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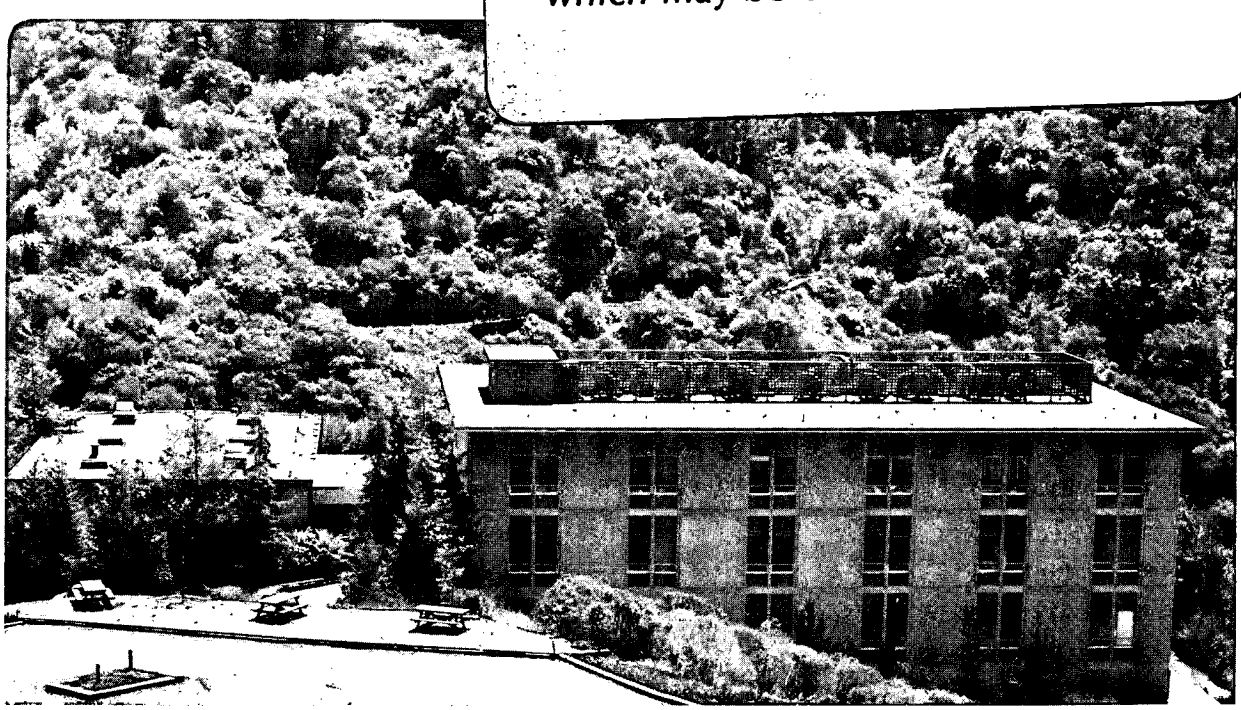

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Oxidative Addition of C-H Bonds in Organic Molecules to Transition Metal Centers

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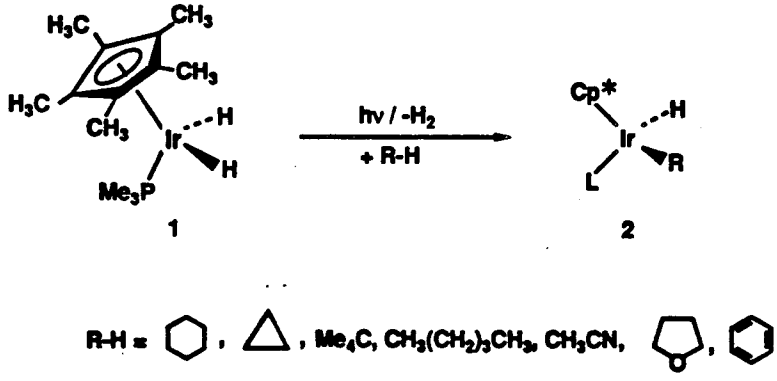
Alkanes are among the most chemically inert organic molecules. They are reactive toward a limited range of reagents, such as highly energetic free radicals and strongly electrophilic and oxidizing species. This low reactivity is a consequence of the C-H bond energies in most saturated hydrocarbons.[1] These values range from 90 to 98 kcal/mole for primary and secondary C-H bonds; in methane, the main constituent of natural gas, the C-H bond energy is 104 kcal/mole. This makes methane one of the most common but least reactive organic molecules in nature.

