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

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The potential for using alkanes–which are among the most chemically inert organic molecules–as feedstocks in chemical synthesis has stimulated a search for metal complexes capable of undergoing the C-H oxidative addition process shown in eq. (1), so that alkane chemistry more selective than that available using free radical reagents might be developed.[1] Intramolecular C-H oxidative addition to metal centers has been known for some time, but despite

$$\text{M} \quad + \quad \text{R-H} \quad \longrightarrow \quad \text{R-M-H} \qquad (1)$$

many efforts a direct observation of the corresponding intermolecular C-H oxidative addition process illustrated in eq. (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, $Cp^* = (\eta^5\text{-}C_5Me_5)$, 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] This reaction is exceedingly general. So far no organic liquid in which $Cp^*(L)IrH_2$ has been irradiated has failed to react with the intermediate generated in the reaction. Some of the solvents that have been observed to give intermolecular C-H insertion products upon irradiation of 1 are illustrated in Scheme I.

Much has been learned about the scope and mechanism of this reaction.[4-8] Following the initial studies with iridium, alkane C-H oxidative addition has been observed at several other

third-row transition metal centers (where M-H and M-R bonds are expected to be relatively strong), 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 selectivity experiments also suggest that steric effects and C-H acidities, rather than bond energies, control the rate of attack of the metal center on particular C-H bonds.

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 ^{o}C. A similar reaction takes place on heating the more stable iridium alkyl hydrides Cp*(L)Ir(R)(H) to temperatures above 100 ^{o}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, giving a very reactive intermediate which can then be trapped by other hydrocarbons.[4] Strong evidence has been obtained that the reactive species responsible for the C-H insertion reaction in benzene and other aromatic solvents are π- (or "η^2-arene") complexes.[5] More recently, evidence has been obtained that analogous, but more weakly bound, alkane "σ-complex" intermediates intervene in the saturated hydrocarbon oxidative addition process before full C-H bond cleavage occurs.[6] In combination with conventional and photoacoustic calorimetric investigations, the thermal reactions have also provided information about absolute iridium-carbon and iridium-hydrogen bond energies. These in turn have given us a quantitative idea of the thermodynamic driving force for the C-H oxidative addition reaction.[7] 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.

The studies summarized above raise a number of important questions about the C-H oxidative addition process. Some of these are being addressed in current work, and preliminary results are illustrated in Scheme 3. One perplexing problem concerns the fact that unlike many C-H oxidative addition systems studied earlier, intramolecular cyclometallation products such as **3** or **4** are never observed in our system; the reactions are exclusively intermolecular. We would like to know 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.[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 CO_2. 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)IrR_1R_2 (R_1 and R_2 = 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. Combined C-H oxidative addition/migratory insertion processes are now being developed using these indenyl systems (Scheme 5).[9]

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 6 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]

As mentioned earlier, 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 liquify 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 Cp*(L)Ir H_2, probably by electron-transfer pathways.[12]

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. Hydrocarbons are known to have reasonable solubility in xenon, and we have found that $Cp^*(L)IrH_2$ exhibits this property as well. Recent experiments have demonstrated that xenon liquified at -70 ^oC and 10 atm pressure does, in fact, serve as an inert solvent for the C-H oxidative addition reaction.[12] The C-H oxidative addition chemistry that we have observed in this medium is summarized in Scheme 7. 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 liquify, such as methane. Finally, we have found that methanol and ethanol give O-H oxidative addition products in liquid xenon, in contrast to their behavior at higher temperatures in neat alcohol solvents, where products believed to be derived from initial C-H activation are observed. The reasons for this unusual change in behavior are not yet understood.

