

## NEW DEVELOPMENTS IN THE ORGANOMETALLIC CHEMISTRY OF THE GROUP IV-VII TRANSITION METALS

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**Abstract-** The homogeneous activation of carbon-hydrogen bonds by tungstenocene and the observation of reversible 1,2-hydrogen shifts in tungstenocene derivatives has led to a widening study of tungstenocene-related chemistry. Many new compounds are described which were designed as tungstenocene precursor analogues and their ability to undergo thermally or photochemically induced C-H activation has been explored. Simple  $d^0$  titanium-alkyls are described in which C-H groups of the alkyl ligand form covalent, three-centered two-electron Ti-H-C bonds. The activation of ethane is described for the first time. Arene-alkylidene-rhenium derivatives are formed and it appears that the reaction is general for many alkanes and  $sp^3$   $CH_2$  groups.

### INTRODUCTION

The chemistry of a number of apparently diverse organometallic compounds will be described. There has been a constant theme underlying each of these studies which has been to work towards an understanding of and to exemplify aspects concerning the activation of carbon-hydrogen bonds by transition metal compounds under homogeneous conditions.

Two initial observations were largely responsible for the direction of the subsequent research. The first of these was the discovery that tungstenocene, made *in situ* either photochemically or thermally, would insert into saturated carbon-hydrogen bonds of many systems including those in tetramethylsilane (Ref. 1 & 2). The second observation was that which led to the postulate that reversible 1,2-hydrogen shifts ( $\alpha$ -elimination) in transition-alkyls was a general and fundamental reaction (Ref 3 & 4). This paper will outline our researches as a consequence of these observations, under the following headings.

#### I. Tungstenocene analogue chemistry

- (a) H/D exchange in  $sp^3$  C-H bonds catalysed by mono-cyclopentadienylmolybdenum derivatives.
- (b) Bent bis-arene derivatives of Zr, Hf and Nb.
- (c) Tertiary phosphine derivatives of Mo, W and Ta.

#### II. Transition metal-hydrogen-carbon Bonds.

- (a) Agostic hydrogens in some titanium alkyls.
- (b) Some *n*-cycloheptatrienyltitanium chemistry

#### III. A general method for the activation of alkanes by rhenium systems.

### I. TUNGSTENOCENE ANALOGUE CHEMISTRY

The sixteen-electron molecule tungstenocene,  $W(\eta-C_5H_5)_2$ , is presently the most fully characterised example of a compound which will insert into many  $sp^2$  and  $sp^3$  carbon-hydrogen bonds. Detailed studies of tungstenocene isolated in a matrix have shown that it has a parallel ring, ferrocene, structure, and a triplet ground state (Ref. 5). The photoelectron spectra of number of tungstenocene derivatives have been determined (Ref. 6) and from this data it may be inferred that the first ionisation potential of tungstenocene will lie near 5.0eV and thus may be classified as having a high-energy metal centre. Space-filling models confirm that tungstenocene is sterically uncrowded as is witnessed by the existence of compounds such as the bis-mesityl derivative  $[W(\eta-C_5H_5)_2(CH_2-3,5-Me_2C_6H_3)_2]$ . Examples of methods of generation and carbon-hydrogen activation reactions of tungstenocene are shown in Fig. 1. Some reactions lead to complex mixtures, e.g. with toluene, whereas *p*-xylene gives only the bis-alkyl derivative. It has not been possible to obtain evidence that tungstenocene will insert into the C-H bonds of fully saturated hydrocarbons, e.g. cyclohexane

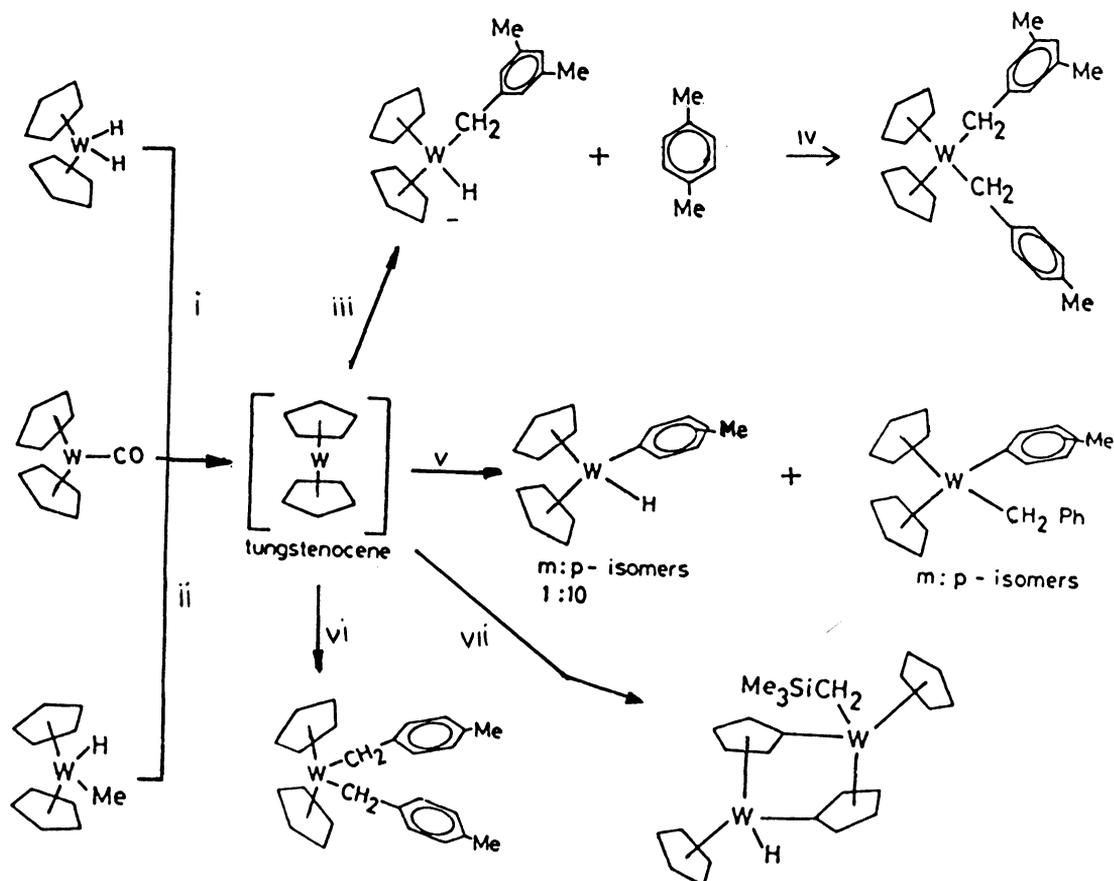


Fig 1. (i) Photolysis. (ii) Thermolysis. (iii) Thermolysis in mesitylene. (iv) Photolysis in p-xylene. (v) Photolysis in toluene. (vi) Photolysis in p-xylene. (vii) Photolysis in tetramethylsilane (cis-isomer also formed).