The potential for using alkanes 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.[2] Intramolecular oxidative addition of C-H bonds to metal centers has been

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

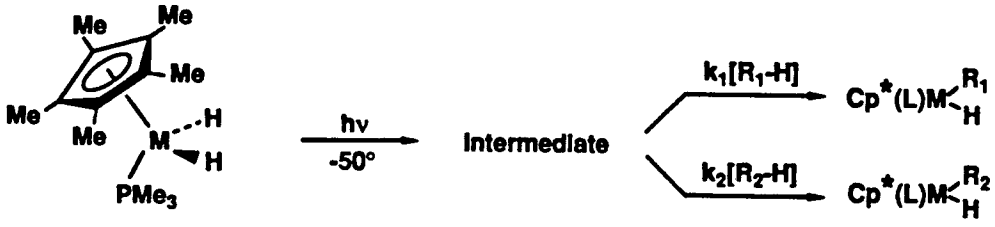
known for some time, but despite many efforts a direct observation of the corresponding intermolecular alkane C-H oxidative addition process illustrated in eq. (1) was not uncovered until 1982. At that time our group and Graham's independently found that irradiation of complexes such as $Cp^*(L)IrH_2$ (**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**).[3] 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 photochemical transformation. Some of the solvents that have been observed to give intermolecular C-H insertion products upon irradiation of **1** are illustrated in Scheme I.

Scheme 1



Much has been learned about the scope and mechanism of this reaction. 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 one first-row metal (iron).[4] The selectivity of the iridium and rhodium C-H oxidative addition reactions have been investigated by carrying out competition studies with various hydrocarbon substrates.[3b, 4b] 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 addition proceeds 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, influence the rate of attack of the metal center on particular C-H bonds.

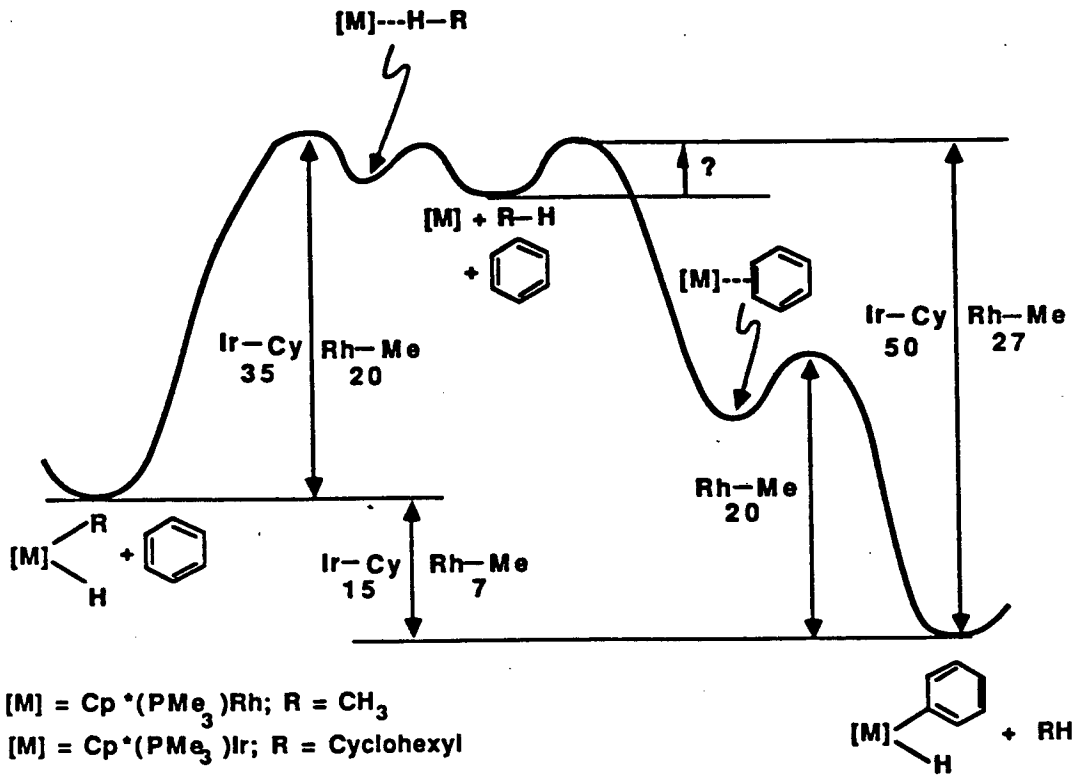
Scheme 2



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

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 Cp*(L)Ir(R)(H) to temperatures above 100 °C. This provides a thermal, rather than photochemical, method for carrying out the C-H insertion reaction. Kinetic, calorimetric and labeling studies have been carried out on these thermal C-H oxidative addition processes.[5] 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 16-electron Cp*ML intermediate, which can then be trapped by other hydrocarbons. Strong evidence has also been obtained that π- (or "η^2-arene") complexes are formed as relatively stable intermediates in the benzene C-H activation process,[6] and more weakly bound alkane "σ-complexes" intervene in the saturated hydrocarbon oxidative addition process before full C-H bond cleavage occurs.[7] 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.[8] The energetics of the processes that occur when cyclohexane and benzene C-H bonds are exchanged at iridium (determined in our work[6,10]), and when methane and benzene C-H bonds are exchanged at rhodium (from the work of Jones and Feher[9]) are summarized and compared in the diagram illustrated in Scheme 3. As shown in the drawing, the overall conversion from alkyl hydride to