In addition to these preparative studies, we have also utilized liquified 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.[13] In this case, $Cp^*Rh(CO)_2$ 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 ^oC gave rise to a transient metal-CO absorption at 1947 cm^{-1}, which decayed rapidly in the presence of cyclohexane, leading to $Cp^*(CO)Rh(H)(C_6H_{11})$. By examining the dependence of the decay rates on the concentration of cyclohexane (Fig. 1) and cyclohexane-d_{12}, 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 $Cp^*Rh(CO)(C_6H_{12})$. 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 $Cp^*(CO)Rh(H)(C_6H_{11})$ 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.[14] 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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3. See, for example, (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1983, *2*, 562; (b) Periana, R. A.; Bergman, R. G. *ibid.*, 1984, *3*. 508; (c) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* 1988, *110*, 7915; (d) Hackett, M.; Whitesides, G. M. *ibid.*1988, *110*, 1449; (e) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *ibid.*, 1985, *107*, 4358; (f) Baker, M. V.; Field, L. D. *ibid.* 1987, *109*, 2825.
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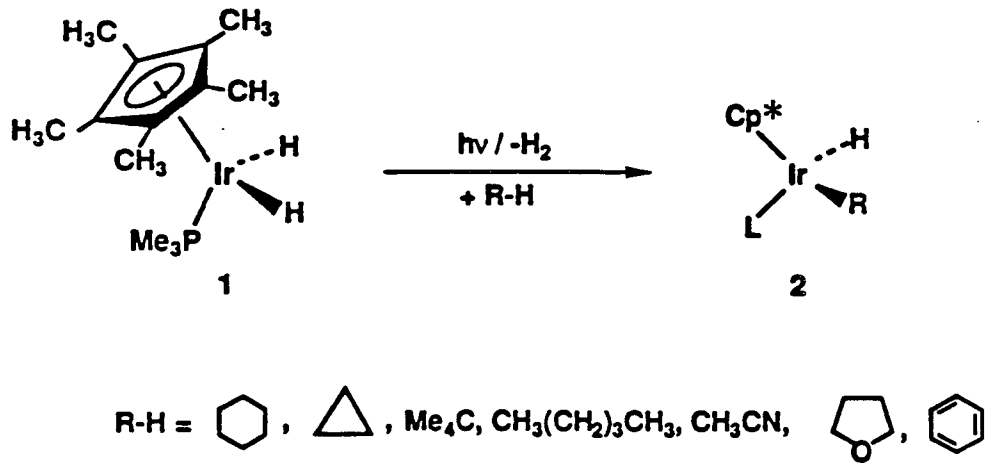
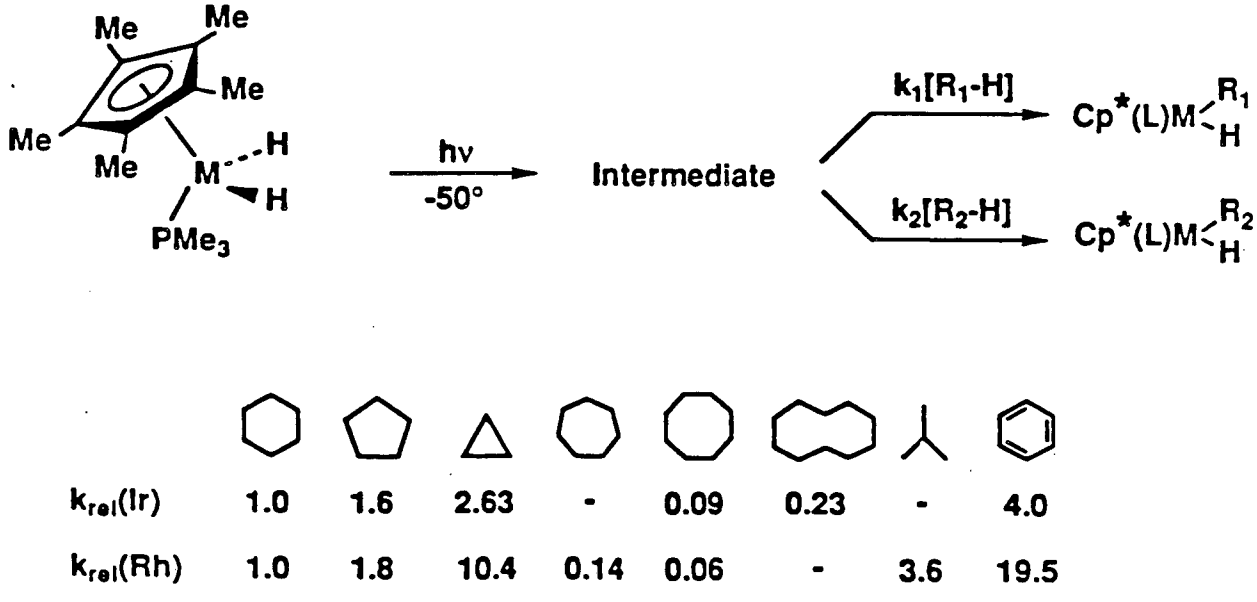
14. Wasserman, E. P.; Bergman, R. G.; Moore, C. B., unpublished results.