or neopentane. This is probably because the expected alkyl-hydride products are either photochemically or thermally unstable under the reaction conditions. In pursuit of systems which would react with alkanes either to form isolable alkyl derived products, or, which would catalyse H/D exchange and thereby show that C-H activation has occurred, we set out to synthesise compounds which would be precursors to tungstenocene analogues. Examples of compounds which can broadly speaking be described as tungstenocene precursor analogues are shown in Fig 2.

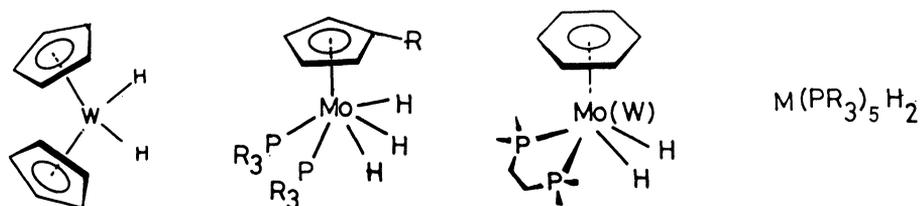


Fig. 2. Examples of compounds which can be regarded as analogues of tungstenocenedihydride. R=Alkyl.

In short, we wished to synthesise high-energy, 18-electron compounds which would undergo thermal or photoinduced loss of a 2e-ligand system leaving a sterically uncrowded and electronically unsaturated, 16-electron metal centre which also had a low lying LUMO. The photoinduced elimination of dihydrogen from a transition metal centre, which was first observed for  $W(\eta-C_5H_5)_2H_2$  (Ref.7), provides a quite reliable method of creating a 16-electron centre so that it was decided to make compounds fitting the above criteria which also had two, or more, cis-oriented dihydrogen ligands. As described below this approach has had mixed success but support for the correctness of the general strategy arises from the exciting

observation that the pentamethylcyclopentadienyl-rhodium and -iridium systems have been shown to undergo photoinduced activation of alkanes giving alkyl-hydride derivatives, see Fig 3. (Ref.8,9 & 10).

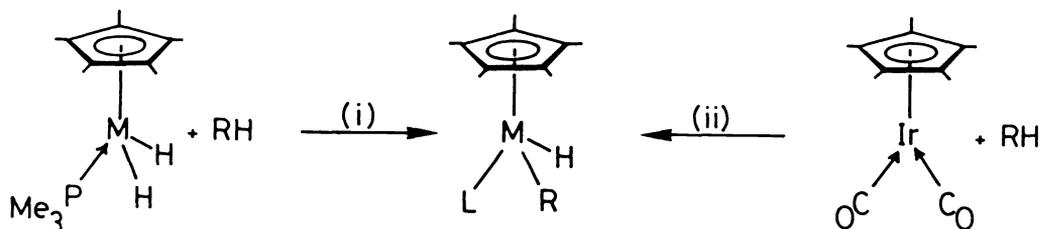


Fig. 3. Alkane activation reactions. (i) where RH = cyclohexane, neopentane. (ii) R= cyclohexane, methane.

(a) H/D exchange induced by mono-cyclopentadienylmolybdenum systems.

Our initial choices for tungstenocene precursor analogues were the compounds  $M(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)_2\text{H}_3$ ,  $M = \text{Mo}$  or  $\text{W}$ . In these compounds the  $\eta\text{-C}_5\text{H}_5$  ligand has been replaced by the groups  $(\text{PR}_3)_2\text{H}$  which also donates five electrons to metal centre and the donor-acceptor properties of tertiary alkylphosphines ensure that the metal centre be electron rich. The compound  $\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})\text{H}_3$  (1) has been found to be an active catalyst for the photoinduced H/D exchange of C-H bonds in a wide variety of substrates (Ref. 11). The proposed mechanism is shown in Equn. 1 & 2 and a selection of substrate reactions is given in Table 1.



where  $[\text{Mo}] = \text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})$

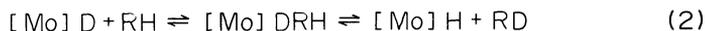


Table 1. H/D Exchange reactions catalysed by  $\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{P}_2)\text{H}_3^{\text{a}}$

Substrate	R=H $\text{P}_2 = \text{dmpe}$	R=Pr <sup>i</sup> $\text{P}_2 = 2\text{PMe}_3$	R=Pr <sup>i</sup> $\text{dprpe}^{\text{b}}$
Benzene	All	All	All
Anthracene	--	All	--
Benz[ a ]anthracene	--	All	--
Toluene	All	Ar	Ar
Mesitylene	Methyl	None	None
Ethylbenzene	Ar	--	--
Hexamethylbenzene	None	--	--
Anisole	All	--	All
Chlorobenzene	--	All	--
Cyclohexane	None	None	None
Dimethylether	All	--	--
Diethylether	None	--	--
1,2-DME	Methyl	--	--
Ethylacetate	All	--	--
Tetramethylsilane	None	--	--
Bis-toluenetungsten	All	--	--

<sup>a</sup> The molybdenum compounds (ca. 20mg) in  $\text{C}_6\text{D}_6$  (ca. 1 cm<sup>3</sup>) and the substrate (ca. 50 mg) were irradiated (500W medium pressure Hg lamp). The <sup>1</sup>H nmr showed evidence for H/D exchange which was confirmed by the mass spectroscopy. Rates of exchange varied from minutes to days (Ref. 11). Ar = only aromatic hydrogens exchanged. Methyl= only methyl hydrogens exchanged. All = all hydrogens undergo exchange. -- = no experiment made. <sup>b</sup> Pr<sup>i</sup><sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPr<sup>i</sup><sub>2</sub>.

