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Activation of Carbon-Hydrogen Bonds in Alkanes and Other Organic Molecules Using Organotransition Metal Complexes

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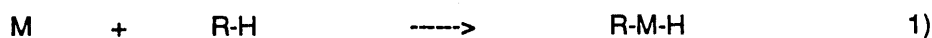
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Presented before the Division of Petroleum Chemistry, Inc.
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**Activation of Carbon-Hydrogen Bonds In Alkanes and Other Organic Molecules
Using Organotransition Metal Complexes**

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Intramolecular C-H oxidative addition to metal centers has been known for some time (1),
but despite many efforts a direct observation of the corresponding intermolecular C-H oxidative



addition process illustrated in Equation 1 was not uncovered until 1982. At that time our group
and Graham's independently found that irradiation of complexes such as $Cp^*(L)IrH_2$ (1, $Cp^* = (\eta^5-C_5Me_5)$, $L = PMe_3$) and $Cp^*Ir(CO)_2$ causes successful insertion of the Cp^*IrL fragment into C-H
bonds in alkanes, leading to stable alkyliridium hydride complexes $Cp^*(L)Ir(R)(H)(2)(2)$. Some of
the solvents that have been observed to give intermolecular C-H insertion products upon
irradiation of 1 are illustrated in Scheme 1.

Following the initial studies with iridium, alkane C-H oxidative addition has been observed
at several other third-row transition metal centers, such as rhodium, rhenium, platinum, and
osmium and even at one first-row metal (iron) (3). The selectivity of the iridium and rhodium C-H
oxidative addition reaction has been investigated by carrying out competition studies with various
hydrocarbon substrates (2a,6). The results are summarized in Scheme 2. Although the absolute
magnitudes of the selectivities are different for Ir and Rh, their trends are parallel, indicating that
C-H oxidative additions proceed by similar mechanisms at these two metal centers, but that the Rh
reactions are less exothermic than their Ir counterparts.

The oxidative addition reaction is reversible--in the rhodium series, most $Cp^*(L)Rh(R)(H)$
complexes are much less stable than their iridium analogues, and eliminate R-H at temperatures
below 0 °C. A similar reaction takes place on heating the more stable iridium alkyl hydrides

$\text{Cp}^*(\text{L})\text{Ir}(\text{R})(\text{H})$ to temperatures above 100 °C. This provides a thermal, rather than photochemical, method for carrying out the C-H insertion reaction. Kinetic studies are consistent with a rate-determining step in which R-H is eliminated from the starting coordinatively saturated (18-electron) alkyl hydride (4,5). Evidence has been obtained that weakly bound alkane " σ -complex" intermediates intervene in the saturated hydrocarbon oxidative addition process before full C-H bond cleavage occurs (6). The energetics of the processes that occur when an alkyl and phenyl C-H bond are exchanged at iridium (from our work (7,10)) and rhodium (from the work of W. D. Jones and coworkers (8)) demonstrate that the overall conversion of alkyl hydride to phenyl hydride is exothermic in both systems, but each alkyl hydride must surmount a significant energy barrier to reach the intermediates that are capable of reacting with C-H bonds in another molecule of alkane or arene.

Our preliminary studies of these systems raised many questions about the mechanism of the intermolecular C-H oxidative addition. Unlike most systems studied earlier, intramolecular cyclometallation products such as **3** or **4** (Scheme 3) are never observed in our system; the reactions are exclusively intermolecular. We do not yet understand the physical basis for this unusual selectivity. Another question concerns whether the photochemical and thermal reactions proceed by analogous mechanisms. As shown in Scheme 3, if thermal decomposition of hydrido(alkyl) complex **1** and photochemical decomposition of dihydride **2** both pass through coordinatively unsaturated species Cp^*IrL , then when mixtures of alkane solvents are used, similar selectivities should be observed in the two reactions. However, it is possible that in the thermal reaction, one alkane complex (e.g., **5**) might be converted to another (**6**) by a direct process that avoids Cp^*IrL . Similarly, irradiation of **1** (which presumably gives initially the electronically excited state **1***) might be attacked directly by a hydrocarbon substrate R-H, leading to intermediate **7** that would subsequently lose H_2 in a second step. In this case, it is possible that the thermal and photochemical reactions would give different selectivities. We are attempting to distinguish these possibilities by developing methods to carefully examine the selectivity

exhibited by the photochemical and thermal iridium reactions in mixtures of alkane solvents under precisely identical conditions.

