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STUDIES ON SYNTHESIS, MECHANISM AND REACTIVITY OF SOME ORGANO–MOLYBDENUM AND –TUNGSTEN COMPOUNDS

Malcolm L.H. Green

Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, England

ABSTRACT. The activation of sp^2- and sp^3- C–H bonds by η-cyclopentadienyl tungsten derivatives is described. Evidence is presented for the reversible elimination of alpha-hydrogen from a tungsten-methyl system. Molybdena- and tungstena- cyclobutane derivatives have been synthesised and their photoinduced evolution of olefins has been investigated. Rules are given for predicting the selectivity of nucleophilic addition to 18-electron organotransition metal cations containing polyene ligands.

The chemistry of the bent bis–η–cyclopentadienyl derivatives of the transition metals of Groups IV, V, VI and Re has proved to be very extensive. Their study has led to considerable development not only in the chemistry of the metals concerned but also in the general context of synthesis, structure, bonding, mechanism and reactivity in organotransition metal chemistry.

The net effect of the two η–C_5H_5 ligands in compounds of the class $[M(\eta\text{–}C_5H_5)_2L_n]$, where L represents any ligand, is to cause the metal d-orbitals to be higher in energy relative to the energies found on these metal atoms in most other common ligand environments. That is to say, in these bent bis–η–cyclopentadienyl complexes, the metal centre may be described as electron rich. Further, the two η–cyclopentadienyl ligands are normally highly inert to inter- and intra- molecular reactions. They are also stereochemically compact so that there remains ample room on the metal for the further coordination of two and up to three ligands of normal dimensions.

In this paper, we are concerned with four aspects of the chemistry of bis–η–cyclopentadienyl molybdenum and tungsten compounds which we consider to have quite general relevance to organotransition metal chemistry.

I. THE ACTIVATION OF C–H BONDS BY η–CYCLOPENTADIENYL–TUNGSTEN DERIVATIVES.

There is now a considerable body of evidence that the 16-electron molecule tungstenocene is able to undergo intermolecular insertions into sp^2- and sp^3 C–H bonds. Figure 1 illustrates synthetic route to the tungstenocene intermediate and some of its reactions with aromatic C–H bonds and other reactions.

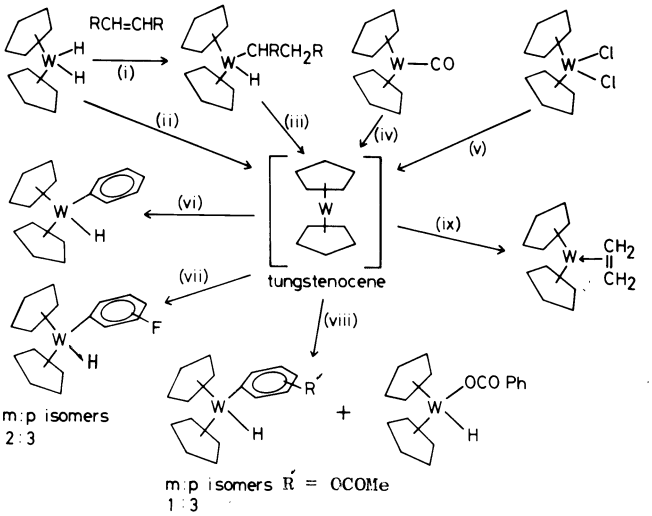


Figure 1. Synthetic routes to tungstenocene and some of its reactions. The tungstenocene is formed *in situ*. (i) R = EtOCO, in toluene at 50°. (ii) Irradiation with a 500W medium pressure Hg lamp at room temperature for 12h. (Ref. 1). (iii) 120° (Ref. 2). (iv) same as (ii) (Ref. 3). (v) Na/Hg at room temperature (Ref. 4). (vi) In benzene (Ref 1). (vii) In C_6H_5F (Ref. 5). (viii) in $C_6H_5CO_2Me$ (Ref. 5). (ix) C_2H_4 in toluene (Ref. 4).

The products of irradiation of solutions of the dihydride $[W(\eta-C_5H_5)_2H_2]$, **1**, in fluorobenzene or methylbenzoate show the tungstenocene to be unselective to normal directional effects in substituted benzenes and the isomeric products appear to be determined more by the steric effects of the substituents.