The low solubility of (1) precluded exploration of alkane activation using cyclohexane as the solvent. It was decided to attempt to increase the solubility of the system by attaching an alkyl side-chain to the cyclopentadienyl ring. After unsuccessfully pursuing more obvious synthetic routes towards this objective a synthesis of iso-propylcyclopentadienyl analogues was achieved via the dimethylfulvene derivative (2), as shown in Fig. 4 (Ref. 12).

The compounds  $\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\text{PR}_3)_2\text{H}_2$  (3) were less successful than (1) in activating C-H bonds (see Table 1) and this we attribute to increase steric problems due to the iso-propyl group and also to the ability of this group to undergo intramolecular C-H addition. The latter is indicated by the rapid exchange of all the hydrogens of the  $\text{Pr}^i$  groups when (3) were photolysed in deuteriobenzene.

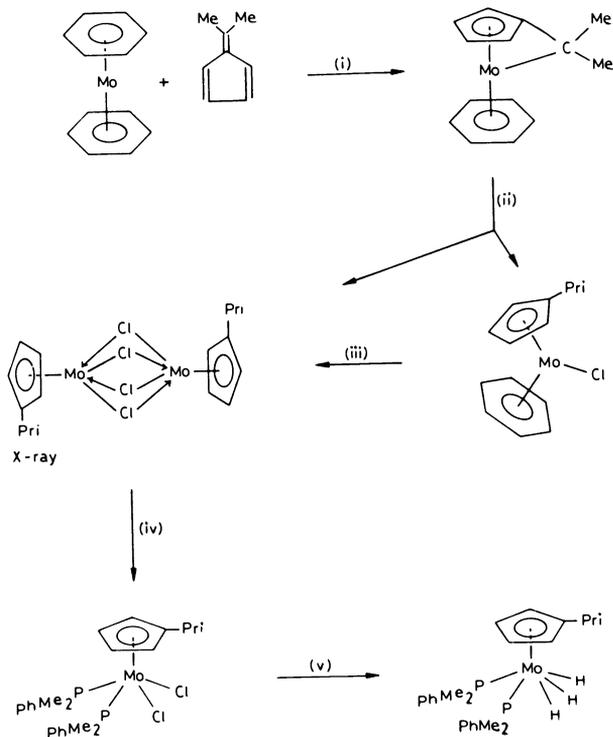


Fig. 4. (i) At r.t. for 4 d. (ii) HCl gas for 1 min. at r.t. (iii) HCl gas for 10 min. (iv)  $\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}$ . (v)  $\text{LiAlH}_4$  in toluene.

Curiously we have so far been unable to prepare any tungsten analogues of the molybdenum compounds (1) and (4). Likely precursors such as (A) and (B) have been isolated (Fig. 5) (Ref. 13) but further attempts to generate cyclopentadienyl-tungsten-trihydrido derivatives led to intractable products.

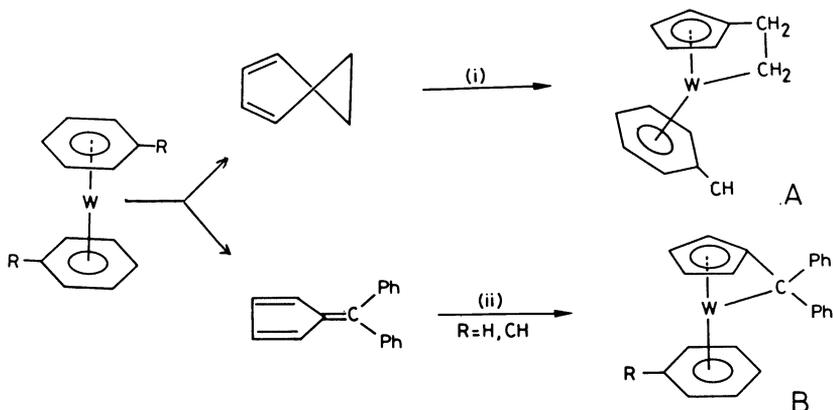


Fig 5. (i) Toluene at  $80^\circ\text{C}$  for 7 days, 25%. (ii) Toluene at  $80^\circ\text{C}$  for 2 week, 20%.

We have prepared mono-cyclopentadienyl-mono-hydrido derivatives of the class  $M(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_3\text{H}$ ,  $M=\text{Mo}$  or  $\text{W}$ , (Fig. 6 & 7) but preliminary studies suggest that they are only weakly active towards intermolecular C-H activation (Ref.14 & 15).

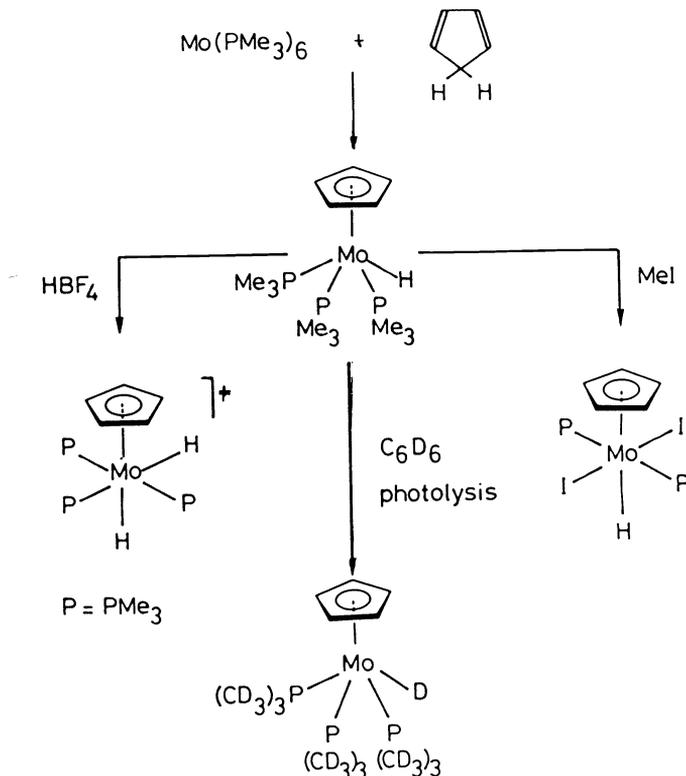


Fig. 6.  $\eta\text{-Cyclopentadienyl}$  tertiary phosphine molybdenum derivatives.