We are also working on the development of methods for the conversion of alkane oxidative addition products to functionalized organic molecules. We have found it possible to convert alkylmetal hydrides to organic halides using the sequences outlined in Scheme 4 (2a,3b,6). However, it would be substantially more useful to generate functionalized molecules by a combination of C-H oxidative addition and migratory insertion reactions with a second molecule, such as CO or CO₂. Unfortunately, it is very difficult to generate an open coordination site in the Cp*(L)M(R)(H) oxidative addition products, and as a result these materials have resisted attempts to induce them to undergo migratory insertion. We have now made some progress on this problem by replacing the Cp* ligand with an indenyl (Ind) ligand. This ligand undergoes much easier interconversion between its η^5 and η^3 configurations, providing a means of opening up a coordination site at the metal center to which it is complexed. Synthetic routes to (Ind)(L)IrR₁R₂ (R₁ and R₂ = alkyl, H) complexes have been worked out, and as expected, migratory insertion of CO and other ligands occurs much more rapidly than in the corresponding Cp* complexes (9). Combined C-H oxidative addition/migratory insertion processes are now being developed using these indenyl systems.

Most of our initial studies were directed toward the investigation of C-H oxidative addition in alkanes. We have recently begun to investigate the interaction of C-H activating iridium and rhodium complexes with functionalized organic molecules, to determine the effect of functional groups on the process, as well as to investigate the propensity of Ir and Rh to insert into C-H versus other types of X-H bonds. Scheme 5 illustrates some of our initial results. Reaction with ethylene gives both a π -complex and a C-H insertion product. Interestingly, the π -complex is stable to the reaction conditions (in fact, it is the thermodynamic product of the reaction), and so cannot be an intermediate in the C-H insertion (10). When the reaction is carried out in alcohol or amine solvents, C-H insertion appears to occur in preference to O-H insertion (11) although with

methanol and ethanol surprising products are produced by subsequent transformation of the proposed initially formed insertion products (12).

We have not yet found an organic liquid that is unreactive toward iridium, so that it might be used as an inert solvent in these reactions. While such ubiquitous reactivity is useful for carrying out chemical transformations on normally recalcitrant substrates, it is a problem in another sense--it has prevented us from investigating the C-H insertion propensity of substrates that are difficult to liquefy under easily accessible conditions (e.g., solids or gases with very low boiling points). Even fluorocarbons, we have found, react with the intermediates generated on irradiation of $\text{Cp}^*(\text{L})\text{Ir H}_2$, probably by electron-transfer pathways.

In order to solve this problem, we have investigated the use of liquid xenon as a potential inert solvent for iridium C-H oxidative addition reactions. Recent experiments have demonstrated that xenon liquefied at $-70\text{ }^\circ\text{C}$ and 10 atm pressure does, in fact, serve as an inert solvent for the C-H oxidative addition reaction (13). We have been able to prepare and isolate, for the first time, C-H oxidative addition products formed from high-melting solid substrates such as naphthalene, adamantane, and even cubane; the latter case represents the first observation of C-H oxidative addition at a tertiary C-H bond. Liquid xenon has also allowed us to carry out more conveniently the C-H oxidative addition reactions of low-boiling gases that are difficult to liquefy, such as methane.