The reactivity of tungstenocene has been compared to that of simple carbenes e.g. CH_2. (Refs. 1 & 4). This is exemplified strongly by the observation that tungstenocene is relatively unselective, even to attack on the sp^3- and sp^2- C—H bonds in toluene, as shown in Figure 2.

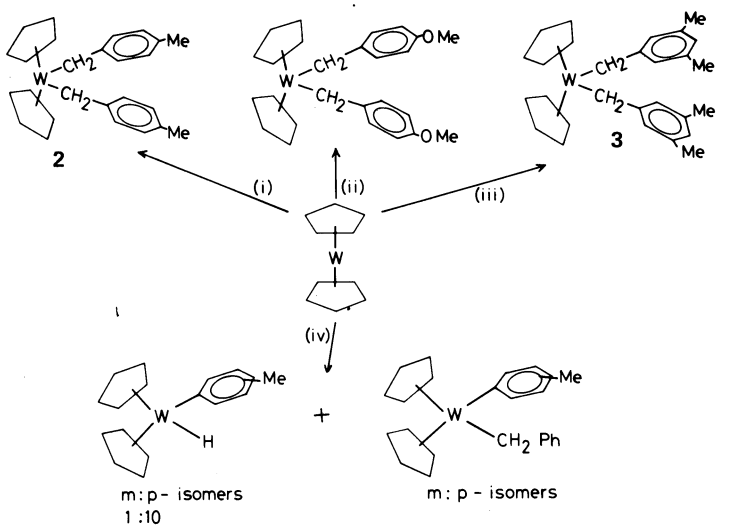


Figure 2. Photoinduced reaction of tungstenocene involving insertion into sp^3 C—H bonds. Irradiation at room temperature of $[(\eta-C_5H_5)_2WH_2]$ in (i) p-xylene (ii) p-anisole (iii) $1,3,5\text{-}Me_3C_6H_3$ (iv) MeC_6H_5.

Figure 2 also shows examples involving insertion of tungstenocene into other sp^3- C—H bonds in p-xylene and mesitylene giving the bis-alkyl derivatives **2** and **3** respectively. (Ref. 6).

We were interested to try to compare the reactions of tungstenocene formed photochemically with those formed by a non-photochemical (i.e. thermal) process. We have found that the methylhydride derivative $[W(\eta-C_5H_5)_2MeH]$ **4**, is stable at room temperature but it decomposes smoothly in solution at 50 - 60° with evolution of methane and the implicit formation of tungstenocene in this reaction is strongly suggested by the thermal reactions of **4**, shown in Figure 3. (Ref. 7).

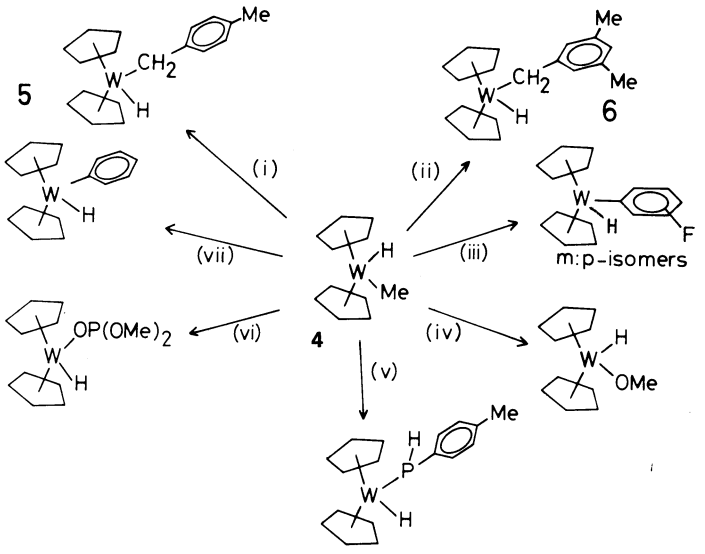
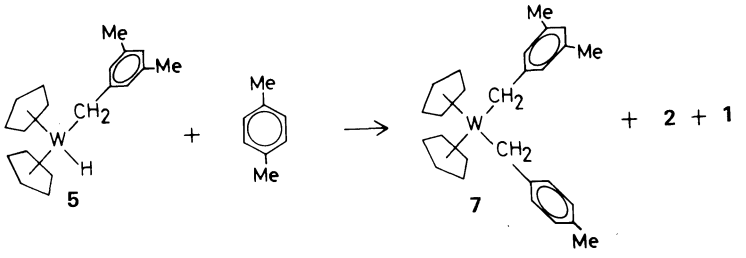