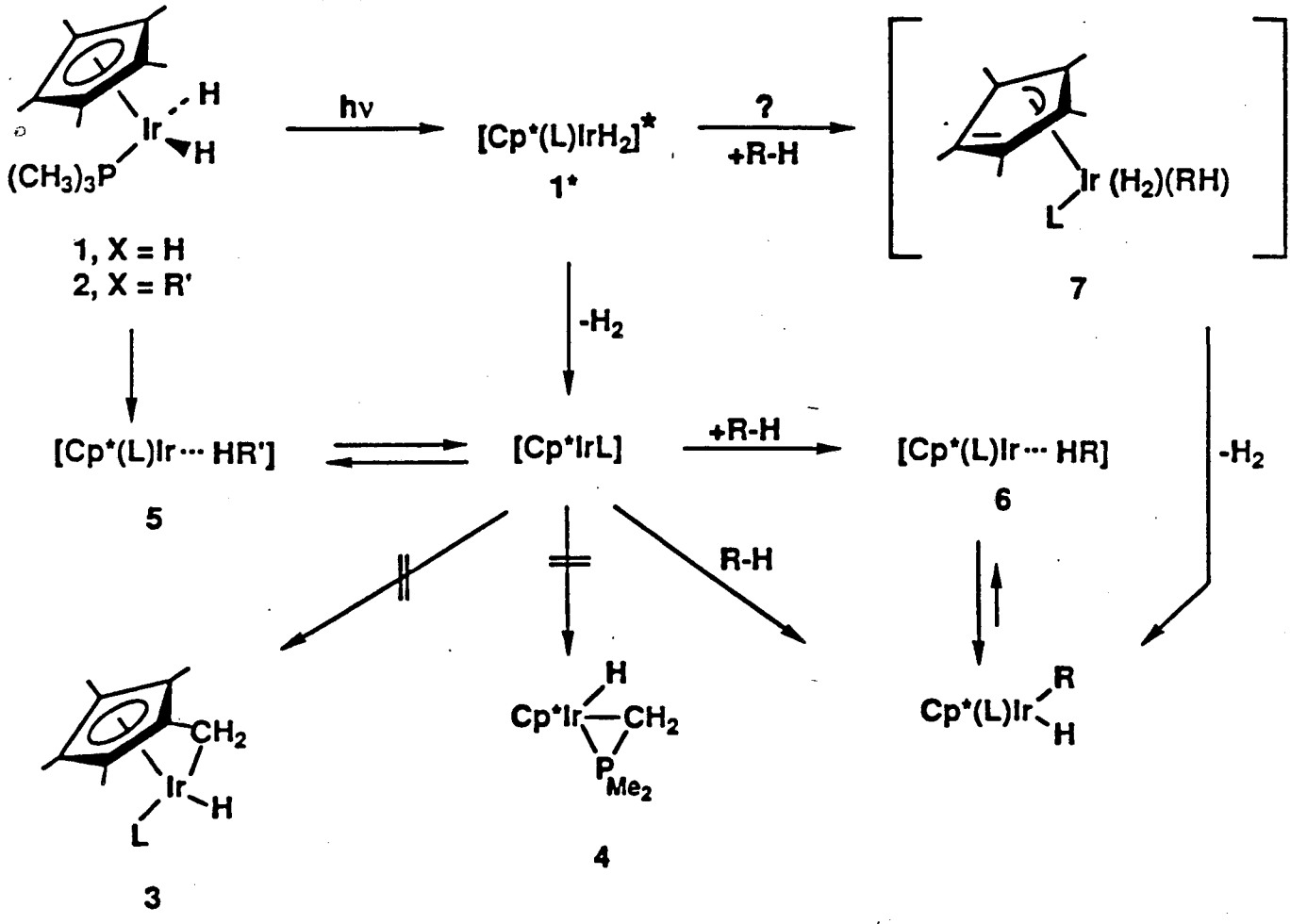
Scheme 1



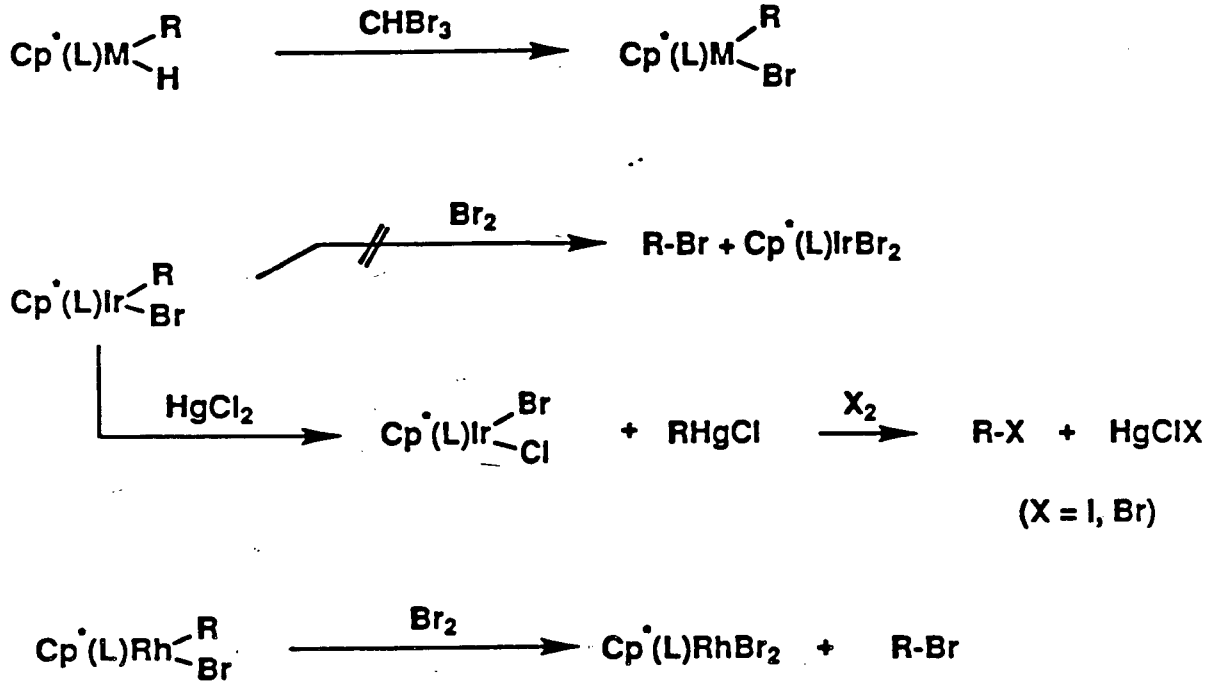
Scheme 2



