

The activation of carbon-hydrogen bonds

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Abstract - The general properties required for a transition metal compound to react with carbon-hydrogen bonds, and especially those of alkanes, are discussed in the light of current examples.

This lecture summarises recent advances in the field and examines some of the current ideas governing the search for homogeneous transition metal catalysts, which it is hoped will lead to the useful and specific functionalisation of carbon-hydrogen bonds.

The carbon-hydrogen bonds which are the primary target for this research are those for which there are no known routes for their functionalization. Paraffins constitute a major group as do the alkyl substituents in many organic compounds. Overall, new methods for the functionalisation of carbon-hydrogen bonds, aliphatic or aromatic, are of general interest. Here we are not concerned with the well-known, non-selective reactions of paraffins, such as chlorination (ref. 1), oxidation, (ref. 2a,b,c), the super-acid catalysed addition of alkanes to olefins (ref. 2d,e,f), nor with the important hydroxylation reactions, catalysed by P450 enzymes (ref. 3), with C-H activation by octaethylporphyrin and related complexes (ref. 4a), or with selective oxidative-coupling reactions such as the recently observed formation of ethylene and ethane from CH₄ and O₂ catalysed by lithium-doped MgO (ref. 4b).

Here we are concerned with those reactions in which the activation step proceeds by the oxidative-addition of a carbon-hydrogen bond to a transition metal centre, followed by subsequent reactions leading to a functionalised product, as shown in fig. 1.

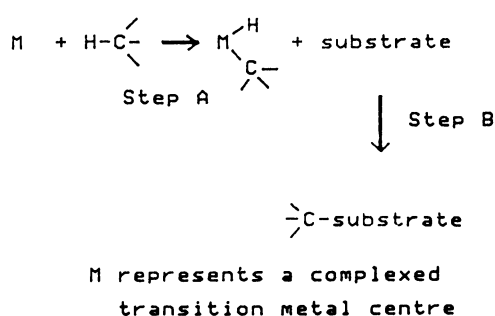


Fig. 1. General inter-molecular alkane activation reaction.

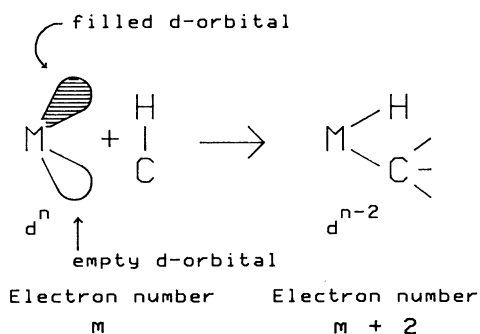


Fig. 2. A symbolic illustration of the two d-electrons and two d-orbitals required for oxidative-addition of a C-H bond to a metal centre M. Note that the reaction results in an increase of electron number of M by two.

GENERAL CONSIDERATIONS OF MECHANISM

For a normal non-radical pathway, there appear to be certain minimal requirements for a transition metal centre which will undergo an oxidative-addition reaction with a C-H bond to form a product intermediate containing two new bonds, i.e. a H-M-C moiety. These requirements are:

The presence on the metal of two or more valency d-electrons, i.e. for dⁿ n must be 2 or greater, and also there must be two available metal orbitals, of essentially d-character. These requirements are illustrated in fig. 2.

If the H-M-C intermediate is an 18-electron system, as will often be the case, then subsequent functionalisation reaction will normally require formation of a 16-electron intermediate in which the M-C-H system is maintained. This intermediate will then be available for subsequent addition reactions with substrate leading to product formation. A schematic reaction sequence is shown in fig. 3, in which several possible functionalisation reactions are exemplified.

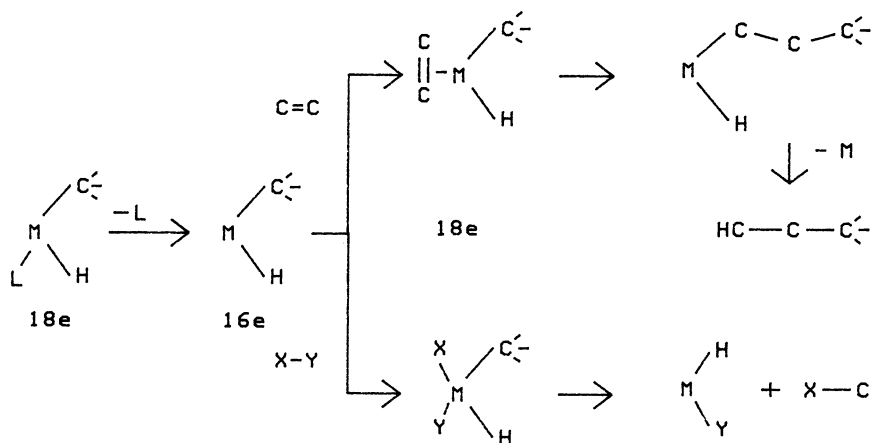


Fig. 3. (i) Addition of an olefin giving, eventually, a new alkane.
(ii) X-Y has many possibilities, for example R-H of an alkane giving R-C, a higher alkane. Such a reaction would be favourable if the resulting dihydrogen intermediate reacted with added olefin forming another alkane.

THERMODYNAMIC CONSIDERATIONS

We first consider Step A (fig. 1), the formation of the H-M-C intermediate. Typically, the carbon-hydrogen bond strengths of simple hydrocarbons decrease in the order aromatic (ca. 110 kcal/mol) > primary (CH_3C) (ca. 98 kcal/mol) > secondary ($\text{C-CH}_2\text{-C}$) (ca. 95 kcal/mol) > tertiary (C-CHR_2) ca. 92 kcal/mol. These substantial C-H bonds strengths require strong

M-H and M-C bonds if the intermediate H-M-C product is to be stable with respect to the reactants. In other words, the 16-electron metal centre must be highly reducing so that the oxidative-addition of the C-H bond is thermodynamically favourable. Metal centres which are highly reducing are often referred to as electron rich (high-energy centres).