Figure 3. Thermal decomposition reactions of bis—η—cyclopentadienyl tungstenmethylhydride at 60° in (i) p-xylene, ca. 35% (ii) mesitylene, ca. 45% (iii) fluorobenzene, ca. 45% (iv) methanol, ca. 70% (v) $Me_2P(4\text{-}MeC_6H_4)$, ca. 35% (vi) $P(OMe)_3$, ca. 25% (vii) benzene, ca. 90%.

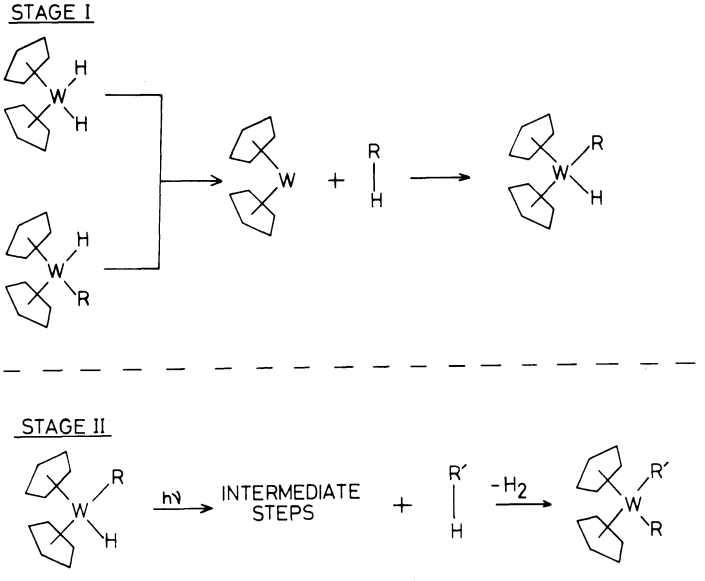
The photochemically and thermally induced reaction of tungstenocene with benzene and fluorobenzene give essentially the same products which suggests the tungstenocene intermediate to be the same under the different conditions. For example, both the thermal and photochemical products from fluorobenzene are a mixture of m- and p- isomers of $[W(\eta\text{–}C_5H_5)_2H(m\text{- or p- } C_6H_4F)$ in the approximate ratio of 2:3 respectively. It seems unlikely that the isomeric ratio would be the same for different intermediate tungstenocene species.

In contrast, the photochemical reactions of tungstenocene with p-xylene and mesitylene give the bis-alkyl derivatives **2** and **3**, whilst the thermal reactions of **4** with p-xylene or mesitylene give only the monoalkylhydrides **5** and **6** respectively. We have found, however, that photolysis of **5** in mesitylene gives the following reaction (Ref. 8).



The formation in this reaction of **7** strongly suggests that **6** and **5** can be intermediates in the formation of **2** and **3** in the photoinduced reactions shown in Figure 2.

We can explain the differences between the photochemical and thermal products of tungstenocene reactions on the basis of the following two stage scheme (Ref. 5).



We propose that Stage 1 is identical for tungstenocene produced either thermally or photochemically. When R = an aryl ligand, the product is thermally and photochemically stable and the reaction rests at Stage 1. However, when R = CH_2Ph, p-$CH_2C_6H_4Me$, or $-CH_2(3,5\text{-}Me_2C_6H_3)$, the monoalkyl compounds $[W(\eta\text{–}C_5H_5)_2RH]$ are thermally stable but photochemically unstable so that on irradiation they proceed to the Stage II reaction giving disubstituted products $[W(\eta\text{–}C_5H_5)_2RR']$.