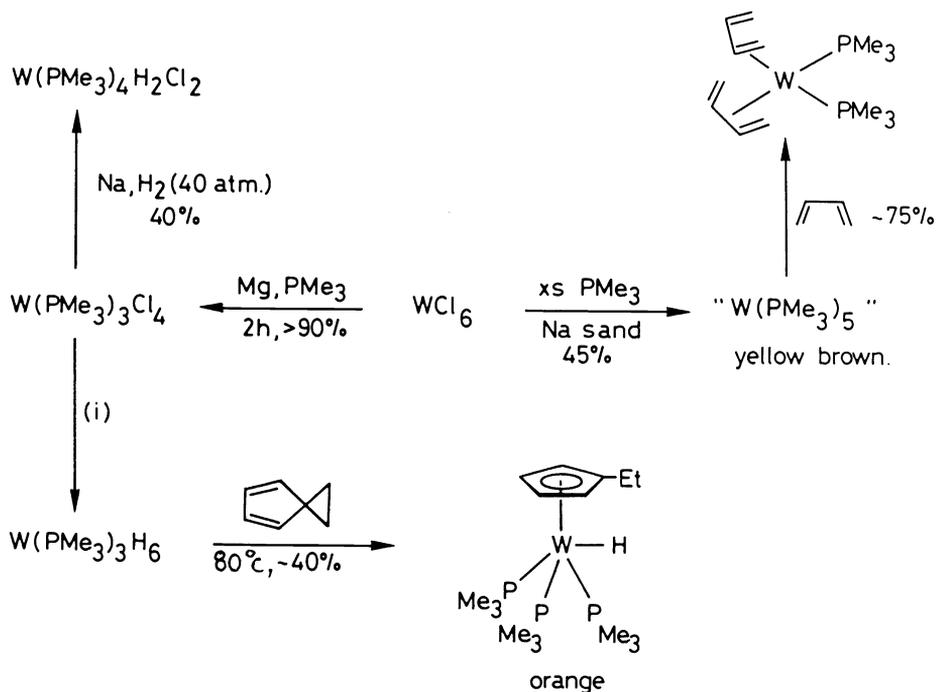


Fig. 7. Synthetic pathways in trimethylphosphine tungsten chemistry. (i)  $\text{LiAlH}_4$ , then hydrolysis using  $\text{MeOH}$  at  $-80^\circ\text{C}$ .

(b) Bent bis- $\eta$ -arene derivatives of Zr, Hf and Nb.

The hypothetical compounds  $M(\eta\text{-arene})_2H_2$ ,  $M=Zr$  or  $Hf$ , can be regarded as tungstenocene precursor analogues. We have not been able to prepare these compounds but have been able to isolate closely related derivatives (see Fig. 8). It was hoped that reaction between hafnium atoms and benzene or toluene would lead *via* intermediate bis-arenehafnium to the compounds  $Hf(\eta\text{-arene})_2(\text{aryl})H$ . In the event, we were unable to isolate stable compounds from the initial deep red and thermally unstable reaction mixtures (Ref. 16 & 17). However, we were able to trap out bis-arene-hafnium and -zirconium derivatives as the trimethylphosphine adducts  $M(\eta\text{-toluene})_2PMe_3$  (Fig. 8) and this observation, coupled with our finding the activation of C-H bonds of toluene, ethane and other hydrocarbons by arene-rhenium systems, which is described below, suggests that the anticipated reactions might have occurred. The iso-electronic niobium cation  $[Nb(\eta\text{-benzene})_2PMe_3]^+$  has also been prepared (Fig. 8).

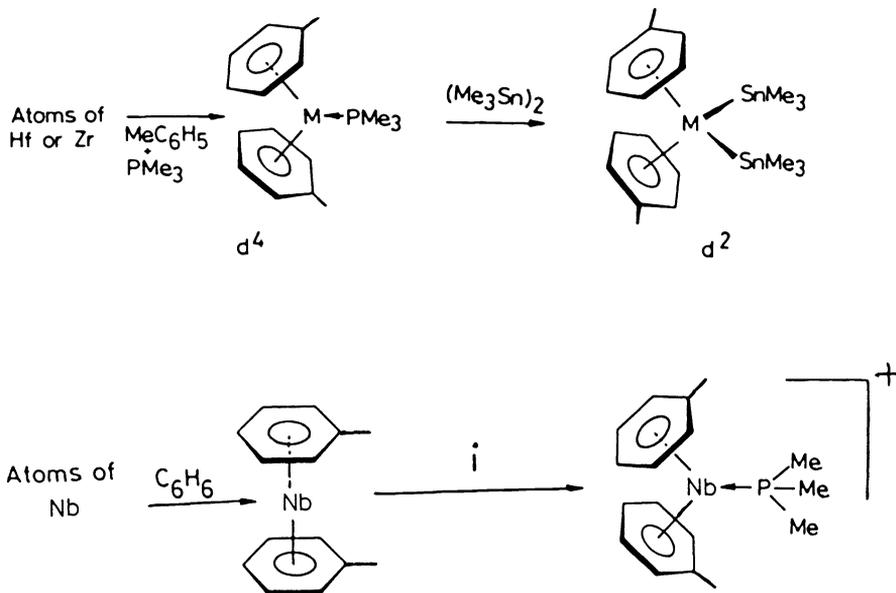


Fig. 8. Synthesis of bis-arene derivatives of hafnium, zirconium and niobium. (i)  $PMe_3$  and  $AgBF_4$  in toluene, (Ref. 18).

(c) Tertiary phosphine derivatives of molybdenum, tungsten and tantalum.

In the context of our approach, 18-electron compounds  $M(PR_3)_yH_y$ ,  $y > 2$ , are tungstenocene precursor analogues. The Fig. 9 summarises some of the new compounds or new routes to known compounds. The key synthetic principle is the absence of the common solvents and trimethylphosphine is used as a reactive solvent allowing many of the syntheses to take place in a one-pot reaction (Ref. 19 & 20). Much of this chemistry is quite recent and we have made relatively few studies of C-H activation by the new compounds. In a preliminary study of the photochemistry of  $W(PMe_3)_4H_2$ , we have found that photolysis in  $C_6H_6$  causes formation *inter alia* of  $W(PMe_3)_3H_2$  (Ref. 21).