For a catalytic reaction, it is not necessary for Step A to have a $-\Delta G$, but of course ΔG must be negative for the overall reaction. There are many possible favourable reactions of C-H bonds which give C-X derivatives. However, the difficulty of achieving specific catalytic C-H functionalisation lies in the choice of substrates and products which will not themselves preferentially react with the metal centre in undesirable ways as discussed below.

TABLE 1 provides some thermodynamic data for the reactions of hydrocarbons (ref. 5)

KINETIC CONSIDERATIONS

Desired selectivity for C-H functionalisation reactions may often require kinetic rather than thermodynamic control. For example, the radical induced chlorination of paraffins proceeds so that the weakest C-H bonds are preferentially chlorinated, giving tertiary and secondary alkyl halides in preference to the more desirable terminal halides.

Jones and Feher have made an elegant study of the well-established preference for metal centres to add to the stronger aromatic C-H bonds rather than the weaker aliphatic C-H bonds (ref. 6). They have shown that kinetic control arises from the greater ability of aromatic molecules to precoordinate to the metal centre (via an η^2 -bond)(ref. 7,8). See fig. 4.

TABLE 1. Gibbs free energy values for hydrocarbon functionalization reactions.

Reaction	Products	ΔG kcal mol ⁻¹
CH ₄ } C ₃ H ₈ } C ₆ H ₆ }	+ Cl ₂ → CH ₃ Cl CH ₃ CH ₂ CH ₂ Cl C ₆ H ₅ Cl	-24.6 -29.4 -30.3
CH ₄ } C ₃ H ₈ } C ₆ H ₆ }	+ $\frac{1}{2}$ O ₂ → CH ₃ OH Pr ⁿ OH C ₆ H ₅ OH	-27.5 -32.9 -39.1
CH ₄ } C ₆ H ₆ }	+ C=C → n-C ₃ H ₈ C ₆ H ₅ CH ₂ CH ₃	- 9.7 -16.1
C ₃ H ₈	+ CO → n-C ₃ H ₇ CHO	+11.0
C ₆ H ₆	+ CO → n-C ₆ H ₅ CHO	+ 9.0
C ₃ H ₈	+ CO + H ₂ → i-C ₃ H ₇ CH ₂ OH	+ 1.0
C ₆ H ₆	+ CO + H ₂ → C ₆ H ₅ CH ₂ OH	+ 0.6
C ₃ H ₆ } c-C ₅ H ₈ } 4c-C ₅ H ₈ }	+ CH ₄ → i-C ₄ H ₁₀ c-C ₅ H ₉ CH ₃ C ₆ H ₆ +3c-C ₅ H ₁₀	- 7.8 - 5.7 -34.9

All values are for gas phase reactions at 298K and n.t.p.

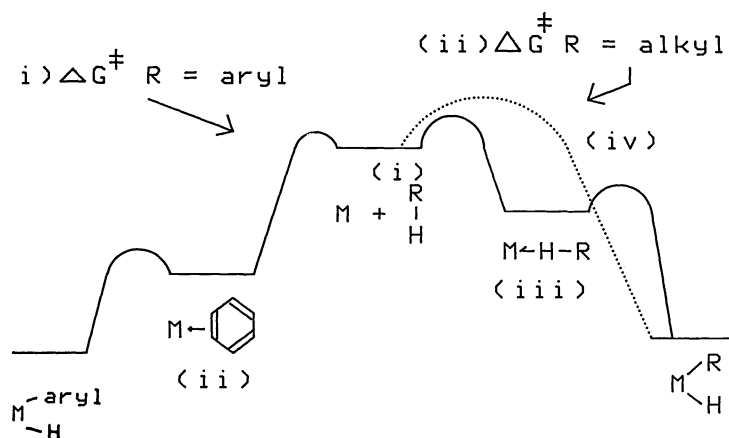


Fig. 4. Schematic energy profile of the reaction of [M] + R-H.

- (i) M at high energy reacts with R-H.
- (ii) ΔG^\ddagger for R = alkyl is greater than for R = aryl so arene rapidly adds giving the [M] - η^2 - arene intermediate.
- (iii) Although they have not yet been detected it seems likely that alkane addition proceeds via prior formation of an agostic intermediate.
- (iv) Rather than a wholly intermolecular pathway.

The precoordination of alkanes is restricted to formation of an agostic $M^{\delta}H-C$ bond. These are now well established in intramolecular systems, e.g. the titanium-ethyl compound in fig. 5 (ref. 9,10), and there is evidence for their occurrence in the bonding of methane to $[Cr(CO)_5]$ and $[Fe(CO)_4]$ (ref. 11).

The formation of these agostic bonds requires the presence of a suitably disposed, empty, and preferably low-lying, metal orbital. A full theoretical discussion of C-H activation has been published (ref. 12b).

The activation of aliphatic C-H bonds of those compounds which may be regarded as paraffin derivatives may proceed via precoordination which involves either agostic $M^{\delta}H-C$ bond formation, or via prior coordination of another more reactive group of the derivative, see fig. 6.

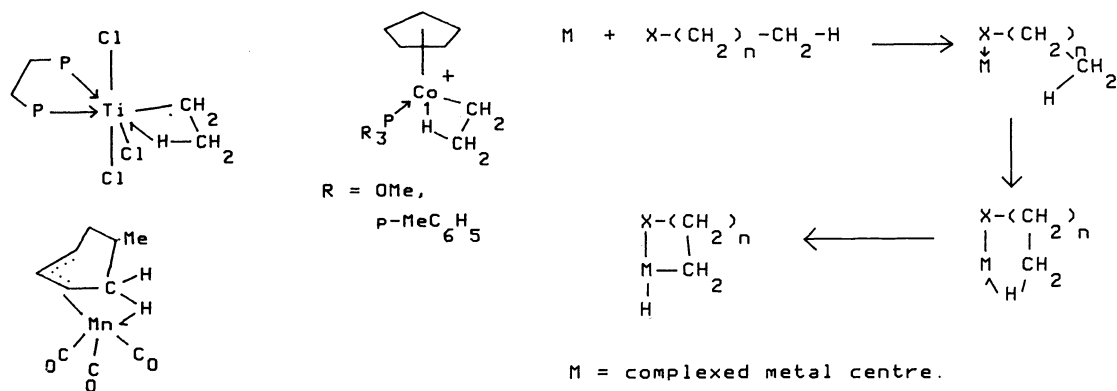


Fig. 5. Examples of simple compounds which contain agostic M-H-C bonds. Many other examples are known (ref. 12a).