In addition to these preparative studies, we have also utilized liquefied noble gases as inert solvents for carrying out time resolved flash kinetic studies using infra-red detection. These experiments are designed to generate transient coordinatively unsaturated C-H activating intermediates, and directly measure the rates of their reactions with C-H bonds (14). In this case, $\text{Cp}^*\text{Rh}(\text{CO})_2$ was utilized to take advantage of the higher quantum yields in the rhodium system and the large IR extinction coefficients observed in metal carbonyl complexes. Irradiation of the rhodium dicarbonyl complex in liquid krypton between -90 and $-120\text{ }^\circ\text{C}$ gave rise to a transient metal-CO absorption at 1947 cm^{-1} , which decayed rapidly in the presence of cyclohexane, leading to $\text{Cp}^*(\text{CO})\text{Rh}(\text{H})(\text{C}_6\text{H}_{11})$. By examining the dependence of the decay rates on the

concentration of cyclohexane and cyclohexane-d₁₂, we have concluded that the transient IR absorption is due to a rapidly equilibrating mixture of the krypton complex Cp*Rh(CO)(Kr) and the cyclohexane σ-complex Cp*Rh(CO)(C₆H₁₂). The latter predominates at high cyclohexane concentrations, and under these conditions the rate of direct conversion of the cyclohexane complex to the C-H oxidative addition product Cp*(CO)Rh(H)(C₆H₁₁) can be measured. From the temperature dependence of this rate constant, we have determined that the activation energy associated with this process is 4.8 kcal/mole.

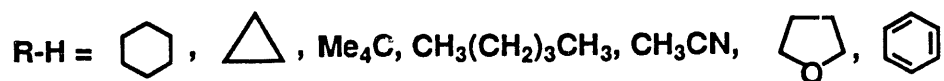
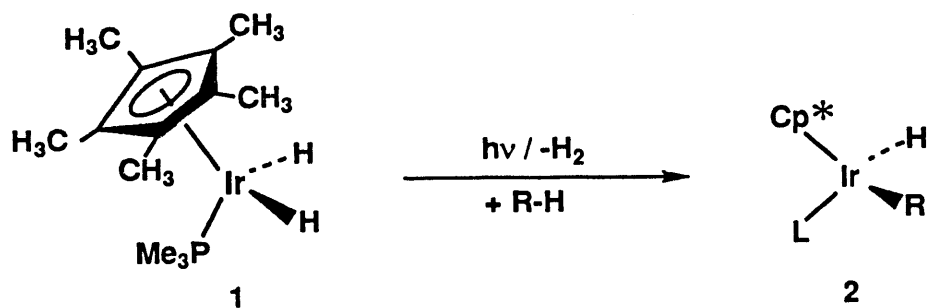
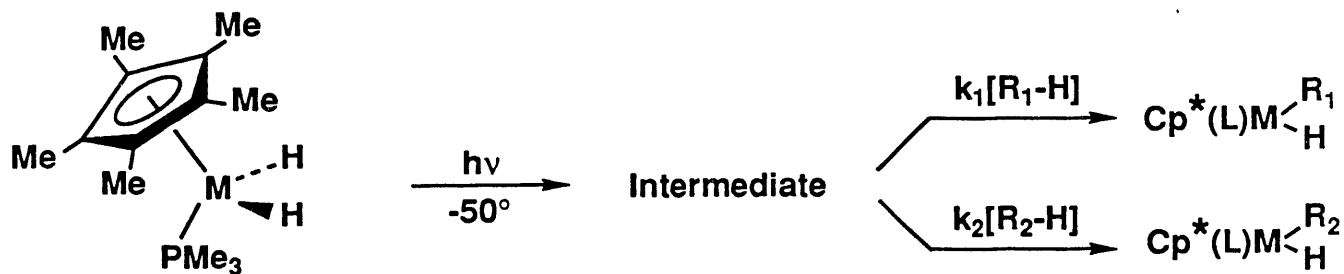
Recently we have also been able to carry out analogous studies in the gas phase. Under these conditions, "naked" rather than solvated Cp*Rh(CO) is formed, and this species reacts with cyclohexane at nearly gas-kinetic rates (15). Under these conditions, collision between Cp*Rh(CO) and cyclohexane is the slowest step in the overall C-H activation process. In contrast, in solution association of solvent with free Cp*Rh(CO) is so rapid that the step involving C-H bond cleavage in the coordinated alkane complex becomes rate-determining.