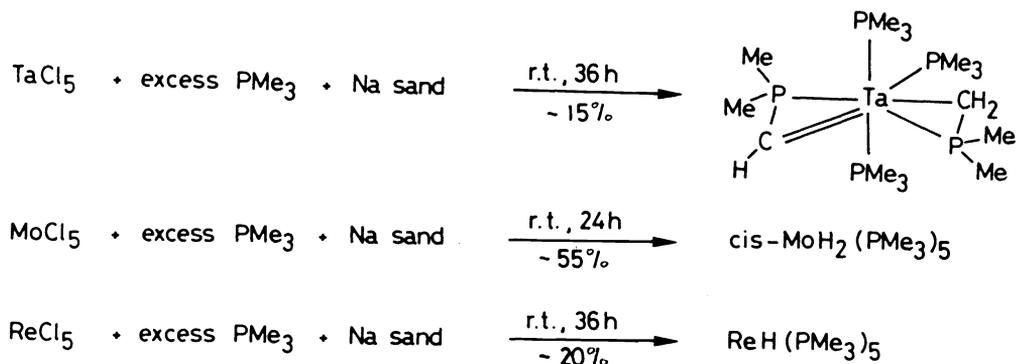
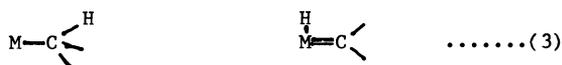


Fig. 9. Syntheses using trimethylphosphine as a reactive solvent.

## II. TRANSITION METAL-HYDROGEN-CARBON BONDS

There is now substantial evidence that the 1,2-hydrogen shift equilibria shown in Equn 1 can occur (Ref. 3 & 4):-



Where [M] has  $d^n, n > 2$  and is a 16-electron centre, or fewer. This reaction can be described as the activation of the C-H bond since it involves the oxidative-addition of the C-H bond to the metal centre. A study of the kinetics of the thermolysis of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CH}_2\text{PR}_3]\text{H}^+$  giving  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{MePR}_3]^+$  shows that reaction to be first order and the rate to be independent of added phosphine. The magnitudes of the parameters (Fig.10) are consistent with the rate determining step being the homolytic breaking of the C-P bond. The data does not distinguish between pathway 1 or 2, providing that the rate of attainment of the equilibrium between A and B is fast compared to  $k_A$  (Ref. 22).

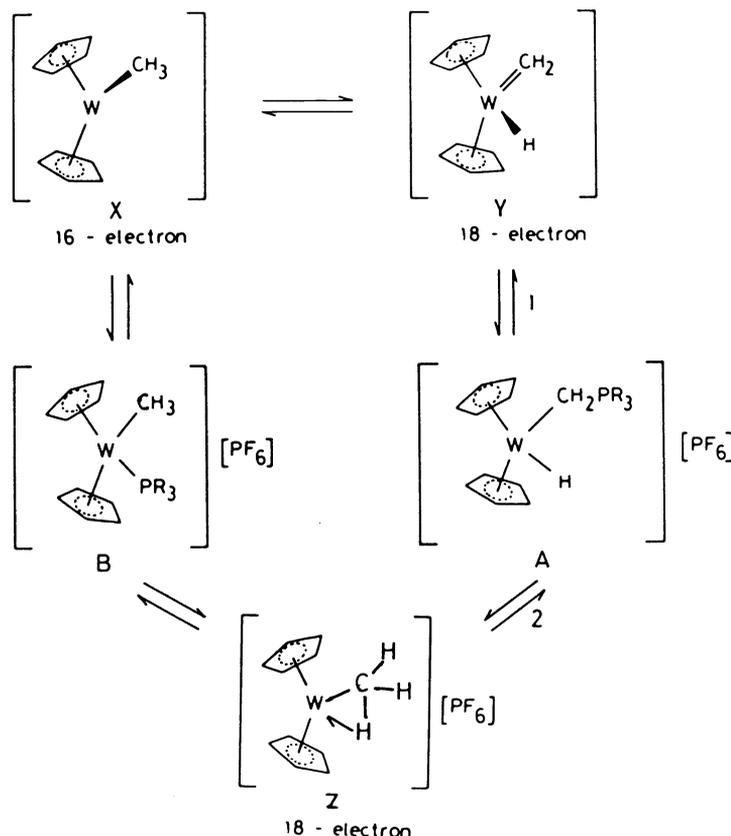


Fig.10 The rate of conversion of A to B in acetone, monitored by  $^1\text{H}$  n.m.r spectroscopy, was  $k = 1.4 \times 10^{-6} \text{ sec}^{-1}$ .  $\Delta E^\ddagger = 145 \text{ kJmol}^{-1}$ ,  $\Delta H^\ddagger = 142 \text{ kJmol}^{-1}$ ,  $\Delta S^\ddagger = +62 \text{ Jmol}^{-1} \text{ degK}^{-1}$ .  $k_D/k_H = 1.23$  at  $65.2^\circ\text{C}$ .

As noted, the equilibrium in Equn. 3 requires that the metal centre had  $d^n$  electrons, where  $n > 2$ . We wondered whether in the case that  $n=0$  the C-H hydrogen would distort towards the metal centre and to examine this possibility we prepared the compounds  $\text{TiRCl}_3(\text{dmpe})$ ,  $\text{R}=\text{Me}$  (C) or  $\text{Et}$  (D) and determined their crystal structures. These compounds were selected since they are  $d^0$ , the titanium has a relatively low atomic number so that nearby hydrogens would be more readily detected and the tertiary phosphine ligand imparts low symmetry which reduces the possibility of molecular disorder in the crystal and assists in thermal stabilisation of the compound (Ref. 23 & 24).

The structures of (C) and (D) with important dimensions (Fig.11)(Ref. 23 & 24) show that there is indeed a Ti-H-C linkage, akin to the covalent two-electron, three centred bonds in their familiar B-H-B systems. The term agostic has been proposed to describe the M-H-C bond (Ref.25). It is now clear that M-H-C bonds can occur widely in organometallic chemistry, as discussed in a recent review (Ref.25) and some typical examples are given in Fig.12.

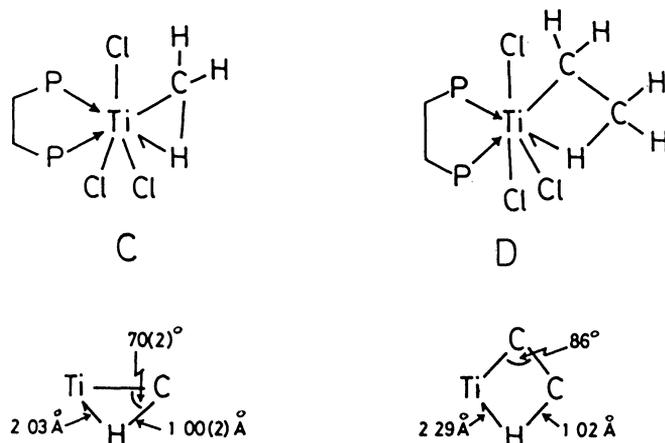


Fig.11. The crystal structures of  $\text{Ti}(\text{dmpe})\text{Cl}_3\text{R}$ ,  $\text{R}=\text{Me}$  or  $\text{Et}$  showing the marked distortions of the alkyl groups and the presence of  $\text{Ti}-\mu\text{-H}-\text{C}$  bonds.