The Stage II must involve intermediates capable of undergoing insertion into sp^3- C–H bonds and we envisage the possibilities shown on the next page:-

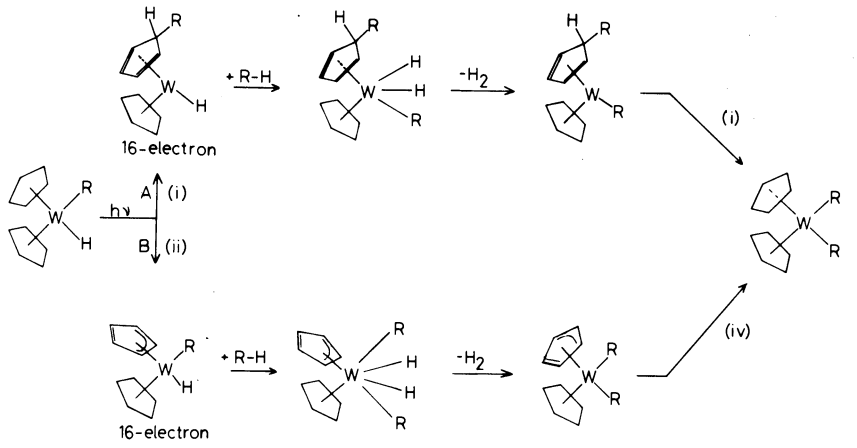
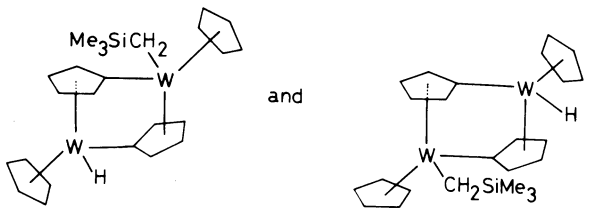


Figure 4. Possible mechanisms for Stage II reactions. (i) Metal-to-ring transfer of R. (ii) η^5–C_5H_5 to η^3–C_5H_5 shift. (iii) Ring-to-metal transfer of R. (iv) η^3–C_5H_5 to η^5–C_5H_5 ring shift.

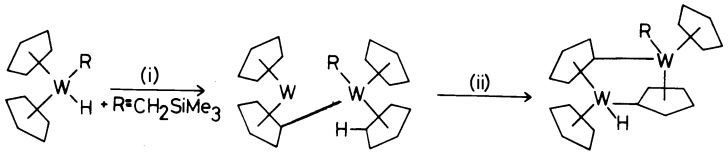
The route A proceeds via a reversible migration of the group R to the η–C_5H_5 ring, as has been observed in the reactions of $[W(\eta\text{–}C_5H_5)_2EtCl]$ (Ref. 9). Route B involves a reversible η^3–$C_5H_5 \leftrightharpoons \eta^5$–$C_5H_5$ ring shift. The feasibility of this equilibrium is supported by the observation that the apparently "20-electron" compound $[W(\eta\text{–}C_5H_5)_2(CO)_2]$ is known and it decomposes thermally to $[W(\eta\text{–}C_5H_5)_2CO]$ (Ref. 10).

Irradiation of solutions of **1** in tetramethylsilane give the cis- and trans-isomers **8** and **9**, whose crystal structures have been determined (Refs. 5 & 11).



8 9

We propose that the reaction proceeds by initial insertion of tungstenocene into a C–H bond of tetramethylsilane, giving the trimethylsilylhydride $[W(\eta\text{–}C_5H_5)_2H(Me_3SiCH_2)]$. A second photoinduced reaction then gives rise to insertion of tungsten into unreacted **1**. An abbreviated mechanism is illustrated below where stage (i) refers to several steps involving type A or B intermediates. The formation of the *cis*- or *trans*- isomers depends on the final step (ii), according to the stereochemistry of the final insertion into the C–H bond of the η–C_5H_5 ring.