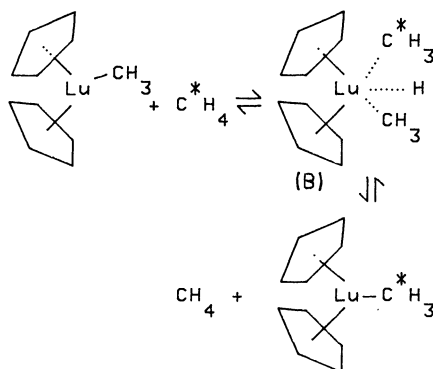


Fig. 7. An example of a homogeneous system which reacts with methane. No intermediate is observed in this d^0 system.

An example of a homogeneous methane activation reaction is shown in fig. 7 (ref. 13). No intermediate was detected, nor indeed is expected, since the metal centre has no d -electrons available for the formation of two new bonds.

The description of the bonding in the intermediate B (fig. 7) must formally resemble that in the stable compounds $[Ta(\eta-C_5H_5)_2H_3]$ (ref. 14) and $[W(\eta-C_5H_5)_2H_3]^+$ (ref. 15), except that there will be two electrons fewer in the $[MH_3]$ fragment, i.e. the HOMO in the Ta and W compounds will be the empty LUMO in the Lu compound $[Lu(\eta-C_5Me_5)_2CH_3]$. The favourable kinetics for methane activation by the lutetium compound indicates the kinetic advantage of a low-lying LUMO which can enhance precoordination of the alkane.

EXAMPLES OF C-H ACTIVATING SYSTEMS

These examples will be restricted to formally intermolecular reactions (see fig. 1). It is interesting to note that the first examples of methane activation were by Pt^{2+} salts (ref. 16) and the lutetium system in which, for different reasons, relatively low-lying empty d -orbitals are present.

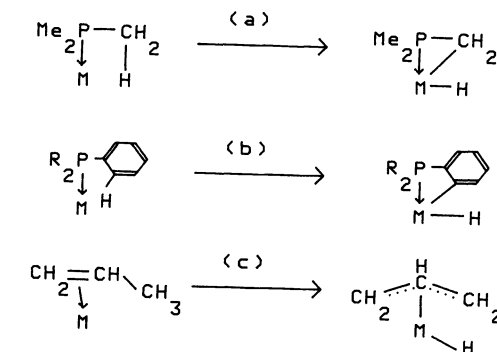


Fig. 6. Examples of intra- or pseudo-intra-molecular oxidative-addition reactions of carbon-hydrogen bonds. When $X=H$ then the reaction is a pseudo-intermolecular reaction. The specific examples (a-d) are intra-molecular reactions. (b) is called the ortho-elimination reaction.

i The oxidative additive of transition metal compounds to carbon-hydrogen bonds giving H-M-C derivatives, which are stable to isolation

TABLE 2 shows the stable starting compounds and the methods by which they are induced to react. With few exceptions, the starting compounds in TABLE 2. are 18-electron compounds and give rise to the reactive intermediate via thermal or photochemical reactions. The most common photoinduced initiation step involves elimination of dihydrogen, as was first demonstrated for $[W(\eta-C_5H_5)_2H_2]$ (ref. 17b). The normal thermal initiation is a simple reductive elimination of alkane from an alkyl-hydride derivative. Most of the implied intermediates have not yet been characterised as extensively as tungstenocene (ref. 20).

The 16-electron tungstenocene has been characterised by matrix-isolation studies which show it to have a parallel-ring, sandwich structure and a triplet ground state (ref. 21).

Most of the products of the C-H additions are 18-electron compounds which are then available for classic M-C cleavage reactions, e.g. with halogens. In this manner, stoichiometric conversion of C-H to C-X can be achieved (ref. 22). There are many metal compounds which will react with C-H bonds, but for which the oxidative addition product is not isolable due to thermal or photochemical instability under the reaction conditions. When polyhydride compounds, $[ML_yH_x]$, ($x=3$ or more), are used, catalytic conversion of C-H to C-D (or C-T) can occur, thereby demonstrating that reaction with C-H substrate has occurred. The general hydrogen-deuterium exchange mechanism is shown in fig. 8. Systems which will catalyse H/D exchange include platinum metal salts (alkane and aromatic C-H) (ref. 16), $[Ta(\eta-C_5H_5)_2H_3]$ (aromatic C-H only) (ref. 14) $[M(PR_3)_3H_3]$ (aromatic C-H only)(ref. 23). The compound $[Mo(\eta-C_5H_5)(dmpe)H_3]$, (where $dmpe = Me_2PCH_2CH_2PMe_2$), is a versatile catalyst for the H/D exchange of C-H bonds in a variety of compounds, as shown in TABLE 3.