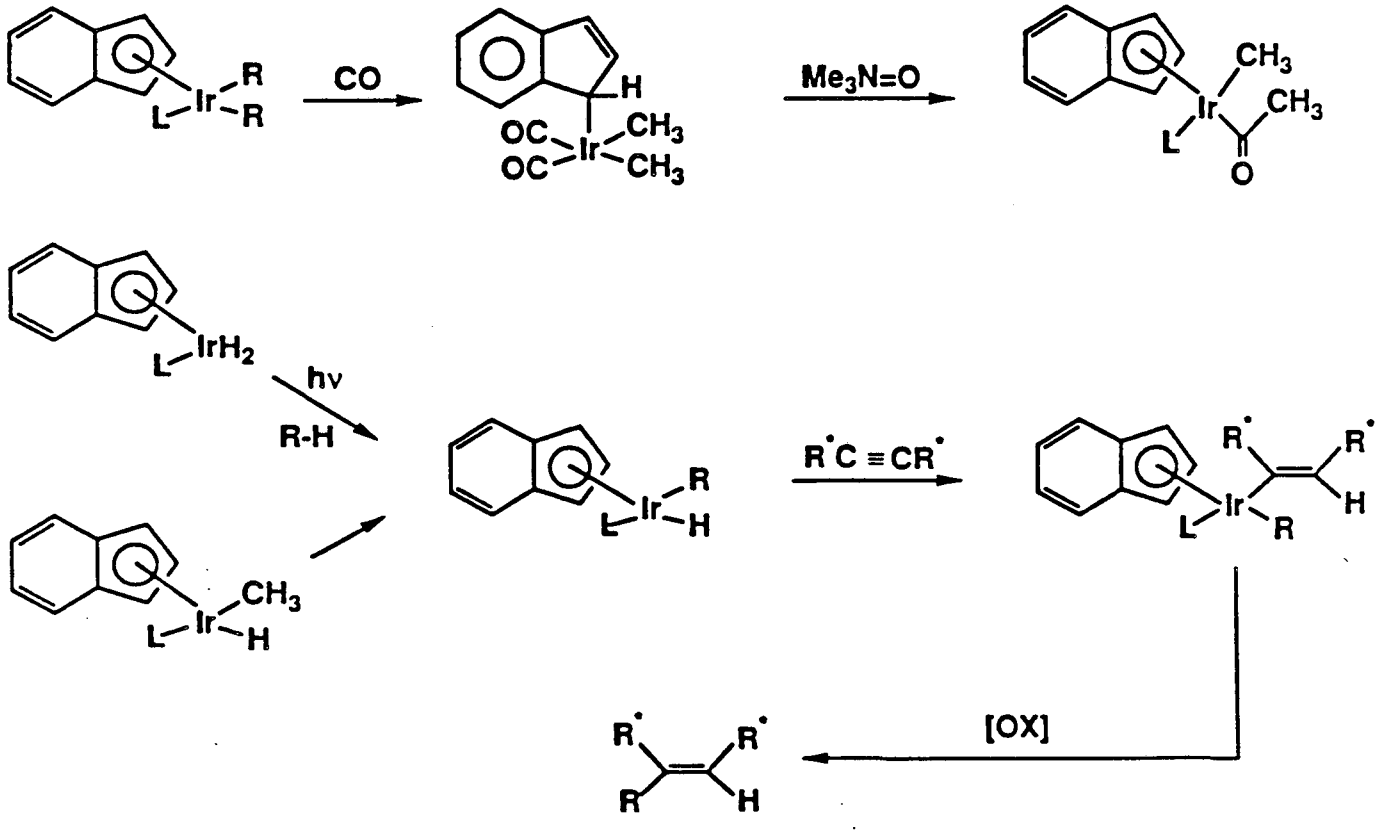
Scheme 3


hν
[Cp*(L)IrH2]*
1*
?
+R-H
Ir (H2)(RH)
L
7
1, X = H
2, X = R'
-H2
[Cp*(L)Ir··· HR']
5
[Cp*IrL]
+R-H
[Cp*(L)Ir··· HR]
6
-H2
R-H
CH2
Ir
H
L
3
Cp*Ir
CH2
PMe2
4
Cp*(L)Ir
R
H