II. EVIDENCE FOR THE REVERSIBLE α–ELIMINATION OF HYDROGEN FROM A TUNGSTEN–METHYL COMPOUND.

Treatment of the compound $[W(\eta\text{–}C_5H_5)_2(\eta\text{–}C_2H_4)Me]PF_6$ in acetone with dimethylphenylphoshine gives, in sequence, the compounds **10, 11** and **12**, which are shown in Figure 5. The deuteriomethyl analogue $[W(\eta\text{–}C_5H_5)_2(\eta\text{–}C_2H_4)CD_3]PF_6$ reacts identically and there is no exchange of deuterium with the hydrogen during the reaction. We have proposed that the reaction can be understood by the suggestion, as the key step, of the following reversible elimination of hydrogen from the methyl group.

$$W\text{–}CH_3 \rightleftharpoons W\overset{H}{\underset{CH_2}{<}}$$

The proposed mechanism is shown in Figure 5 where $k_1 \gg k_2 \gg k_3$ (Ref 12).

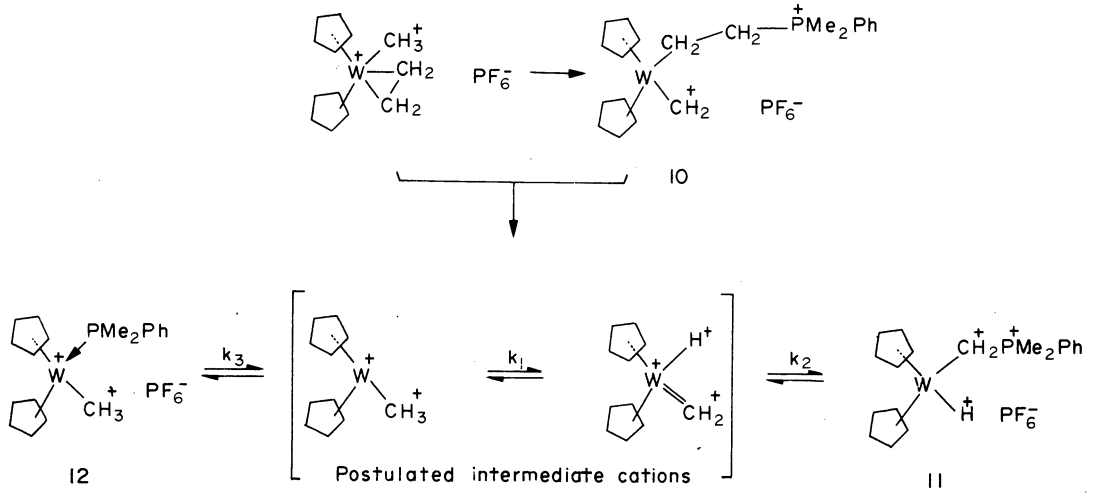
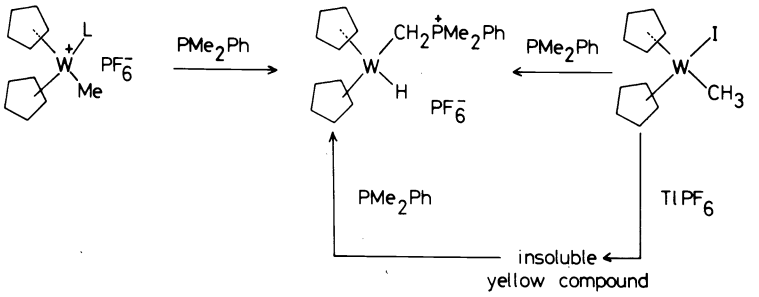


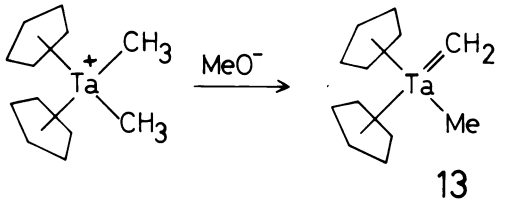
Figure 5. * denotes H or D.

This mechanism is supported by the following observations:-

a) The ethylene ligand is not essential for the formation of the compound **11** since we obtain this compound from several other tungsten methyl compounds (Refs 13 & 14), viz:



b) Elegant studies by Schrock have shown extraction of α–hydrogen from tantalum alkyls (Ref. 15) in the following reaction (Ref 16):



The compound **13** is isoelectronic with the proposed intermediate $[W(\eta\text{–}C_5H_5)_2(=CH_2)H]^+$.