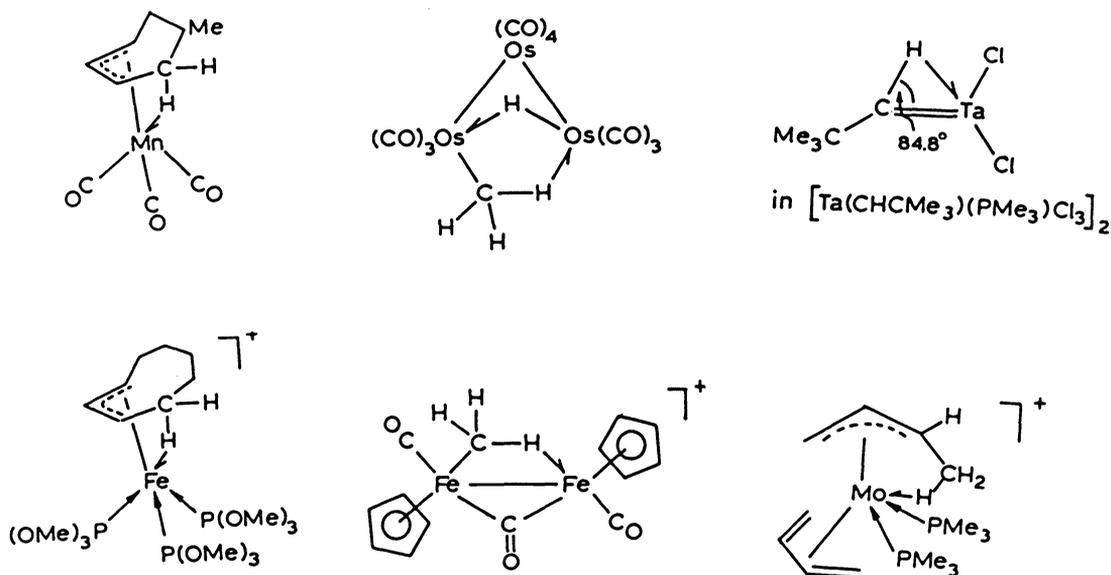


Fig.12. A selection of compounds which have covalent, three-centred, two-electron  $\text{C}-\text{H}-\text{M}$  bonds (Ref.25).

The  $\text{C}-\text{H}-\text{M}$  bonds can be regarded as ground state representations for what in many  $\text{C}-\text{H}$  activation process will be the transition state, e.g. for the  $\text{Ti}$ -ethyl compound (D) the "stabilised transition state" for  $\beta$ -elimination. It is important to realise that the agostic  $\text{C}-\text{H}-\text{M}$  structure may be the ground state structure for many equilibria, see Fig. 13.

Previously, it was proposed that the agostic species (column 2) only occurred as transition states in the formation of the hydride derivatives (column 3) from the 16-electron systems (column 1). However it is now clear that the agostic structures (column 2) can be the ground state structures. In the agostic structures of metal-alkyls the alkyl ligand acts as a bidentate ligand to the metal centre and this clearly has implications in the stereochemical control of the reactions of transition metal-alkyl compounds.

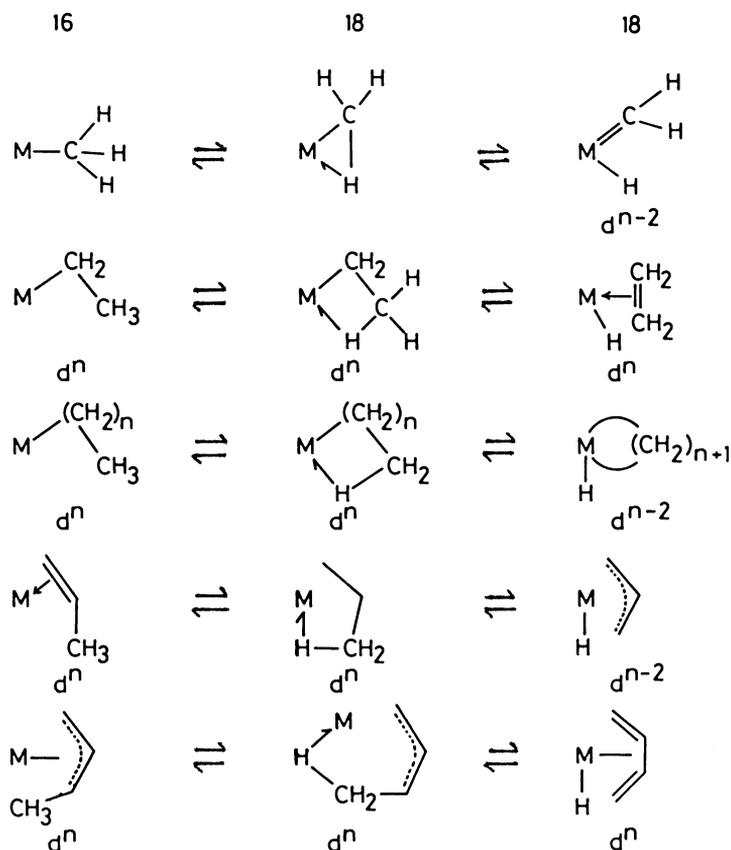


Fig.13 For any 18-electron M-olefin-hydride or related  $\eta$ -unsaturated -hydride there is the possibility for the equilibria shown. The agostic structures (column 2) may be the ground state structure this may be readily detected by  $^1\text{H}$  n.m.r. spectroscopy (Ref.25).

(b) Some  $\eta$ -cycloheptatrienyltitanium chemistry

It seems probable that the minimum requirement for formation of an agostic C-H-M bond is that the metal centre should have a low-lying LUMO coupled with appropriate steric unsaturation. As part of a separate study we have developed the chemistry of the mono-cycloheptatrienyltitanium system, as shown in Fig. 14.

