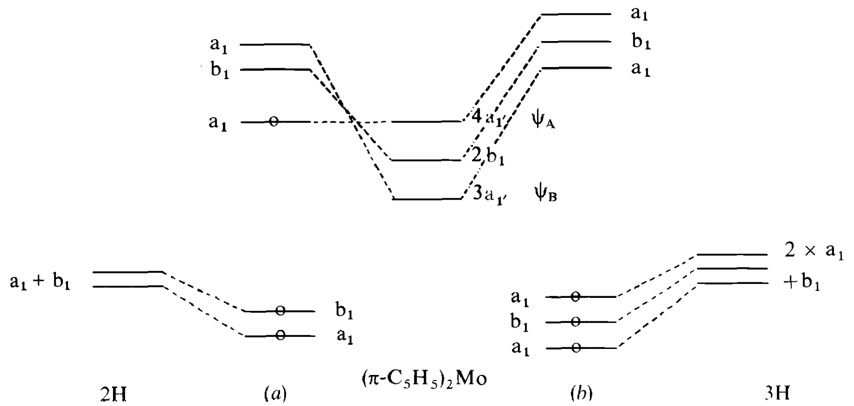


Figure 3. (*a*) The M.O.'s resulting from interaction between the $(\pi\text{-}C_5H_5)_2Mo$ system and two hydrogen ligands, showing the 'lone pair' in the ψ_A (Alcock) orbital.
(*b*) The M.O.'s resulting from interaction between the $(\pi\text{-}C_5H_5)_2Mo$ system and three hydrogen ligands, showing that all three metal orbitals are employed. For simplicity, all other M.O.'s arising from the $(\pi\text{-}C_5H_5)_2Mo$ system are omitted

The *Figure 3* shows that the bonding of a d^2-system, such as $(\pi\text{-}C_5H_5)_2Mo$ with two hydrogen ligands giving the dihydride $(\pi\text{-}C_5H_5)_2MoH_2$, places the ψ_A $(4a_1)$ orbital as the highest filled 'non-bonding' orbital. The 'lone pair' is therefore located in the Alcock-type orbital. The *Figure 3* also shows how interaction of the $(\pi\text{-}C_5H_5)_2M$ system with three hydrogens, forming $[(\pi\text{-}C_5H_5)_2MoH_3]^+$, gives rise to three bonding M.O.'s, as would be anticipated from the Balhausen model, and there are now no 'lone pair' electrons.

Several other points of interest arise from crystal structure studies made on bis π-cyclopentadienyl molybdenum compounds and related systems. Of eighteen bent bis π-cyclopentadienyl metal compounds studied recently in Oxford by Dr C. K. Prout and co-workers, thirteen have staggered configurations and five were eclipsed. The compounds $(\pi\text{-}C_5H_5)_2MCl_2$, $M = Mo$ or Nb, have very similar structures and in both cases two molecules are found in the asymmetric unit, one of which is eclipsed and the other staggered. The ring–metal–ring angles are 131° (eclipsed) and 129° (staggered). These data suggest that there can only be very small energy differences between the two configurations and that crystal forces are an important factor in determining the configuration.

The six most accurate structures have been examined to see if there were any significant differences between the C–C distances of the C_5 rings, as has been suggested. The data come from structure determinations (R values in parenthesis) on the compounds $(\pi\text{-}C_5H_5)_2MoCl_2$ (0.026), $[(\pi\text{-}C_5H_5)_2MoCl_2]^+BF_4^-$ (2.60), $[(\pi\text{-}C_5H_5)_2ReBr_2]^+BF_4^-$ (5.0), $[(\pi\text{-}C_5H_5)_2NbCl]_2O]^{2+}[BF_4]^{2-}$ (3.0), $(\pi\text{-}C_5H_5)_2Mo(SBu)_2FeCl_2$ (0.07)[45], $[\{(\pi\text{-}C_5H_5)_2Mo(NH_2CH(CO_2)CH_2S\}_2H^+PF_6^-$ (0.038) and $[(\pi\text{-}C_5H_5)_2Mo(NHMe.CH_2.CO_2)]^+Cl^-$ (0.072)[46]. The mean C–C distance were found to be 1.402 Å with a standard deviation of 0.028 Å and there were no significant differences which could be attributed to regular unequal distances in the rings.