III. METALLOCYCLOBUTANE DERIVATIVES OF MOLYBDENUM AND TUNGSTEN.

Treatment of η^3–allylic cations of the type $[M(\eta\text{–}C_5H_5)_2(\eta^3\text{–}CHRCR'CH_2)]^+$ with nucleophiles $N^- = H^-$, Me^- or $C_3H_5^-$ causes addition of the nucleophile to the 2-carbon of the allyl group and thermally stable, crystalline metallocyclobutane derivatives are isolated (Figure 6), (Ref. 17).

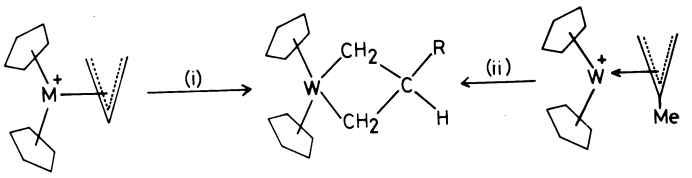


Figure 6. (i) M = Mo when R = H; M = W, R = H, D, Me or C_3H_5 (ii) M = W, $NaBH_4$ in THF.

Irradiation of solutions of some of the metallocyclobutane compounds gives rise to high yields of olefins which have *one carbon less* than in the original metallocyclobutane ring. The data is given in Table 1 (Ref 18).

TABLE 1

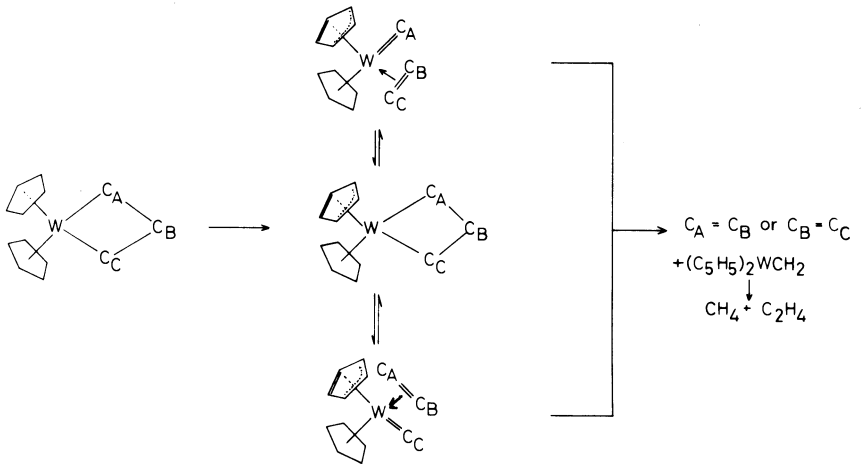
Volatile products of photolysis of some tungsten cyclobutane compounds (Ref. 18).

Compound	Reaction time /h[a]	Volatile products[b]	
		Major	Minor
$[W(\eta\text{–}C_5H_5)_2(\text{–}CH_2CH_2CH_2\text{–})]$	21	Ethylene, 10	Propene, 5 Methane, 1
$[W(\eta\text{–}C_5H_5)_2(\text{–}CHMeCH_2CH_2\text{–})]$	4	Ethylene, 10 Propene, 8	Butene, 6 Methane, 1
	21	Propene, 10 Ethylene, 5	Butene, 4 Methane, 1
$[W(\eta\text{–}C_5H_5)_2(\text{–}CH_2CHMeCH_2\text{–})]$	18	Propene, 10	Methane, 6 Butene, 3 Ethylene, 1

a). Reactions were in hexane (ca. 10 mmol l^{-1}), at room temperature in a Pyrex vessel; irradiation by a Hanovia 500W medium-pressure lamp.

b). G.L.C. on a KCl/alumina column, peak intensities are relative to the most intense peak = 10. Combined yield of products, ca. 50%.

We propose that the photo-decomposition of the metallocyclobutane compounds proceeds by the following mechanism:-



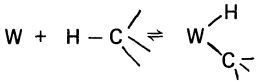
A crucial step in the mechanism is the opening of the metallocyclobutane ring, giving the olefin-carbene systems. (Ref. 19). It is this equilibrium, namely:-

which is thought to be the key step in olefin metathesis catalysis and our observations on the above metallocyclobutane compounds strongly support this proposal.