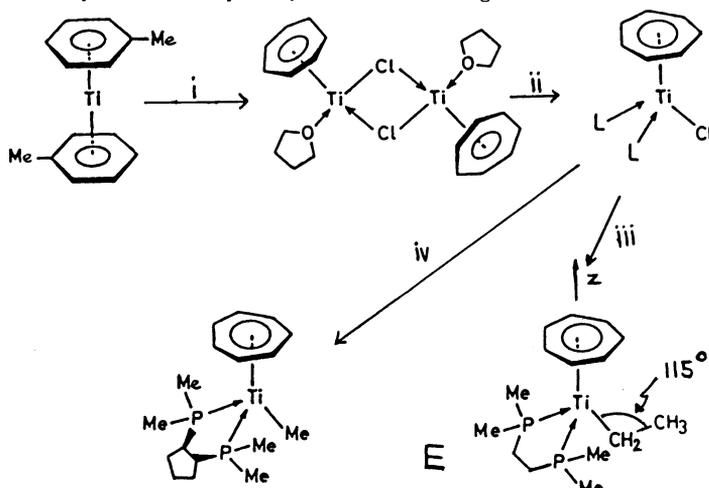


Fig. 14. New synthetic routes to  $\eta$ -cycloheptatrienyl-titanium derivatives (Ref.26) (i) Cycloheptatriene,  $[\text{EtAlCl}_2]_2$  in thf at r.t. (ii)  $\text{L}_2 = (\text{PMe}_3)_2, \text{dmpe}, \text{dppe}, 1,2-(\text{Me}_2\text{P})_2\text{C}_5\text{H}_8$ , or  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ . (iii)  $\text{EtMgBr}$  in  $\text{Et}_2\text{O}$ . (iv)  $\text{MeMgBr}$  in  $\text{Et}_2\text{O}$ .

The thermally stable titanium-ethyl compound  $Ti(\eta-C_7H_7(dmpe)Et)$ , (**E**), is a 16-electron compound and so is a possible candidate for the presence of an agostic ethyl group. However, the crystal structure shows that the Ti-C-C angle of the Ti-ethyl moiety is normal ( $115^\circ$ ) and the Ti-C<sub>b</sub> distance (3.170(6)Å) is too great for the formation of a Ti-H-C<sub>b</sub> bond. The electronic structure of molecules such as (**E**) is generally well understood and it can be argued with confidence that the LUMO of (**E**) is an a<sub>1</sub> orbital which is located along the metal-C<sub>7</sub>-ring axis and pointing mainly towards the C<sub>7</sub>-ring. In this case the LUMO would not be suitably directed towards the CH<sub>3</sub> group for formation of an agostic interaction.

In contrast the compound  $Co(\eta-C_5H_5)(\eta-C_2H_4)(\eta-CH_2CH_2-H)$ , (**F**) has an agostic ethyl group (Fig. 15), and this is in accord with the anticipated location of the LUMO that would be present in the anagostic compound  $Co(\eta-C_5H_5)(\eta-C_2H_4)(CH_2CH_3)$ .

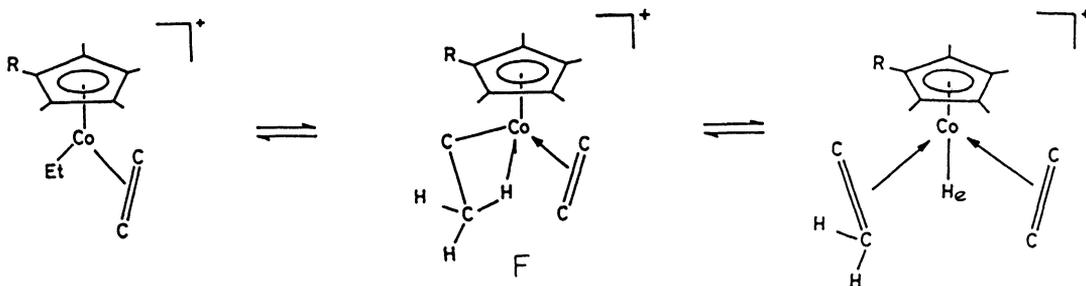


Fig. 15. The equilibria are shown by variable temperature  $^1H$  nmr spectroscopy: the spectra show the central agostic structure to be the most stable at  $-60^\circ C$ .

### III.A GENERAL METHOD FOR THE ACTIVATION OF ALKANES BY INVOLVING ARENE-RHENIUM COMPOUNDS

In section II we described our studies on tungstenocene precursor analogues in the search for systems which would activate saturated hydrocarbons. Several homogeneous transition metal systems have been described which will react with saturated hydrocarbons under mild conditions (Ref. 28). More recent examples include, iridiumtertiaryphosphine derivatives (Ref.29), rheniumtertiaryphosphinehydrido compounds (Ref.30), rhodium- and iridium-pentamethylcyclopentadienyl compounds (Ref. 8,9 & 10). Activation of methane by  $Lu(\eta-C_5Me_5)_2Me$  (Ref.31) and in matrices by atoms or clusters of metals such as Al, Fe, Co, Ag, Au and Zn (Ref. 32) and many years ago by solutions of Pt(II) salts (Ref. 33) has also been described.

In a continuing search for alkane activating systems we set out to prepare arene-rhenium compounds, e.g.  $Re(\eta\text{-arene})(PR_3)_3H_3$  and proposed to employ a metal atom route. The co-condensation of rhenium atoms with the arenes, toluene, p-xylene and mesitylene led to the compounds (**F**), (**G**) and (**H**) shown in Fig.16. Ethylbenzene reacts giving two products derived from attack on the CH<sub>2</sub> or the CH<sub>3</sub> of the ethyl group.