It has been shown that the compounds $(\pi\text{-}C_5H_5)_2M(SR)_2$, where R = Ti, Mo or W, may act as ligands to transition metals. Typical examples are given in *Figure 4*.

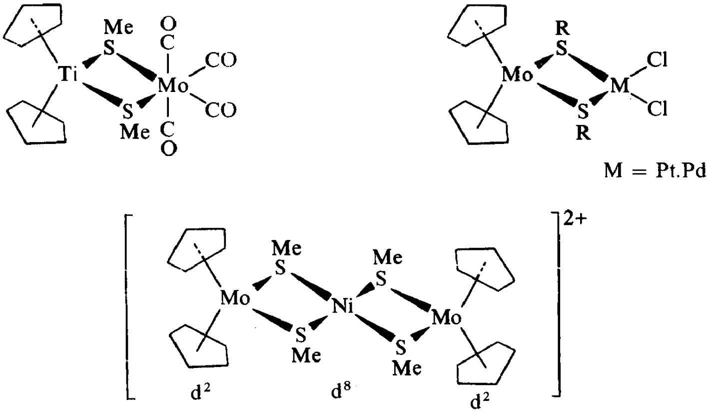
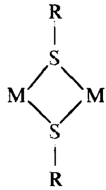


Figure 4. Some mixed-metal complexes containing bridging thiol ligands[47, 48, 49]

The crystal structure data for some complexes where these ligands coordinate to Group VI metal carbonyl residues are shown in *Table 2*.

Table 2. Distances and angles in some bridging  systems[50, 51]

M M'	M–S–M'	S–M–S	S–M'–S	M–M', pm
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2Mo(CO)_4$	82.8°	99.9°	94.6°	332
$(\pi\text{-}C_5H_5)_2W(SPh)_2Cr(CO)_4$	104.2°	71.2°	72.0°	393
$(\pi\text{-}C_5H_5)_2W(SPh)_2Mo(CO)_4$	105.0°	72.6°	69.0°	406
$(\pi\text{-}C_5H_5)_2W(SPh)_2W(CO)_4$	104.9°	72.8°	69.4°	401
$[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni]^{2+}[BF_4]^{2-}$	72.3°	98.2°	117.2°	277

It appears from the bridging angles that the complexes formed from the d^2-tungsten system $(\pi\text{-}C_5H_5)_2W(SPh)_2$ do not have a bonding W–M′ interaction, whereas the complex formed by the d^0-titanium complex $(\pi\text{-}C_5H_5)_2Ti(SMe)_2$ appears to have a Ti—Mo bond. It was, therefore, of interest to examine the reactions of a d^1-ligand of the above type. For this reason the paramagnetic ($\mu_{eff} = 1.71$ B.M.), red complex $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (I) was prepared (*Figure 5*).