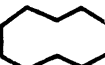


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Reference and Notes

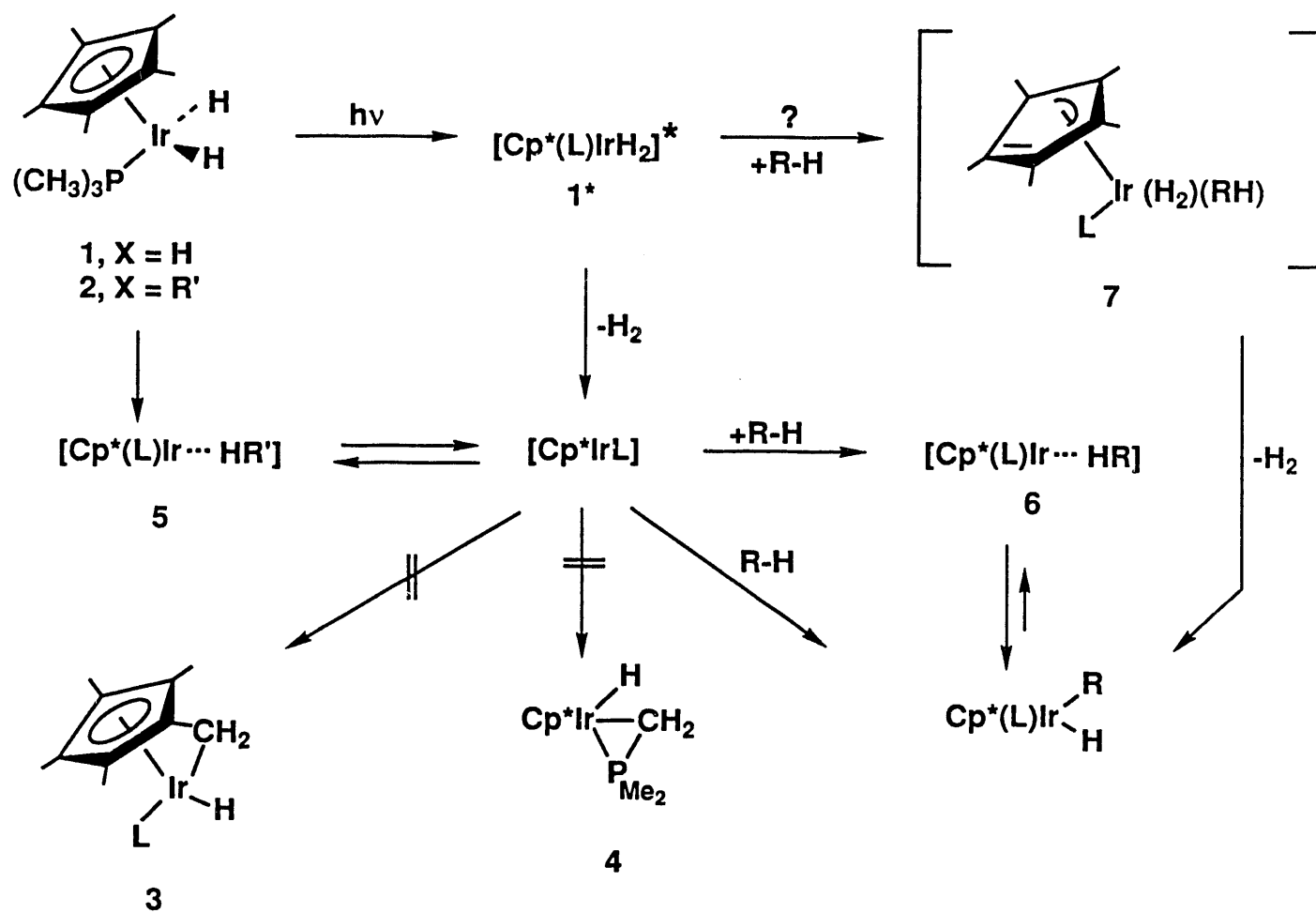