The reaction between rhenium atoms and benzene alone gave no tractable products. However when rhenium atoms were added to a mixture of benzene and trimethylphosphine then good yields were obtained of the compound  $[Re(\eta-C_6H_6)(PMe_3)_2]_2$ , (**I**). We imagined that the rhenium atoms reacted with the arene forming a highly reactive rhenium-arene species which was then trapped either by reacting further with trimethylphosphine, or, for the compounds (**F-H**), with the methyl groups of the arene. Therefore, we thought to react rhenium with benzene in the presence of other added sources on methyl groups, including those of saturated hydrocarbons. As is shown in Fig. 15 this approach has been successful and we have been able to activate ethane and 2-methylpropane and isolate the compounds (**J-K**) in up to 20% yields (Ref.34)

The rhenium- $\mu$ -alkylidene dimers (**F-K**) are all highly air-sensitive, volatile, orange-yellow crystals: they may be sublimed at  $80-110^\circ C, 10^{-4}$  torr. The formation of the dimers involves the removal of two hydrogens from a CH<sub>3</sub> or CH<sub>2</sub> group of the alkane or alkyl groups and the reaction is a remarkable advertisement for the exciting and unpredictable nature of transition metal atoms as synthetic reagents. The alkane activation occurs in the presence of a very large excess of benzene, the ligands are derived from two separate components in the matrix and the product is a binuclear compound. Further, after what must be a very complex and multi-step mechanism the yields are typically around 20% (based on the quantity of rhenium arriving as atoms on the reaction surface). The molten rhenium in the furnace acts as a black-body source ( $3,200^\circ C$ ) and we estimate that the radiation emitted is rather greater than from a 500 watt tungsten lamp. It is, therefore, possible that some stage(s) of the reaction are photoinduced.

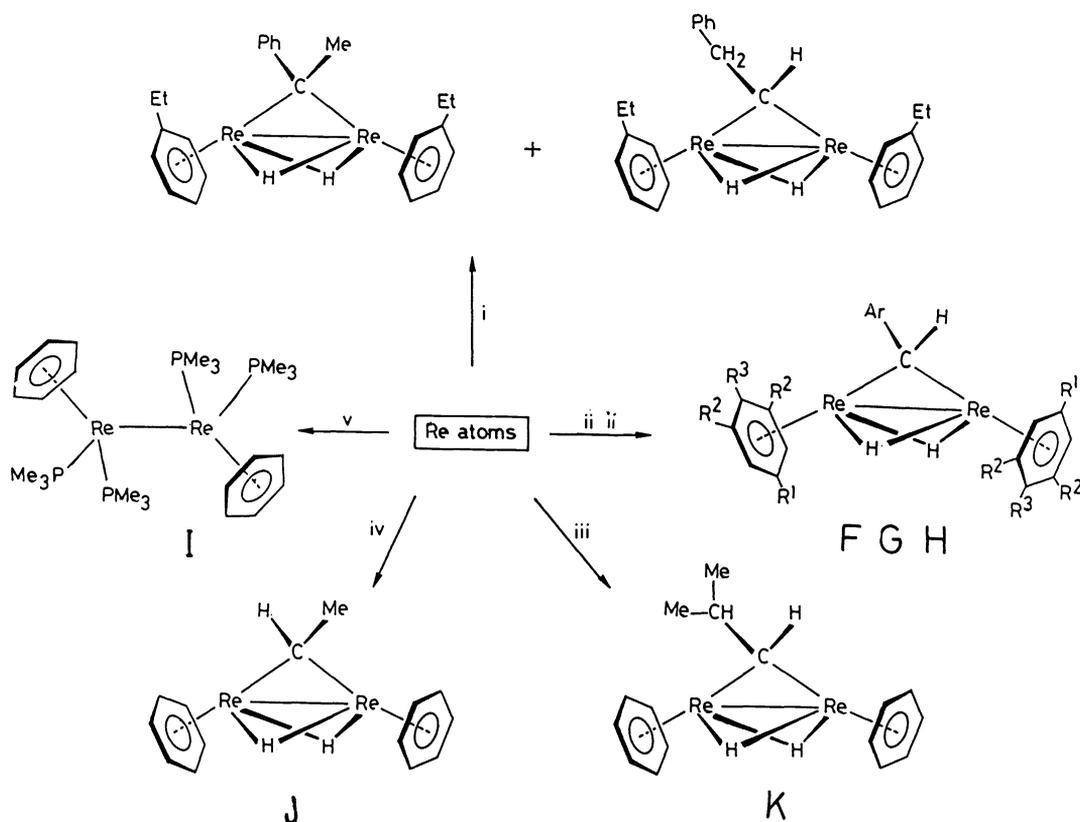


Fig.16. Rhenium atoms (ca 1-3 g.), generated from a positive-hearth electron gun furnace supplied by G.V.Planer Ltd., were co-condensed with the indicated substrates. i. Ethylbenzene gives a ca. 1:1 mixture, in overall 20% yield. ii.  $R^1, R^3 = Me, R^2, R = H; Ar = Ph$  (F);  $R^1, R^2 = Me, R^3 = H; Ar = 4-Me-C_6H_4$  (G);  $R^1, R^2 = Me, R^3 = H; Ar = 3,5-Me_2C_6H_3$  (H). iii. Me<sub>3</sub>CH, 20%. iv. Ethane, 12%. v. Benzene + PMe<sub>3</sub>, 40%.

## CONCLUSION

We have described systems which will activate C-H bonds both in fully saturated hydrocarbons and in functionalised alkyl derivatives. We have provided examples where transition metal alkyls form M-H-C covalent bonds. The activation of methane by Watson's Lu( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Me system apparently involves only a d<sup>0</sup> system, whereas all the other C-H activating systems have d<sup>n</sup>-electrons n>2.

We can speculate that the activation of a C-H bond by a transition metal centre proceeds via approach of the C-H bond to the mandatory LUMO on the metal centre with initial formation of a M-H-C bond. The formation of intermolecular M-H-C bonding between the Cr(CO)<sub>5</sub> moiety and methane has been suggested from matrix isolation studies by Perutz and Turner. (Ref.35) If the LUMO-HOMO gap is small then orbital mixing leading to oxidative-addition of the C-H bond can follow giving a metal-alkyl-hydride adduct. Tungstenocene has a triplet state and molecules such as Ir( $\eta$ -C<sub>5</sub>H<sub>5</sub>)PR<sub>3</sub> and Fe(PR<sub>3</sub>)<sub>4</sub> would also be expected to have a triplet state. If the adduct is to be isolable then it must be photochemically stable in those reactions where the transition metal centre is formed by a photochemical process. Since it is generally the case that third row transition metals form more thermally stable hydrides and alkyl derivatives than their lighter congeners it would normally be expected that for a particular ligand environment e.g. M( $\eta$ -C<sub>5</sub>R<sub>5</sub>)(PR<sub>3</sub>)<sub>x</sub> then the stability to isolation of the C-H addition product would follow the order first row<second row<third row. A high energy (electron-rich) metal centre would clearly encourage the oxidative addition of a C-H bond as a means to lower the electron density at the metal.

Finally, a further goal will be to achieve the selective, functionalisation of C-H systems catalysed by homogeneous transition metal compounds.

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