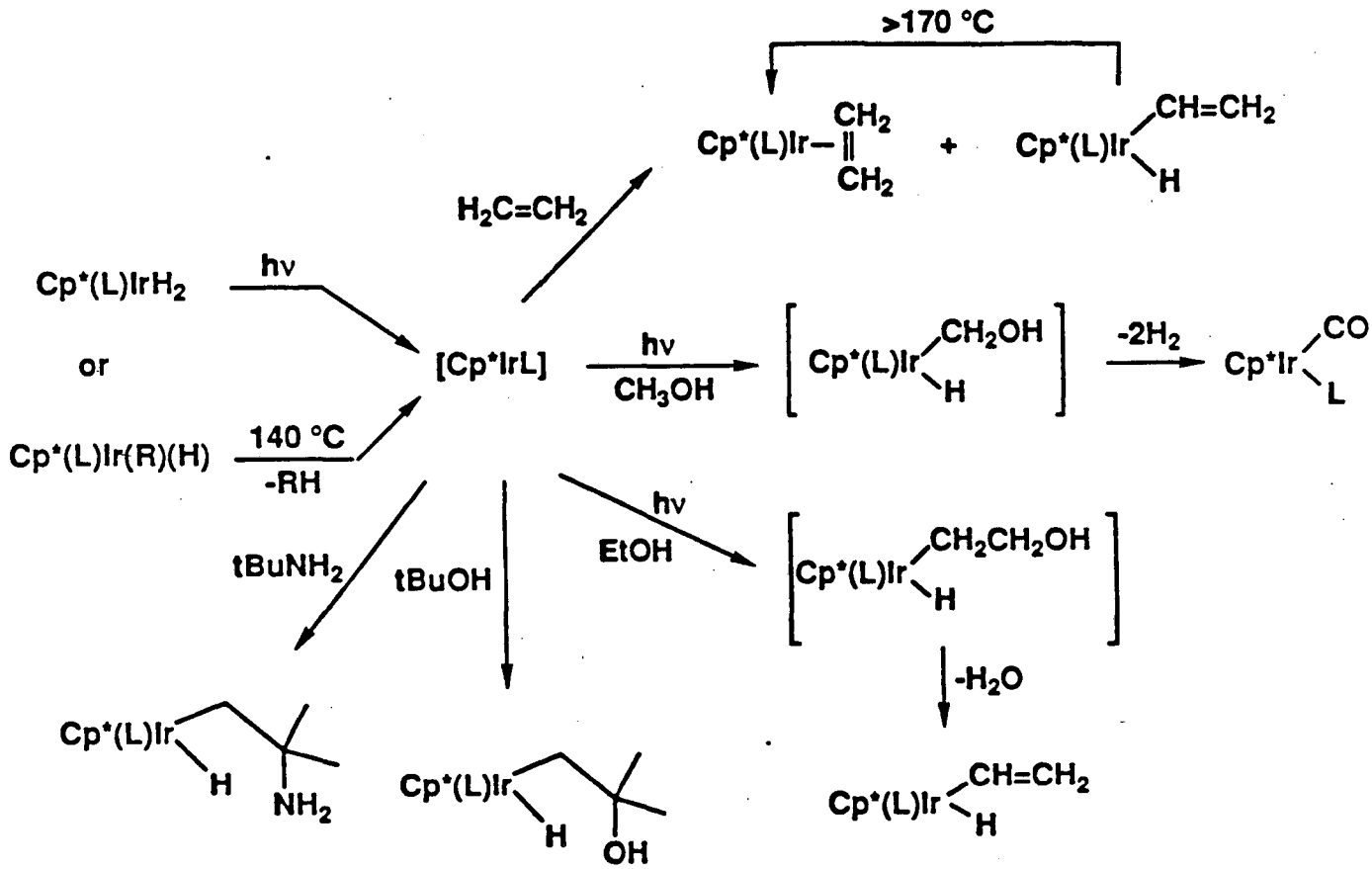
Scheme 4



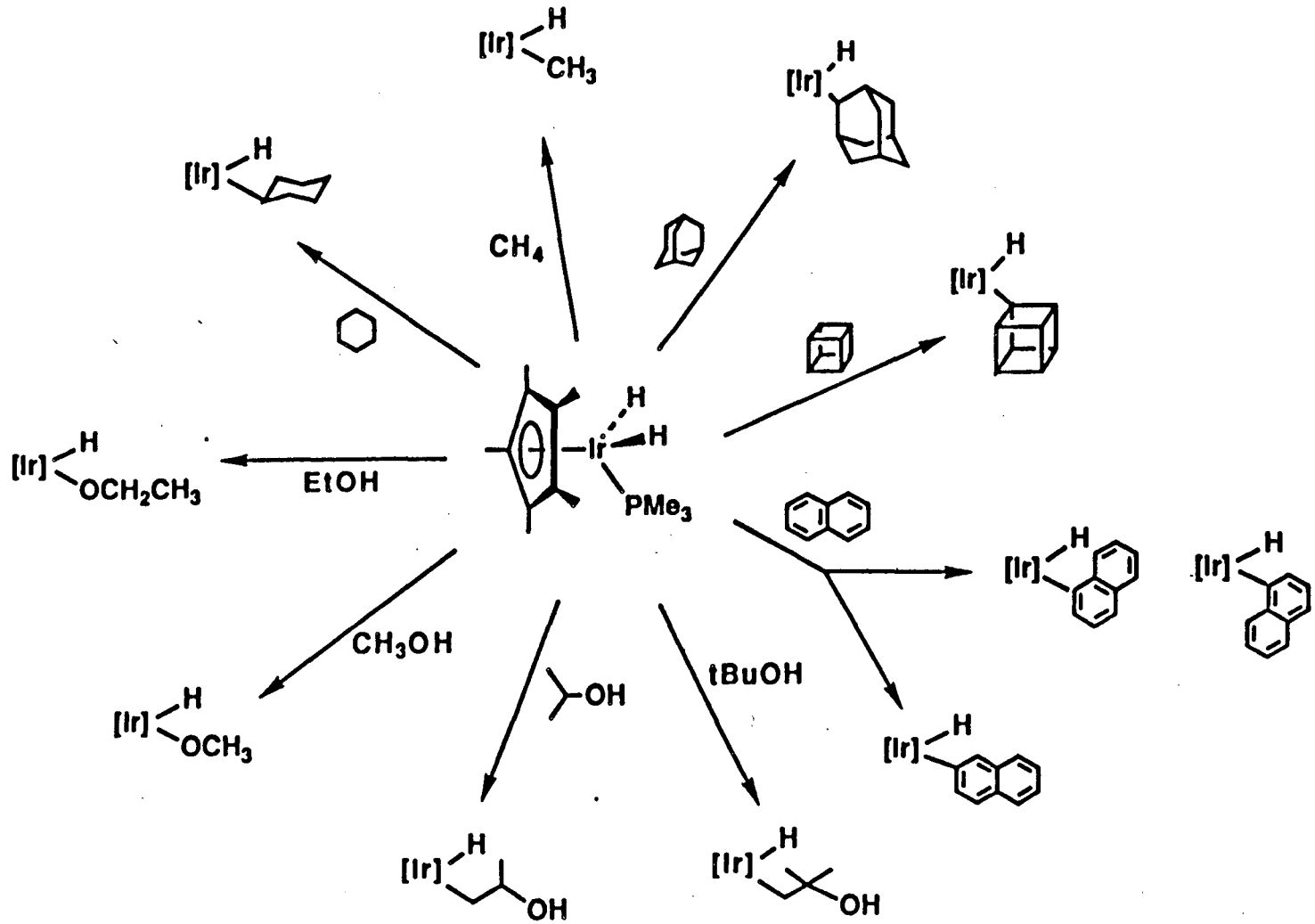
Scheme 5



Scheme 6


>170 °C
Cp*(L)Ir—CH2=CH2
+
Cp*(L)Ir(CH=CH2)(H)
H2C=CH2
Cp*(L)IrH2
hν
or
Cp*(L)Ir(R)(H)
140 °C
-RH
[Cp*IrL]
hν
CH3OH
Cp*(L)Ir(CH2OH)(H)
-2H2
Cp*Ir(CO)(L)
tBuNH2
tBuOH
hν
EtOH
Cp*(L)Ir(CH2CH2OH)(H)
-H2O
Cp*(L)Ir(H)(NH2)
Cp*(L)Ir(H)(OH)
Cp*(L)Ir(CH=CH2)(H)

Scheme 7: Products formed on irradiation of solutions of 1 and the indicated organic molecules in liquid xenon at –60 to –75 °C.