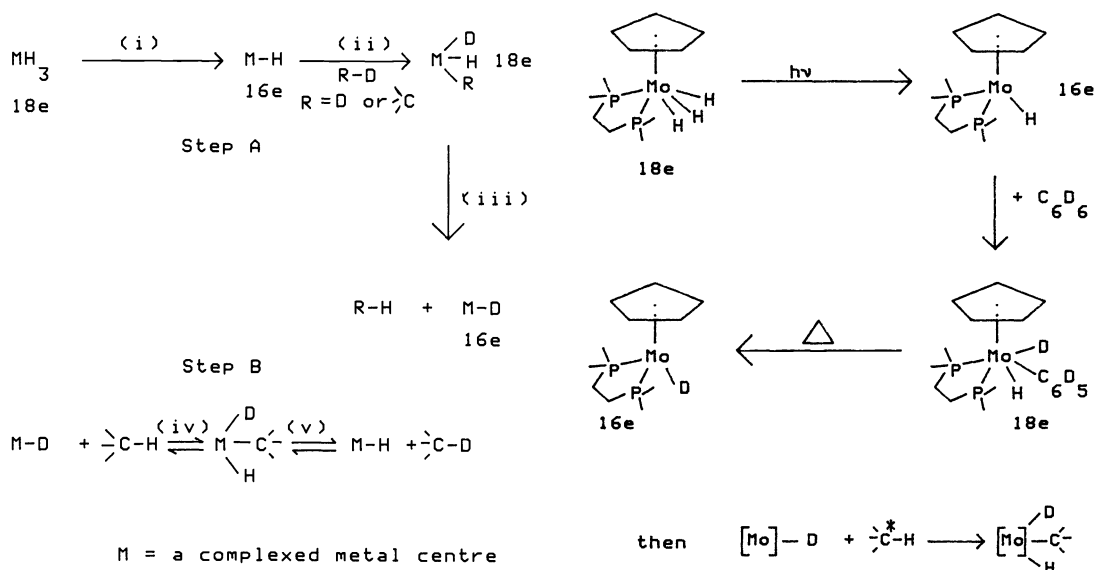


Fig. 8a.


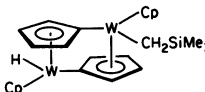
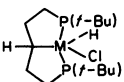
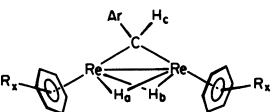
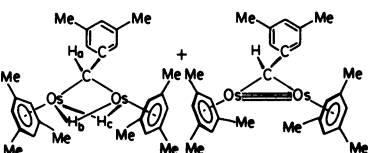
Fig. 8b.

Fig. 8a. A general mechanism for hydrogen-deuterium exchange catalysed by transition metal-polyhydrides, exemplified by a trihydride.

- (i) Thermal or photoinduced dissociation of dihydrogen.
- (ii) Oxidative-addition of a carbon-deuterium or D-D bond.
- (iii) Reductive-elimination of a C-H or H-D bond.
- (iv) Addition of a new C-H bond.
- (v) Reductive-elimination of a C-D bond.

Fig. 8b. Proposed mechanism for photoinduced H/D exchange catalysed by $[Mo(\eta-C_5H_5)(dmpe)H_3]$. The reactions indicated in TABLE 3 were carried out in solution of the C-H substrate and a catalytic amount of the compound in an excess of deuterobenzene, as the source of deuterium.

TABLE 2 Examples of transition metal compounds which add to C-H bonds giving isolable H-M-C products.

Reaction	Products	Ref
(i) Aromatic C-H bonds		
$[\text{Ru}(\text{dmpe})_2\text{Cl}_2]$ + 	$\xrightarrow{\Delta}$ $[(\text{dmpe})_2\text{Ru}^{\text{H}}\text{Naph}]$	17a
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ + Ph-H	$\xrightarrow[-\text{H}_2]{h\nu}$ $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{Ph})\text{H}]$	b
$[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2\text{H}_2]$ + Ph-H	$\xrightarrow[-\text{H}_2]{h\nu}$ $[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2(\text{Ph})\text{H}]$	c
$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2\text{H}_2]$ + Ph-H	$\xrightarrow[-\text{H}_2]{h\nu}$ $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2(\text{Ph})\text{H}]$	d
$[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2]$ + Ph-H	$\xrightarrow[-\text{H}_2]{h\nu}$ $[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{Ph})\text{H}]$	e
$[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{PPh}_2\text{Me})]$ + Ph-H	$\xrightarrow{\Delta}$ $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{Ph})\text{H}]$	f
$[\text{Lu}(\eta\text{-C}_5\text{Me}_5)_2\text{H}]$ + Ph-H	$\xrightarrow{\Delta}$ $[\text{Lu}(\eta\text{-C}_5\text{Me}_5)_2\text{Ph}]$	g
$[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{PPr}^i)_3\text{H}_2]$ + Ph-H	$\xrightarrow[-\text{H}_2]{h\nu}$ $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{PPr}^i)_3(\text{Ph})\text{H}]$	h
(ii) Aliphatic C-H bonds (excluding alkanes)		
$[\text{M}(\text{dmpe})_2(\text{Aryl})\text{H}]$ M = Fe, Ru	+ $\text{CH}_3\text{COCH}_3 \xrightarrow{\Delta}$ $[\text{M}(\text{dmpe})_2(\text{CH}_2\text{COCH}_3)\text{H}]$	18a
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ + SiMe_4	$\xrightarrow{h\nu}$ 	b
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{Me})\text{H}]$ + $\text{C}_6\text{H}_3\text{Me}_3$	$\xrightarrow[-\text{CH}_4]{\Delta}$ $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{-C}_6\text{H}_3\text{Me}_2)\text{H}]$	c
$[\text{MCl}_3]$ + $(\text{Bu}^t)_2\text{P}(\text{CH}_2)_5\text{P}(\text{Bu}^t)_2$ M = Ir, Rh	$\xrightarrow{\Delta}$ 	d
$\text{Re}(\text{atoms})$ + $\text{C}_6\text{H}_6\text{-xMe}_x$ x = 1, 2, 3	$\xrightarrow{\text{m.v.s.}^*}$ 	e
$\text{Os}(\text{atoms})$ + $\text{C}_6\text{H}_3\text{Me}_3$	$\xrightarrow{\text{m.v.s.}^*}$ 	f

m.v.s.* = via metal vapour synthesis.