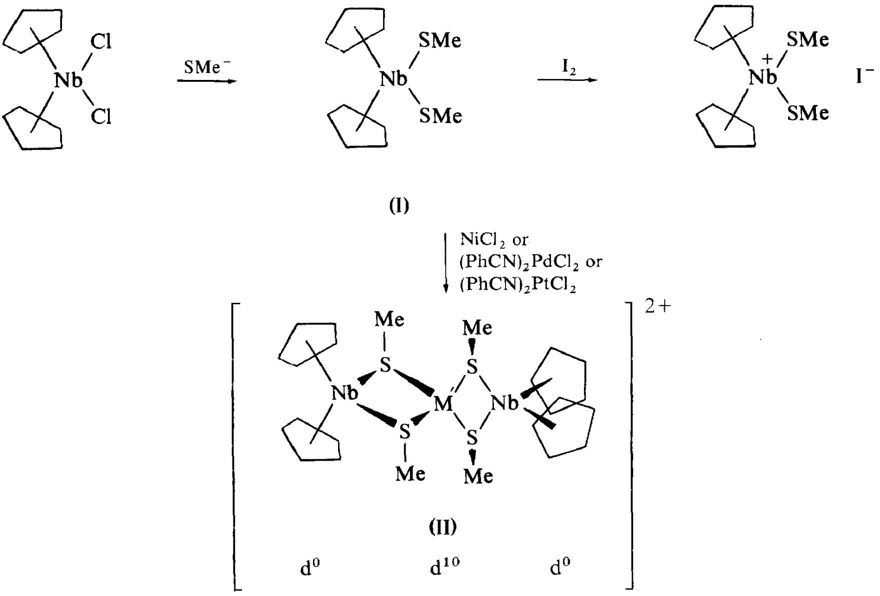


Figure 5. Preparation and reactions of some bis π-cyclopentadienyl niobium compounds

The molybdenum and tungsten complexes $\{[(\pi\text{-}C_5\text{-}H_5)_2M(SMe)_2]_2Ni\}^{2+}$ (see *Figure 4*) are diamagnetic and are thought to contain square-planar, d^8-nickel. The niobium analogue (II, M′ = Ni) is also found to be diamagnetic ($\chi_m = -607 \times 10^6$ e.m.u. at 22°C) and determination of the crystal structure shows that the nickel has a tetrahedral environment (see *Figure 5*)[51]. It therefore appears that in the compound (II, M′ = Ni) the nickel may be formally described as zero-valent, d^{10} and the two niobium atoms as five-valent, d^0. The dimensions of the NiS_2Nb rings, given in *Table 2*, suggest there is substantial niobium–nickel bonding in the complex and the bonding may be represented as donor bonds from the d^{10}-nickel atom to the 16 electron d^0-niobium systems. It is normally found that saturated sulphur ligands may not stabilize low-valent, electron-rich metal systems as readily as, for example, tertiary phosphine ligands. This is attributed to a greater ability of tertiary phosphine ligands to act as electron acceptors. The niobium complexes (II) represent the first examples of zero-valent compounds of nickel, palladium and platinum which might appear to be stabilized by sulphur ligands and we propose that this arises as a result of an acceptor role for a niobium–nickel bond of essentially σ-symmetry.

Therefore, in the complexes (II) it appears that the system $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+$ is acting as a 2 × 2 electron σ-donor and a 2 electron σ-acceptor: an unusual type of donor–acceptor ligand. The bonding between the nickel and the niobium can be understood by analogy with the trihydride cation $[(\pi\text{-}C_5H_5)_2MoH_3]^+$ and, in the light of the M.O. scheme in *Figure 3*, this description is not inconsistent with the proposal that the odd electron in compound (I) is placed in an orbital of location ψ_A.