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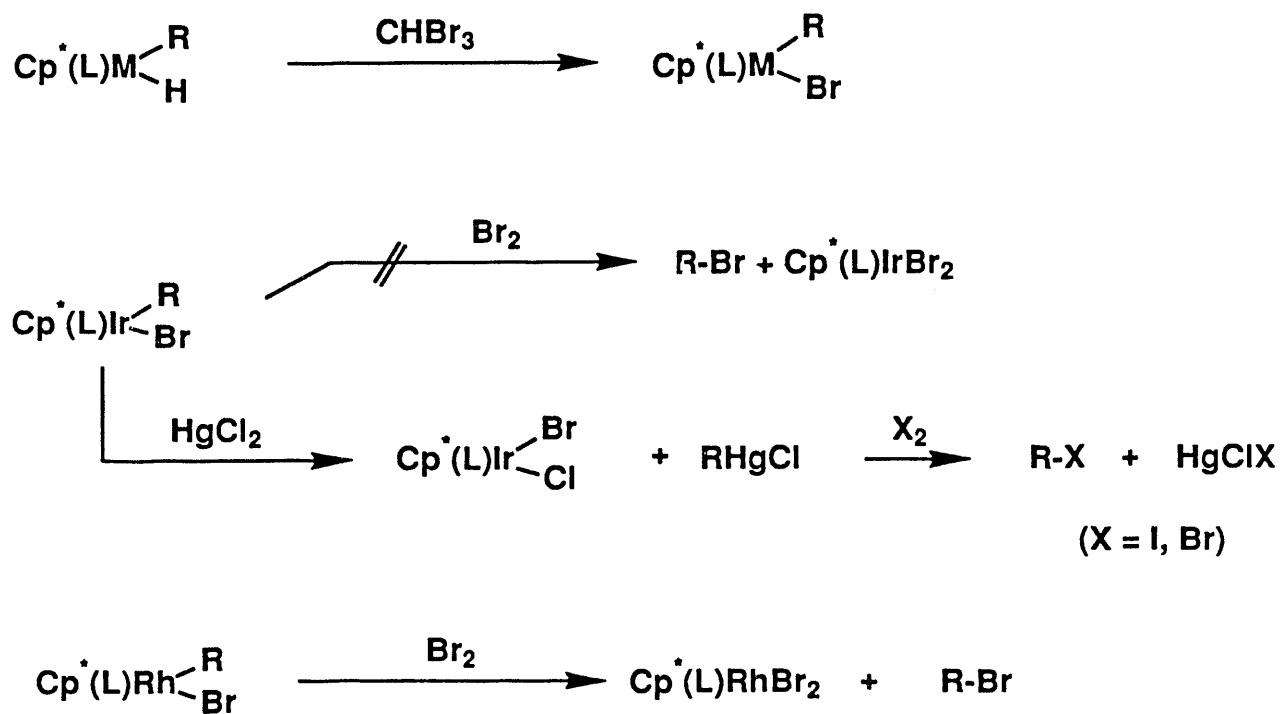
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Scheme 1Scheme 2