TABLE 2 cont'd

Reaction	Products	Ref
(iii) Alkane C-H bonds		
$[\text{IrS}_2\text{L}_2\text{H}_2]^+ + \text{Bu}^t\text{-CH}_2=\text{CH}_2 + \text{c-C}_5\text{H}_{10} \xrightarrow{\Delta} [\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{L})\text{H}_2]^+$ $\text{L}=\text{PPh}_3, \text{S}=\text{H}_2\text{O} \text{ or } (\text{CH}_3)_2\text{CO}$		19a
$[\text{Re}(\text{L})_2\text{H}_7] + \text{Bu}^t\text{-CH}=\text{CH}_2 + \text{c-C}_5\text{H}_{10} \xrightarrow{\Delta} [\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{L})_2\text{H}_2]$ $\text{L}=\text{PPh}_3, \text{PEt}_2\text{Ph}$		b
$[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{H}_2] + \text{c-C}_6\text{H}_{12} \xrightarrow[\text{-H}_2]{h\nu} [\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{C}_6\text{H}_{11})\text{H}]$		c
$[\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{C}_6\text{H}_{11})\text{H}] + \text{CH}_4 \xrightarrow{\Delta} [\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{Me})\text{H}]$		d
$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{H}_2] + \text{R-H} \xrightarrow{h\nu} [\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{R})\text{H}]$ $\text{R}=\text{C}_6\text{H}_{11}, \text{C}_3\text{H}_5, \text{C}_5\text{H}_9$		e
$[\text{Lu}(\eta\text{-C}_5\text{Me}_5)_2\text{-CH}_3] + {}^{13}\text{CH}_4 \xrightarrow{\Delta} [\text{Lu}(\eta\text{-C}_5\text{Me}_5)_2{}^{13}\text{CH}_3] + \text{CH}_4$		f
$[(\eta\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2] + \text{R-H} \xrightarrow{\Delta} [\text{Ir}(\eta\text{-C}_5\text{Me}_5)\text{CO}(\text{R})\text{H}]$ $\text{R}=\text{C}_6\text{H}_{11}, \text{CH}_2\text{Bu}^t, \text{CH}_3$		g
$\text{Re}(\text{atoms}) + \text{C}_6\text{H}_6 + \text{alkane} \xrightarrow{\text{m.v.s.*}} \text{see fig. 10.}$		h
alkane = ethane propane, butane, neopentane, 2-methylpropane cyclohexane, cyclopentane, cyclopropane		
$[\text{Th}(\eta\text{-C}_5\text{Me}_5)_2(\eta^2\text{-(CH}_2)_2\text{CMe}_2)] \xrightarrow{\Delta} [\text{Th}(\eta\text{-C}_5\text{Me}_5)_2(\text{Me})\text{CH}_2\text{Bu}^t]$		i
$\text{W}(\text{atoms}) + \text{PMe}_3 + \text{c-C}_5\text{H}_{10} \xrightarrow{\text{m.v.s.*}} [\text{W}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{H}_5]$		j
$\text{Re}(\text{atoms}) + \text{PMe}_3 + \text{c-C}_6\text{H}_{12} \xrightarrow{\text{m.v.s.*}} [\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}]$		k
$[1,10\text{-B}_{10}\text{H}_8(\text{N}_2)_2] + \text{CH}_4 + \text{CO} \xrightarrow{\Delta} [\text{CH}_3\text{B}_{10}\text{H}_7(\text{CO})_2] + [(\text{CH}_3)_2\text{B}_{10}\text{H}_6(\text{CO})_2]$		l
$\text{Os}(\text{atoms}) + \text{C}_6\text{H}_6 + \text{isobutane} \xrightarrow{\text{m.v.s.*}} \text{see fig. 11.}$		m

m.v.s.* = via metal vapour synthesis.

TABLE 3. H-D exchange with $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})\text{H}_3]$ (ref. 24).

Substrate	Deuteriated product	Hydrogen undergoing exchange and approximate rates ^a
(a) Aromatic hydrocarbon substrates		
$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{D}_5\text{CD}_3$	CH_3 : 4 days C_6H_5 : obscured by solvent
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$	$\text{C}_6\text{D}_5\text{CH}_2\text{CH}_3$	C_6H_5 : 6 hours
$1,4\text{-C}_6\text{H}_4(\text{CH}_3)_2$	$1,4\text{-C}_6\text{D}_4(\text{CD}_3)_2$	C_6H_4 : 2 days, CH_3 : 4 days
$1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$	$1,3,5\text{-C}_6\text{H}_3(\text{CD}_3)_3$	CH_3 : 7 days
$\text{C}_6(\text{CH}_3)_6$	none	
$\text{CH}_3\text{OC}_6\text{H}_5$	$\text{CD}_3\text{OC}_6\text{D}_5$	CH_3O : 8 hours, C_6H_5 : 6 hours
$1,4\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3$	$1,4\text{-CD}_3\text{C}_6\text{D}_4\text{OCD}_3$	CH_3 : 10 days, C_6H_4 : 6 hours OCH_3 : 6 hours
(b) Non-aromatic substrates		
$(\text{CH}_3)_2\text{O}$	CD_3OCD_3	CH_3 : 7 days
$(\text{CH}_3\text{OCH}_2)_2$	$(\text{CD}_3\text{OCH}_2)_2$	CH_3 : 14 days
$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	$\text{CD}_3\text{CO}_2\text{CD}_2\text{CD}_3$	CH_3CO_2 : 1 day, CH_2 : 15 days CH_3 : 5 days. Integration obscured by dmpe.
Cyclohexane	none	
$(\text{CH}_3)_4\text{Si}$	none	
(c) Organometallic substrates		
$\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$	$\text{Fe}(\eta\text{-C}_5\text{D}_5)_2$	C_5H_5 : 12 hours
$\text{W}(\eta\text{-C}_6\text{H}_5\text{CH}_3)_2$	$\text{W}(\eta\text{-C}_6\text{D}_5\text{CD}_3)_2$	C_6H_5 : 2 hours, CH_3 : 3 days
$\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2$	$\text{W}(\eta\text{-C}_5\text{D}_5)_2(\text{CH}_3)_2$	C_5H_5 : 3 hours

^a The times given are the times required to achieve statistical equilibrium with deuteriobenzene.