2. SOME REACTIONS OF BIS π-CYCLOPENTADIENYL MOLYBDENUM AND TUNGSTEN COMPOUNDS

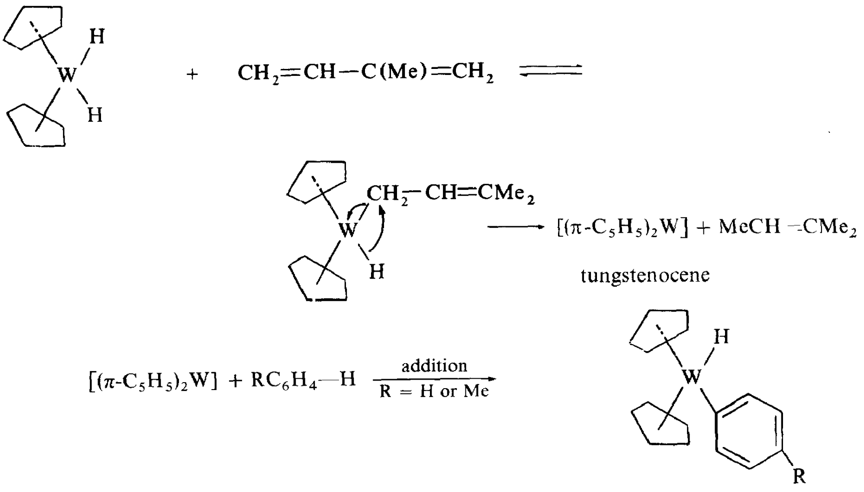
It is found that the bis π-cyclopentadienyl molybdenum and tungsten systems are very robust and can form inert, thermally stable compounds with a surprising range of ligands. For example, neutral, d^2-complexes $(\pi\text{-}C_5H_5)_2MoX_2$, where X_2 is H_2, Me_2[52], $(SH)_2$[53], $(SR)_2$[54], S_4[55], Cl_2[56], Br_2[56], $(N_3)_2$[57] and even =O[58], are known. The unusual nitrosyls $(\pi\text{-}C_5H_5)_2Mo(NO)I$[59] $(\pi\text{-}C_5H_5)_2Mo(C_5H_5)NO$[60] have been described. These may be either 20 electron compounds if the NO is treated as a 3 electron ligand, or 18 electron compounds if the NO is regarded as a 1 electron ligand. The substitution of a $\pi\text{-}C_5H_5$ ring is observed when the dihydride $(\pi\text{-}C_5H_5)_2MoH_2$ is treated with $MeMn(CO)_5$ and the binuclear derivative $(\pi\text{-}C_5H_5)_3\overline{Mo\text{-}\pi\text{-}C_5H_4\text{-}Mn}(CO)_4$ is formed[61].

The d^2-system may exist as mono-cations $[(\pi\text{-}C_5H_5)_2MoLX]^+$ where LX represents ligands such as $Cl(PR_3)$[62], $Me(PR_3)$[52], $Br(SMe_2)$[54], $Br(CO)$[52], $SCH_2CH_2NH_2$[63], SCH_2CH_2SMe[54], $MeC_6H_4S_2$[64], and other chelate ligands such as amino acid residues[65]. Even di-cations are found, as in $[(\pi\text{-}C_5H_5)_2MoNH_2CH_2CH_2NH_2]^{2+}$[65].

The inertness of the bent $(\pi\text{-}C_5H_5)_2M$ system is demonstrated by the observation that treatment of the dihydrides $(\pi\text{-}C_5H_5)_2MH_2$ with chlorine or bromine does not cause immediate destruction, instead the paramagnetic, d^1, five-valent compounds $[(\pi\text{-}C_5H_5)_2MX_2]^+$, X = Cl or Br, are formed in good yield[56]. The six-valent, d^0-compounds $[(\pi\text{-}C_5H_5)_2MoH_3]^+$ are also known[33, 34]: this observation demonstrates that with hydrogen ligands a central atom may achieve a higher valency than with halogen ligands.

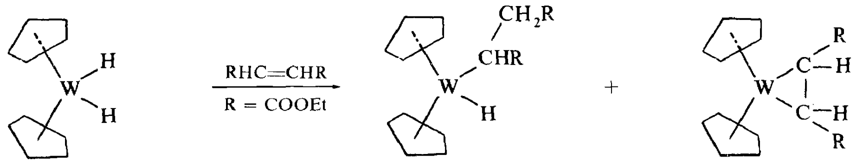
The ease and variety of stable compounds that can be formed might suggest that the bis π-cyclopentadienyl molybdenum and tungsten system held no surprises and would not take part in catalytic reactions. This is, however, not the case and two examples of unexpected reactivity are shown below.

(i) Treatment of the dihydride $(\pi\text{-}C_5H_5)_2WH_2$ with isoprene in benzene at 120°C for three days causes the reduction of the isoprene to isomeric pentenes. Chromatography of the less volatile products gives the volatile phenyl hydride derivative $(\pi\text{-}C_5H_5)_2WH(C_6H_5)$ (III) in up to 5 per cent yields. The *p*-tolyl analogue of compound (III) is made in the same way using toluene as a solvent. The reaction is thought to involve the homogeneous substitution of benzene or toluene by 'tungstenocene' formed as an intermediate species and the following mechanism may be written[66].