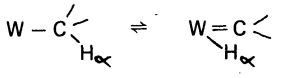
SUMMARY OF PARTS I, II & III.

On the basis of the above observations, we have proposed that bis-cyclopentadienyl tungsten derivatives can undergo three simple processes:

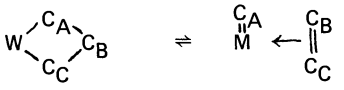
(a) Reversible insertions into saturated sp^3 C–H bonds:-



(b) Reversible elimination of alpha-hydrogen forming a carbene-hydride:-

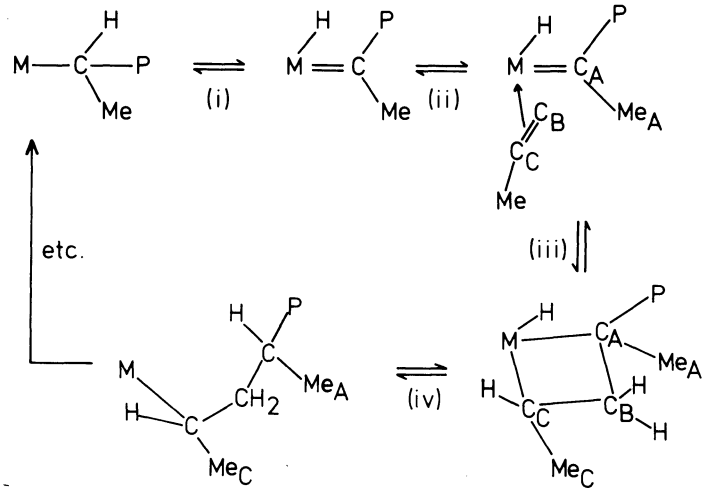


(c) The opening of a tungstencyclobutane ring giving carbene-olefin intermediates:-



This, together with related studies on olefin metathesis reactions (Ref. 19) on the activation of C–H bonds and on other α-hydrogen elimination studies, (Refs. 15, 16 & 20), suggests that these three processes may occur in widely differing compounds so that they are *general* and *characteristic* properties of suitable transition metal centres.

Combinations of these three processes give rise to exciting new mechanisms not hitherto thought to be likely. For example, the following scheme for polymerisation of propylene, giving stereo-regular polymers can be written, which is consistent with known data.



P represents polymer chain.

Figure 7. A new mechanism for head-tail polymerisation on propylene. (i) Reversible α-elimination of hydrogen. (ii) Addition of propylene with $MHC_AC_BC_C$ approximately coplanar and the Me_C group *trans* to P. (iii) *cis* opening of $C_C{=}C_B$ giving a metallocycle with Me_AMe_C cisoid. (iv) Reductive elimination with retention of stereochemistry at C_A. This process gives the *syndiotactic* polymer. Alternatively, if the propylene adds at stage (ii) placing the Me_C *trans* to Me_A, then the polymer grows as the *isotactic* isomer.

A mechanism for vicinal interchange rearrangements in the biochemical catalysis by coenzyme B-12 has been proposed involving reversible insertions into sp^3 C–H bonds and reversible α-elimination of hydrogen. (Ref. 21).

In this context, we note that the biochemical oxidation of alkanes and other C—H systems e.g. of octane to octanol by a P450 cytochrome (Ref 22), may proceed by initial insertion of the transition metal centre into the C—H bond, followed by insertion of oxygen into the metal-alkyl bond. It is normally suggested that oxidation proceeds via oxygen attack from a metal-activated oxygen system on the unactivated C—H bond.

IV. RULES FOR PREDICTING THE REGIOSELECTIVITY OF NUCLEOPHILIC ADDITION ON 18-ELECTRON ORGANOTRANSITION METAL CATIONS CONTAINING POLYENE LIGANDS.

Nucleophilic addition to the η-allylic cation $[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CHCH_2)]^+$ or to the cation $[Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_7H_7)]^+$ are regiospecific and give exclusively $[W(\eta\text{-}C_5H_5)_2(\text{-}CH_2CHNCH_2]$ (Ref. 17) and $[Mo(\eta\text{-}C_6H_6N)(\eta\text{-}C_7H_7)]$ (Ref. 23) respectively, where N is the nucleophile. It was surprising observations such as these that led us to inquire into the factors responsible for regiospecificity of nucleophilic addition to organometallic cations containing polyene ligands.