The conversion of $[\text{Ir}(\text{PPh}_3)_2(\text{solvent})_2\text{H}_2]^+$ in the presence of cyclopentane and neo-hexene into $[\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]^+$ was an early example of a homogeneous alkane activation reaction (ref.19a) (see fig. 9). This reaction must proceed via many intermediate steps, the crucial step being initial insertion of iridium into a cyclopentane C-H bond.

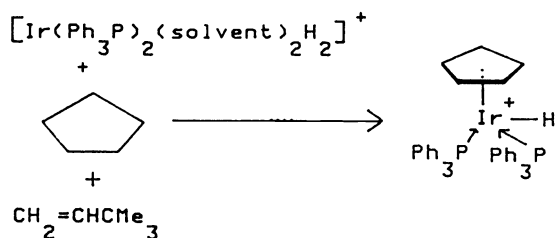
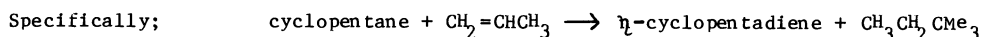
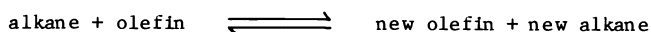


Fig. 9. Early example of homogeneous alkane activation.

It is important to note that thermodynamic control is assisted by the hydrogen transfer reaction which is essentially thermoneutral.



A contributory driving force for the overall reaction can be associated with the the stable $[\text{Ir}(\eta\text{-C}_5\text{H}_5)]$ bond. The acceptor olefin neo-hexene, $\text{CH}_2 = \text{CHCMe}_3$ was chosen since such alkyl-substituted olefins are poor ligands.

ii Alkane activation by transition metal atoms leading to alkyl derivatives

There is evidence for the the photoinduced insertion of atoms of Cu and Fe into methane under matrix isolation conditions, but no products were isolated (ref. 25a,b,c). Co-condensation of atoms of Cr (ref. 19k), W (ref. 19j), Re (ref. 19h,k) and Os (ref. 19m) with alkanes in the presence of potential ligand molecules such as benzene and trimethylphosphine have led to compounds containing ligands derived from the alkanes. Some interesting examples are shown in fig. 10.

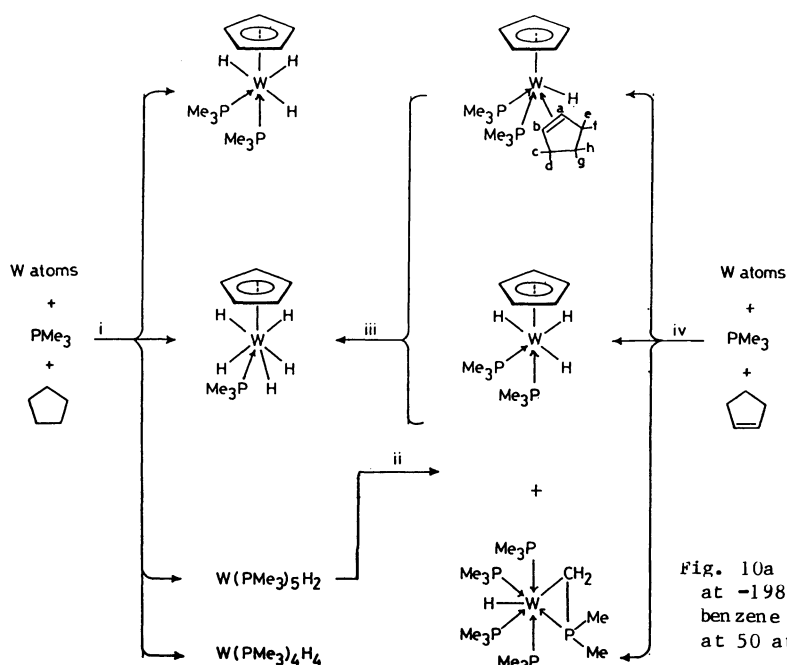


Fig. 10a (i) and (iv) Co-condensation at -198°C , (ii) cyclopentadiene in benzene at -60°C , (iii) dihydrogen at 50 atm.

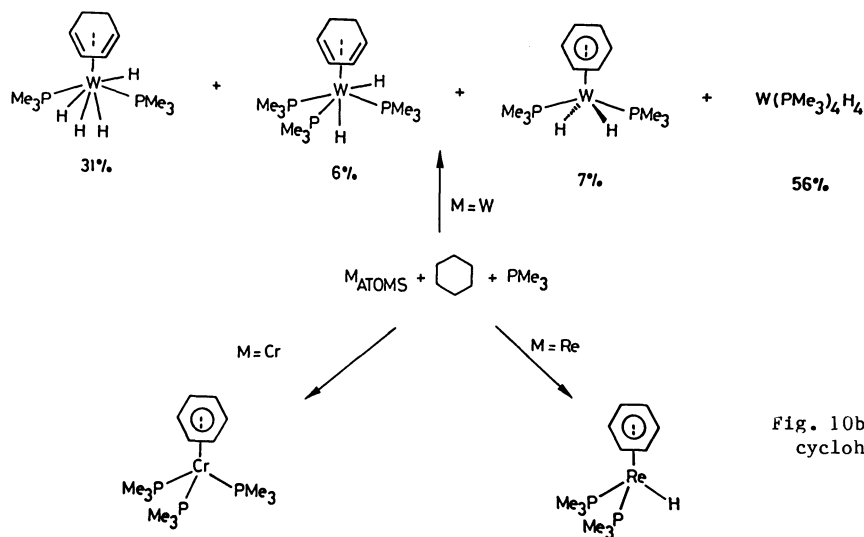


Fig. 10b. Activation of cyclohexane via metal atoms.