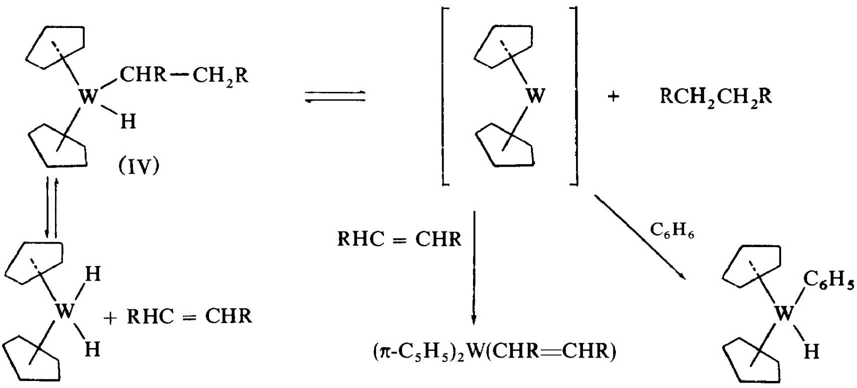
(III)

Support for the first step in this mechanism arises from the observations that the hydrides $(\pi\text{-}C_5H_5)_2MH_2$ are known to add across unsaturated systems such as acetylenes[67] and, in particular, with diethylmaleate the tungsten dihydride gives the succinyl derivatives (IV), and the cyclic product (V)[68]. Further, if a solution of the succinyl derivative (IV) in benzene is heated at 120°C for six hours then the phenyl hydride is formed in 6 per cent yield together with some of the dihydride $(\pi\text{-}C_5H_5)_2WH_2$ and the cyclic derivative (V). The equilibria shown in *Figure* 6 may be envisaged:



(IV) (V)

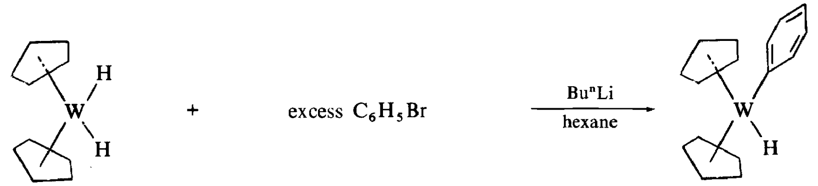
In a separate experiment it was found that heating solutions of the phenyl hydride compound (III) in deuterobenzene for two days at 120°C did not give any deuterophenyl derivatives. This suggests that the phenyl hydride is not a good source of the 'tungstenocene' intermediate. Attempts to isolate tungstenocene by several routes, including reduction of the dichloride $(\pi\text{-}C_5H_5)_2\text{-}WCl_2$ with metals, have been unsuccessful.



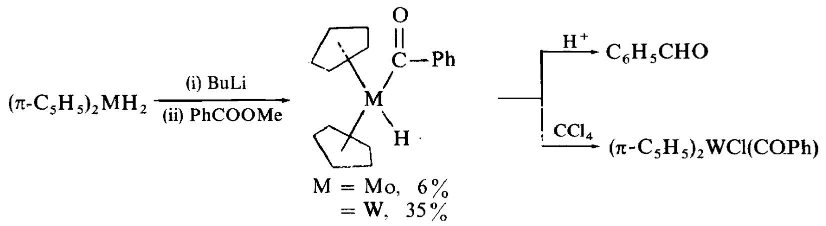
(V) (III)

Figure 6

In a search for an improved route to the phenyl hydride (III) the following reactions were found[69]:



~50%
(III)