We have arrived at three simple rules for predicting the *kinetically* controlled products of such additions. The rules depend on the classification of coordinated polyenes as *odd* or *even* according to their hapto number and as *closed* or *open* according to whether they are cyclically conjugated (e.g. $\eta^6\text{-}C_6H_6$) or not (e.g. $\eta^6\text{-}C_7H_8$). The rules apply to 18-electron cations and should be applied sequentially. They are:-

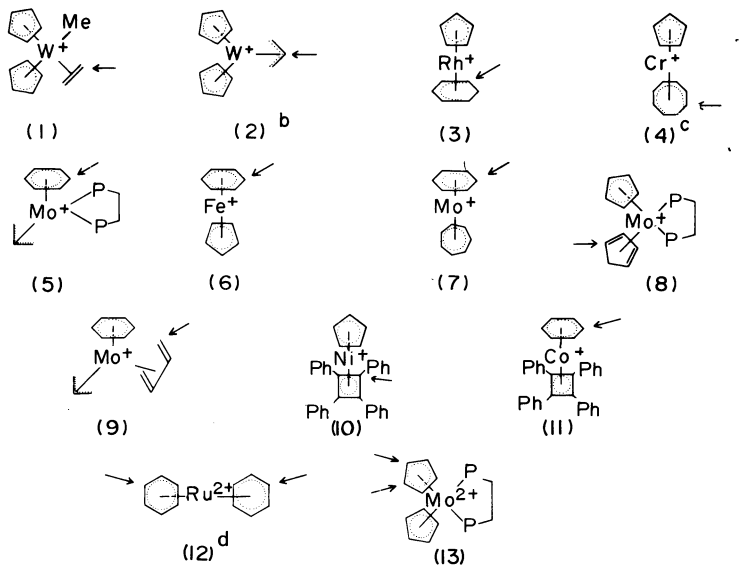
Rule 1. Nucleophilic attack occurs preferentially at *even* coordinated polyenes which have no unpaired electrons in the highest occupied molecular orbitals.

Rule 2. Nucleophilic addition to *open* polyenes is preferred to addition to *closed* polyenes.

Rule 3. For *even open* polyenes, nucleophilic attack at the terminal carbon is always preferred; for *odd open* polyenes, attack at the terminal carbon occurs only if the transition metal centre acts as a strongly electron-withdrawing group.

The Table 2 illustrates the site of nucleophilic attack in representative 18-electron cations, which do not contain carbonyl ligands. In all cases, the product observed is that predicted by the above rules. Example (9) illustrates the need to apply the rules sequentially. The rules also account for the very different products obtained from the successive addition of 2 moles of nucleophiles to the di-cations (12) and (13).

TABLE 2. Regioselectivity of Nucleophilic Attack on Organotransition metal cations containing polyene ligands.[a]



a). P⌒P is 1,2-bis(diphenylphosphino)ethane. The arrows indicate the positions of attachment of the nucleophiles in the product.

b). In contrast, nucleophilic attack to the relatively electron poor cation $Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CO)(NO)$ (Ref. 24) occurs at the terminal allylic carbon atom.

c). This example demonstrates that the rules may also apply to $17e^-$ systems.

d). The indicated positions are for Ph^- addition, which may be presumed to be kinetically controlled. However, addition of H^- gives both $[Ru(\eta\text{-}C_6H_7)_2]$ and $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)]$. The latter is presumably the thermodynamically most stable product, which arises from the former by intramolecular hydrogen migration.

These rules also apply to polyene-transition metal cations which contain carbonyl ligands. However, the position is more complicated since nucleophilic addition may occur both on the polyene ring or to the carbonyl ligand. When the addition is likely to be irreversible (i.e. is kinetically controlled), the rules apply well. Nucleophiles which normally add irreversibly include alkyl and aryl anions. Nucleophiles such as NH_3, RNH_2, NCS, NCO, N_3 and OMe, may add reversibly, in which case the products may reflect thermodynamic control. A detailed discussion of these rules will be presented elsewhere (Ref. 24).

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