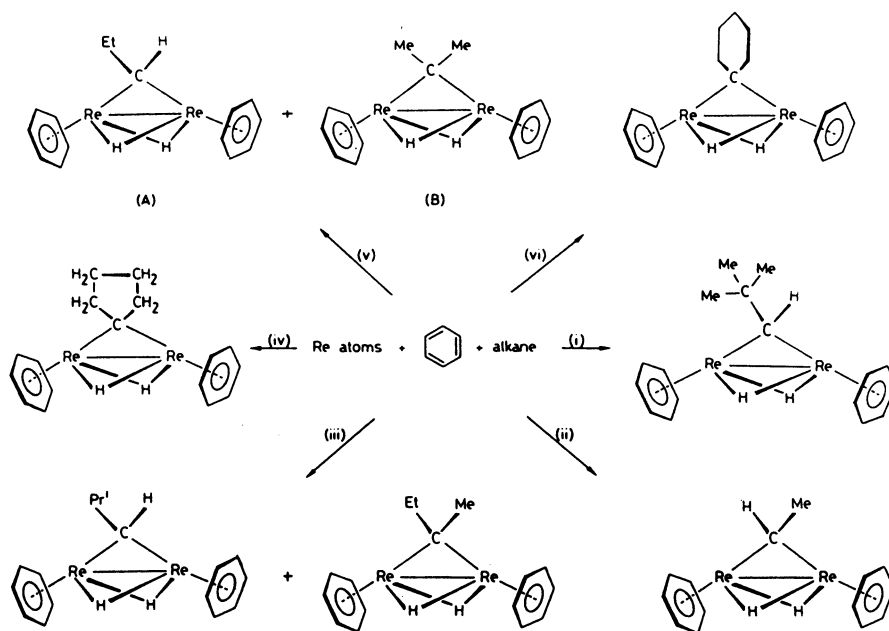
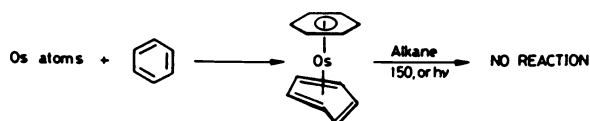


Fig. 10c. Activation of alkanes by rhenium atoms; where alkanes (R)=
(i) neopentane, (ii) ethane, (iii) butane, (iv) cyclopentane, (v) propane.

The mechanisms for these reactions are unknown and must be complex. Photochemically initiated steps may be envisaged since under the conditions of the co-condensation experiments the co-condensate is exposed to the radiation from the molten metal sample (e.g. ca. 3600°C for rhenium). However, it seems reasonable to assume the reactions are homogeneous, especially in the light of the catalytic processes discussed below. The conditions of the atom reactions are such that the potential ligand molecules, benzene or PMe_3 , are present in a large molar excess over both the metal atoms and the alkane. Nonetheless, the oxidative-addition of the C-H bonds of the alkanes competes very successfully with the potential ligand molecules. This is well illustrated by the reaction between osmium atoms, benzene and isobutane in which a triple C-H activation of isobutane occurs giving A (fig. 11), and there is essentially no $\text{Os}(\eta\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_6)$ (ref. 26) detected in the reaction product.



BUT

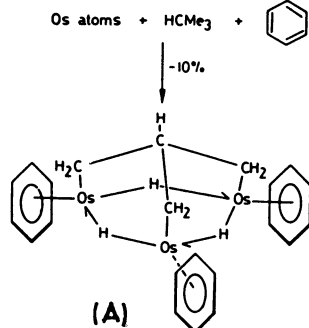


Fig. 11. Formation of trinuclear osmium cluster via osmium atoms.

In contrast, when isobutane is absent osmium atoms react with benzene giving $\text{Os}(\eta\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_6)$ in excellent yield. These metal atom-alkane activation reactions imply that suitably unsaturated transition metal compounds, i.e. of low electron number, can readily react with alkane C-H bonds.

iii Catalytic alkane activation

Alkane-olefin hydrogen transfer reactions can be carried out selectively and in some cases catalytically using polyhydride tertiaryphosphine transition metal compounds (ref. 27). An example is shown in Figure 12.

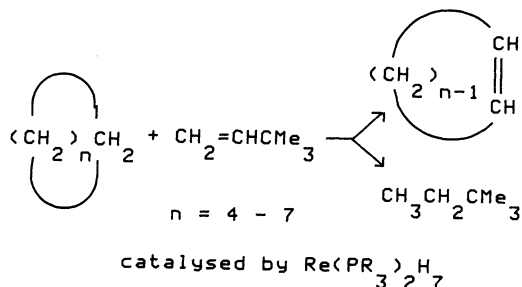


Fig. 12. Examples of catalytic hydrogen transfer reactions of alkanes giving cyclic olefins (ref. 19a,b).

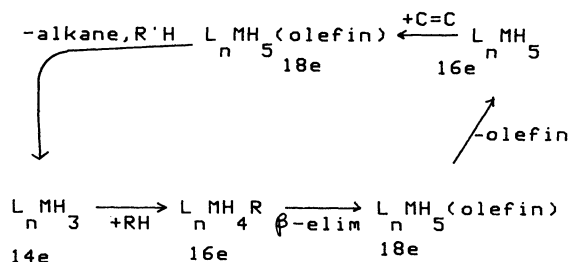


Fig. 13. Key intermediates in the proposed mechanism for alkane dehydrogenation by rhenium polyhydride complexes.

TABLE 4. Ionisation potentials for some tungsten phosphine complexes.

Compound	1st Ionization Potentials/eV	d ⁿ number
$[\text{W}(\text{PMe}_3)_3\text{H}_6]$	---	0
$[\text{W}(\text{PMe}_3)_4\text{H}_4]$	5.5	2
$[\text{W}(\text{PMe}_3)_5\text{H}_2]$	5.37	4

Felkin has proposed the active intermediate to be a 14-electron complex $[\text{L}_2\text{ReH}_3]$ (ref.28) (fig. 13). Thus the proposed key equilibria are given in (fig. 13).