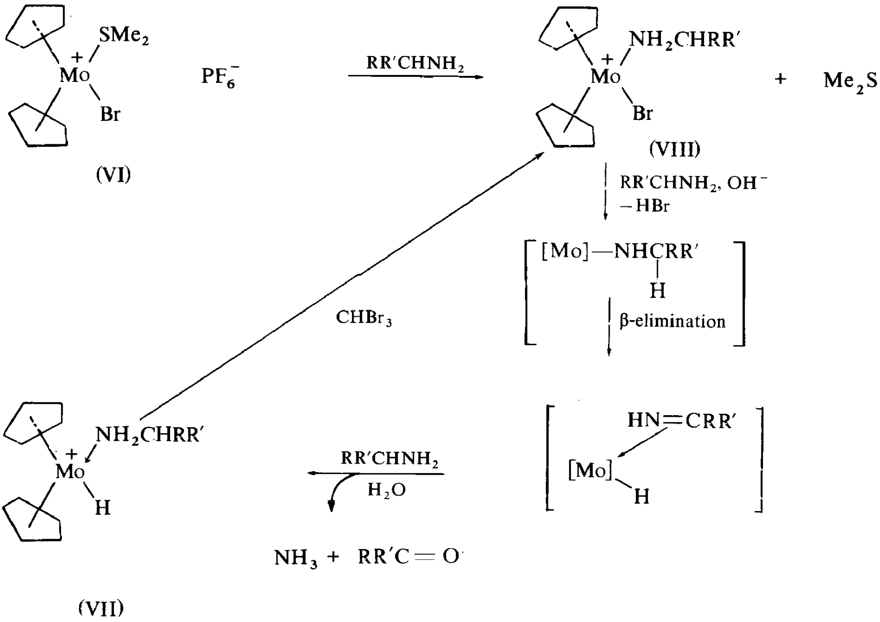


$$(\pi\text{-}C_5H_5)_2WH_2 \xrightarrow[\substack{\text{(ii) PhCOOMe } 35\% \\ \text{or PhCOCl } 35\% \\ \text{or PhCHO } 10\%}]{\text{(i) Bu}^n\text{Li}} (\pi\text{-}C_5H_5)_2WH(COPgh$$

The mechanisms of these reactions are not clear and they are being studied further.

(ii) Another reaction which illustrates the diversity of behaviour of the $(\pi\text{-}C_5H_5)_2Mo$ (or W) systems involves the oxidation of amines to aldehydes and ketones. Treatment of the dimethylsulphide cation (VI) with aqueous solutions of amines RNH_2 at ~50°C gives a smooth reaction and the amine hydrides $[(\pi\text{-}C_5H_5)_2MH(RNH_2)]^+$ (VII) and the corresponding aldehyde or ketone are formed[52].

The following mechanism is proposed: it closely resembles that given for the formation of transition metal hydrides using alcohols in the presence of a base.

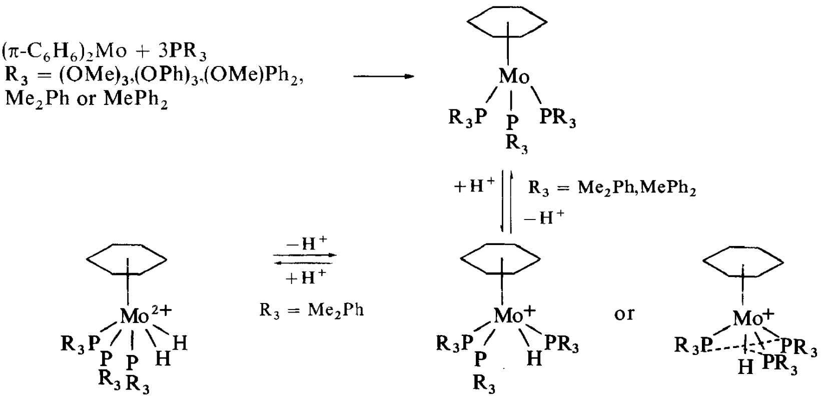


The mechanism is supported by the observations that the amine bromide (VIII) can be prepared from the dimethylsulphide complex using anhydrous amine (shown when $RR'NH_2 = MeNH_2, Bu^nNH_2$), and that treatment of several of the amine bromides with aqueous sodium hydroxide gives aldehydes or ketones as before.