([Ir] = Cp^*IrPMe_3)

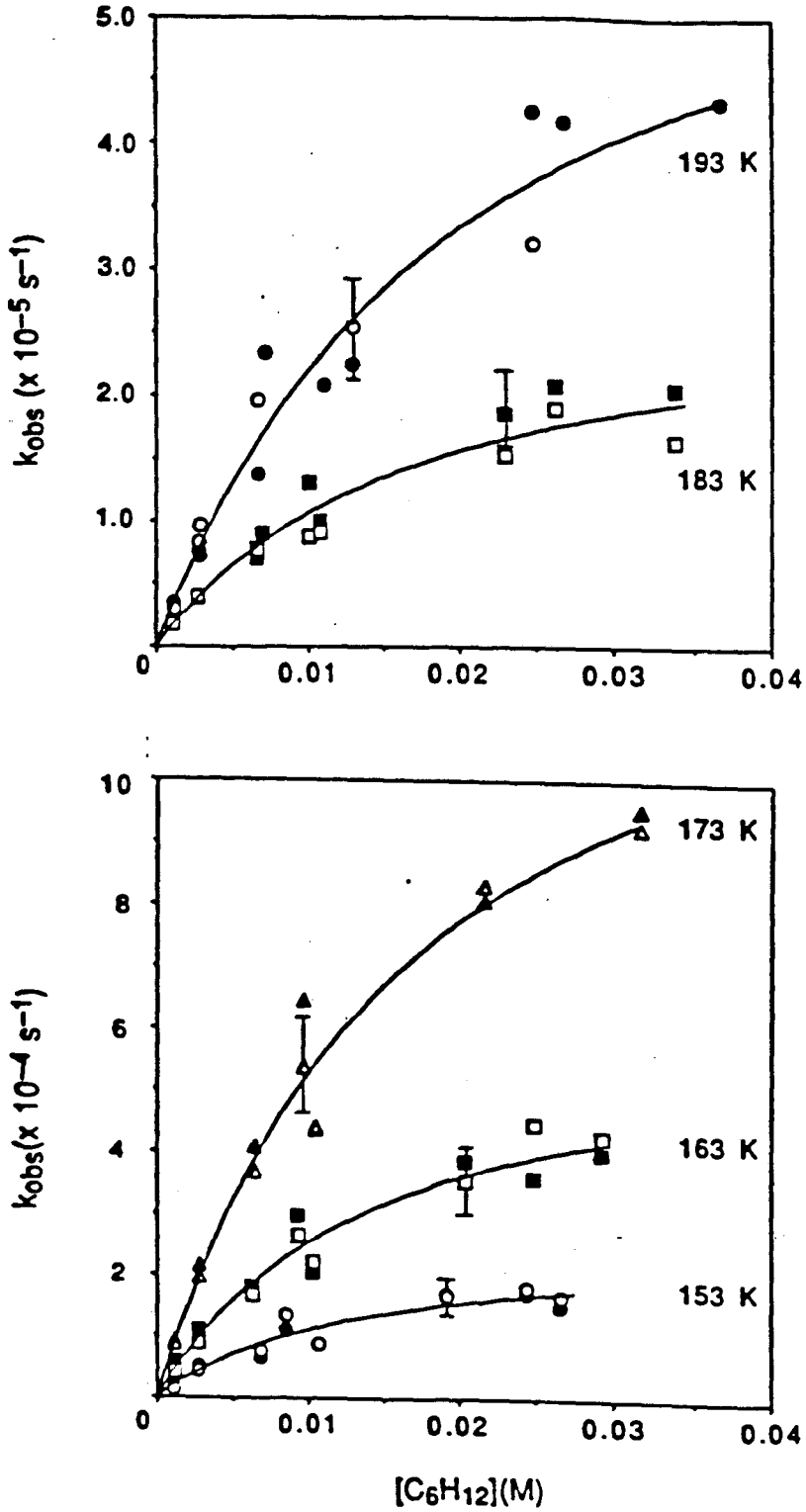


Figure 1. The observed rate constants (k_{obs}) for the decay of the transient at 1947 cm^{-1} (filled symbols) and for the formation of the product at 2003 cm^{-1} (open symbols) as a function of cyclohexane concentration and temperature. For clarity, only representative error bars are indicated explicitly.

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