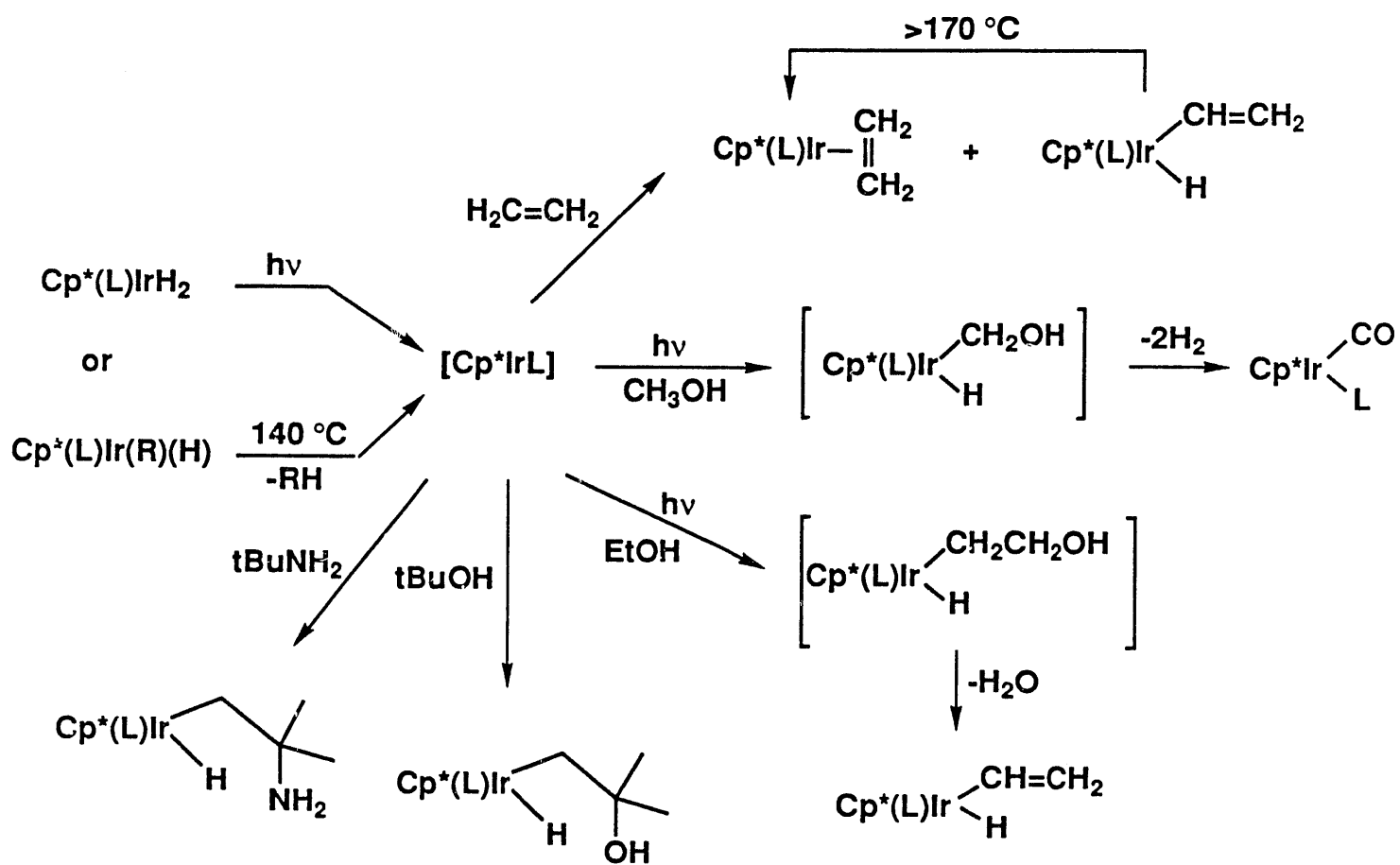
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|-----------------------------|---|---|---|---|--|---|---|---|
| |  |  |  |  |  |  |  |  |
| $k_{\text{rel}}(\text{Ir})$ | 1.0 | 1.6 | 2.63 | - | 0.09 | 0.23 | - | 4.0 |
| $k_{\text{rel}}(\text{Rh})$ | 1.0 | 1.8 | 10.4 | 0.14 | 0.06 | - | 3.6 | 19.5 |

Scheme 3



Scheme 4

Scheme 5



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