3. SOME ARENE MOLYBDENUM CHEMISTRY

In view of the interest in the role of molybdenum in catalytic reactions such as olefin dismutation and nitrogen fixation it seemed worthwhile to try to prepare and study low-valent and very electron-rich molybdenum systems. The bisarene molybdenum complexes first prepared by E. O. Fischer[70] were chosen as starting materials.

Treatment of bisbenzene molybdenum with several tertiary phosphines or phosphites R_3P causes smooth displacement of one benzene ring and the complexes $C_6H_6Mo(PR_3)_3$ are formed in good yield[71]. Examples are:

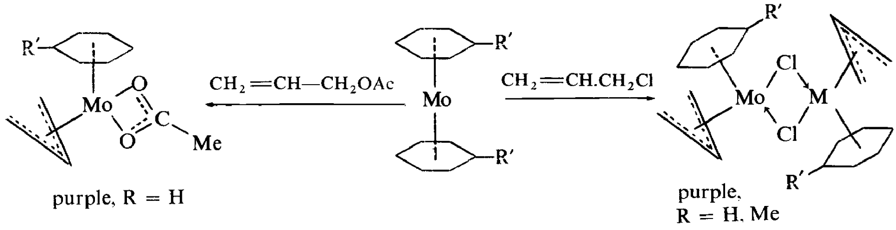


(X) (IXa) (IXb)

The tertiary phosphine complexes R_3 = Me_2Ph or $MePh_2$ are basic and may be protonated in a stepwise manner forming a monohydride derivative (IX) and the dihydrides (X). The i.r. and ^1H n.m.r. data do not permit unequivocal distinction between the two structures (IXa) and (IXb) for the monohydride cations. The hydride resonances appear as 1:3:3:1 quartets from room temperature to −96°C consistent with coupling of the three equivalent hydrogen ^{31}P nuclei. However, it may well be that even at −96°C the phosphorus and hydrogen ligands are rapidly interconverting so that they appear equivalent. Interconversion of stereochemistry has been observed for many tertiary phosphine hydrides[72] and for $C_6H_6V(CO)_3H$[73]. By analogy with the structure proposed for $C_6H_6V(CO)_3H$, and with the structures of many π-cyclopentadienyl complexes π-$C_5H_5MoL_3H$, the structure (IXa) seems the most likely.

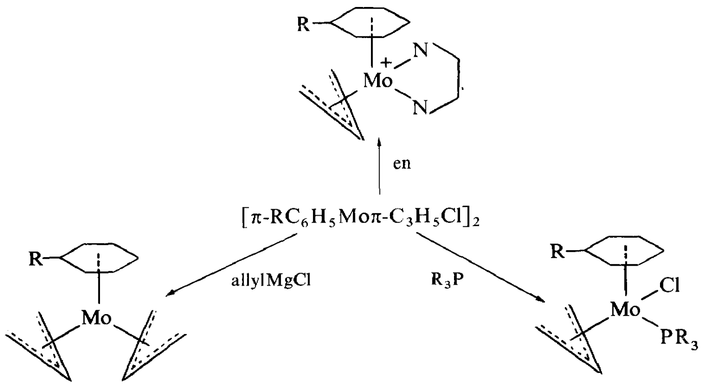
In contrast to the above observations it was found that the triphenylphosphine compound $C_6H_6Mo(Ph_3P)_3$ could not be prepared by the above route. However, a dinitrogen compound of stoicheiometry $C_6H_5MeMo(Ph_3P)_3N_2$[74] has been isolated.

Further studies on the reactivity of bisarene molybdenum led to the observation that treatment of bisarene molybdenums with allyl chloride[75] or allyl acetate[76] forms the π-allyl derivatives (XIa or b). The structure of the complex (XIa, R′ = H) shown below has been determined by x-ray diffraction studies[77].