The advantage of starting from a 14-electron intermediate is that the 16-electron alkylhydride adduct can add another olefin ligand. Effective catalysis involving a multi-step sequence of intermediates is normally associated with the requirement that no intermediate should be unduly stable, and that no activation energy should be unduly high. In this context, it is pertinent to comment on the photoelectron spectra (ref. 29) of the compounds $[\text{W}(\text{PMe}_3)_5\text{H}_2]$, and $[\text{W}(\text{PMe}_3)_4\text{H}_4]$. The first ionisation energies are, $[\text{W}(\text{PMe}_3)_5\text{H}_2]$ IP = 5.37eV and $[\text{W}(\text{PMe}_3)_4\text{H}_4]$ IP = 5.5eV, and are remarkably similar despite the apparent "oxidation" of the metal centres. The values of the first I.P.'s correspond to electron-rich metal centres.

This trend would not be expected for a similar sequence where, for example, the hydrido-ligands were replaced by chloride. It seems as though transition metal-hydrogen bonds may have sufficient flexibility to buffer against charge build-up at the metal centre. Some buffering role can also be associated with the PMe_3 ligands. Unlike, for example, the M-CO system, one can envisage positive charge delocalisation from the metal to the phosphorus by an increased contribution to the M-P bond of the canonical form $[\text{Me}_3\text{P} \rightarrow \text{M}]$. If the energies of the HOMOs of series such as $[\text{M}(\text{PR}_3)_x\text{H}_y]$, ($y=0, 2, 4$) and $[\text{W}(\text{PR}_3)_m\text{H}_n]$, ($m+n = 2, 4$) remain essentially constant then such a "plateau effect" would be suitable for catalytic C-H activation by the metal centre.

iv Selectivity in C-H activation with respect to deactivation

A transition metal centre which has the required properties to oxidatively-add to an alkane will clearly be reactive towards many other bonds C-X, X-Y, and to other donor ligands. In particular, reactivity towards other C-H bonds inevitably present in the metal complex by either intra- or intermolecular processes can compete with the desired intermolecular reaction with alkane. This is illustrated by the numerous compounds which, while apparently closely related to the rhodium and iridium systems $[\text{M}(\eta\text{-C}_5\text{Me}_5)\text{LH}_2]$, do not react with alkanes, (although some will react with many other C-H bonds).² Examples are $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})\text{H}_3]$, $[\text{W}(\eta\text{-C}_5\text{Me}_5)_2\text{H}_2]$, and $[\text{W}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_3\text{H}]$. Tungstocene, for example, does not give a product with cyclohexane but rather forms the dimer $[(\eta\text{-C}_5\text{H}_5)\text{W}(\mu\text{-H})_2(\eta\text{-C}_5\text{H}_4)]_2$ (ref. 30).

photolysis of decamethyltungstocenedihydride (fig. 14) gives the stepwise formation of "tuck-in" (ref. 31) products arising from the intramolecular oxidative-addition of C-H bonds of the ring-methyl groups to the tungsten centre (Figure 14) (ref.32, and 33). These reactions contrast with those of photolysis of $[M(\eta-C_5Me_5)LH_2]$, (M= Rh, Ir, L=CO, PMe_3) from which no dimers or "tuck-in" products are observed.

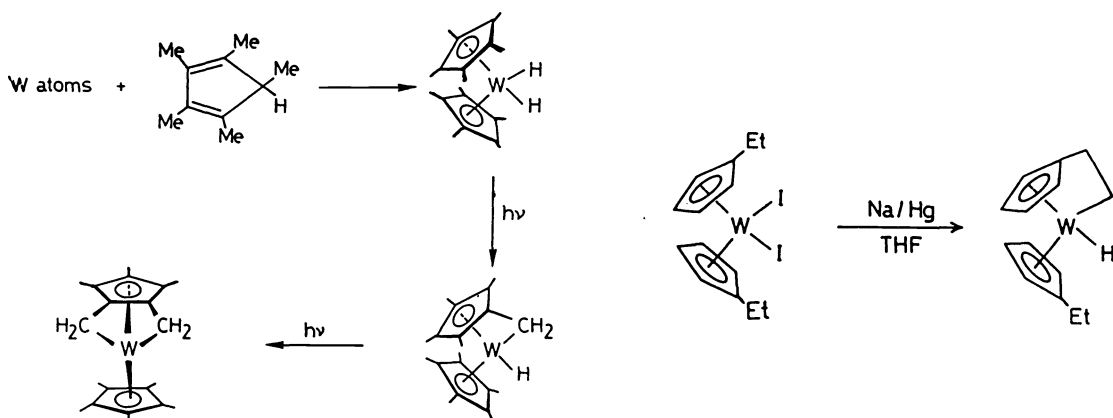


Fig. 14. Examples of intramolecular oxidative-addition of the C-H bonds of alkyl substituents on η -cyclopentadienyl rings.

The short life-time of the polyhydride catalysts illustrated in fig. 12 may be attributed to bi-nuclear decomposition pathways. Indeed these reactions are carried out in dilute solutions in order to reduce the importance of these pathways.

The major problem for homogeneous catalysts which will add C-H bonds of alkanes is the control and restriction of their reactivity towards alternative substrates, destructive dimerisation and intra-C-H activating processes.

v The carbene CR_2 analogy with C-H activating metal centres

The chemical analogy between tungstocene and carbenes was noted first many years ago and has been amply justified by the characterisation of tungstocene as a triplet (ref. 21). We have noted above the desirability, on thermodynamic grounds, for a C-H activating metal centre to have a high energy HOMO. In contrast, alkane precoordination via an agostic bond, which is kinetically desirable, requires a low-lying LUMO. These conditions are maximised when the HOMO and LUMO are degenerate, i.e. a triplet state. Perutz has observed that many of the proposed intermediates which oxidatively-add to C-H bonds can be expected to have triplet states on grounds of their expected symmetry, e.g. $[M(\eta-C_5R_5)L]$, (M = Rh, Ir), and $[Fe(dmpe)_2]$.

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