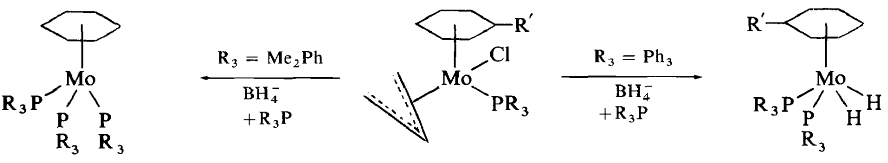
(XIb) (XIa)

The purple crystals of the dimeric allyl complexes (XIa) are slightly soluble in benzene. The bridging chloride dimer is readily cleaved by a variety of ligands: it also reacts with allyl magnesium chloride forming an air sensitive, yellow bis π-allyl complex (XII), examples are:



(XII)

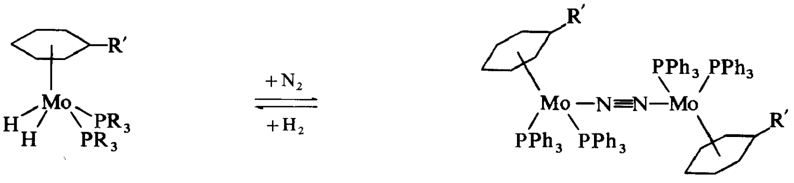
Treatment of the complex $C_6H_6Mo(\pi\text{-}C_3H_5)(Me_2PhP)Cl$ (XIII, $R_3 = Me_2Ph$) with sodium borohydride in the presence of excess of the tertiary phosphine gives the trisphosphine complex $C_6H_6Mo(R_3P)_3$. This observation, coupled with knowledge of the existence of the dinitrogen compound described above led us to study the reaction using triphenylphosphine. It was found that reduction with sodium borohydride of the complex (XIII, $R_3 = Ph_3$) under hydrogen or argon in the presence of excess triphenylphosphine gave red crystalline complexes. Analysis, i.r. and especially the ^{1}H n.m.r. data suggest these complexes to be the dihydrides (XIV) shown below.



(XIII) (XIV)

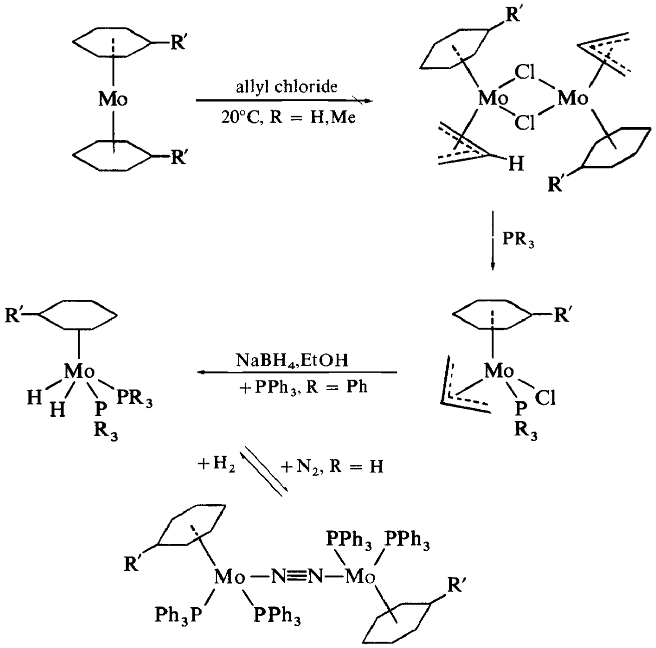
R′ = H or Me

The dihydride (XIV, R′ = H) in benzene reacts readily with nitrogen gas at room temperature and at one atmosphere forming a binuclear, maroon dinitrogen complex (XV) in essentially quantitative yield. The reaction is reversible and treatment of the dinitrogen complex with hydrogen gas reforms the dihydride. The symmetrical structure for the dinitrogen complex is proposed on the basis of analytical data, infrared spectra and the observation of an intense band in the Raman spectrum at 1910 cm^{-1} assignable to a symmetric N=N stretch. There is no band assignable to an N=N stretching frequency in the infrared spectrum.



(XIV) (XV)

The overall reaction scheme for the preparation of the molybdenum dinitrogen compounds is as follows:



These reactions show that the arene molybdenum bond is chemically robust and can survive in a wide range of ligand environments. This may well be true for other second and third row transition metals.

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