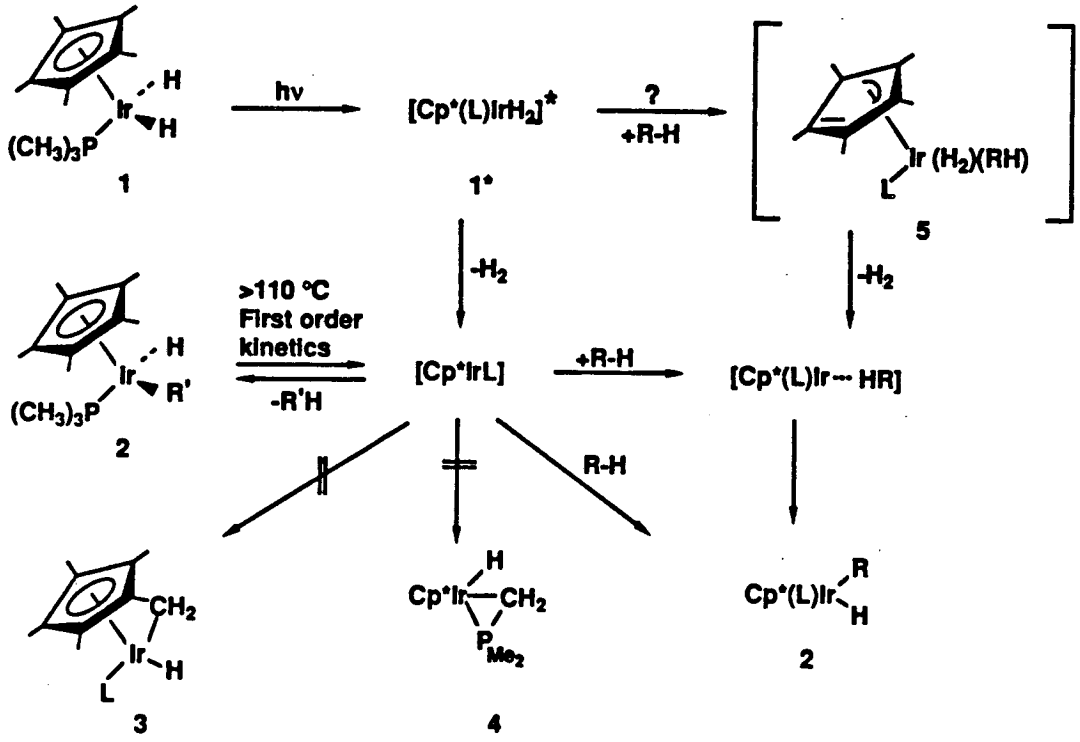
Scheme 3



phenyl hydride is exothermic in both systems, but each alkyl hydride must surmount a significant energy barrier to reach the 16-electron Cp*ML species that is capable of reacting with the C-H bond of benzene.

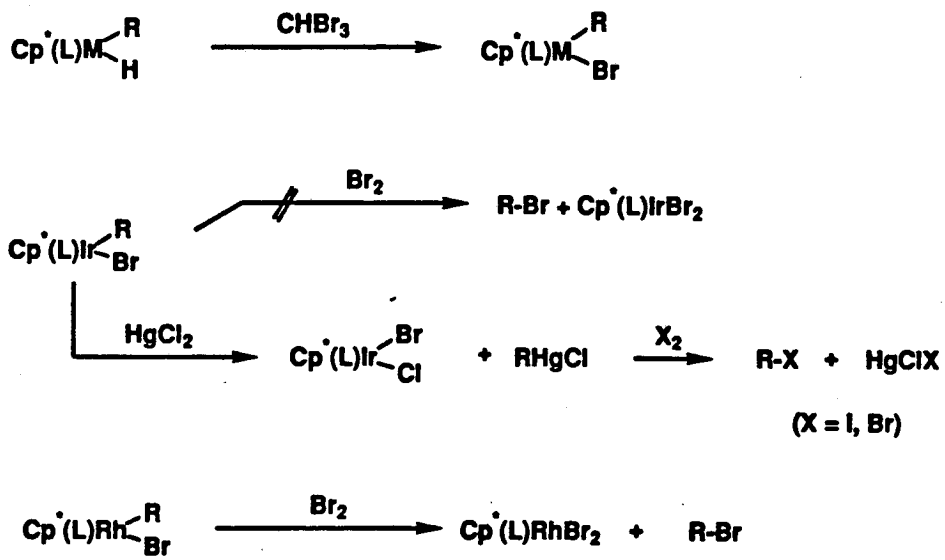
The studies summarized above raise a number of important questions about the C-H oxidative addition process. Some of these are being addressed in current work, and preliminary results are illustrated in Scheme 4. One perplexing problem concerns the fact that unlike many C-H oxidative addition sytems studied earlier, intramolecular cyclometallation products such as **3** and **4** are never observed in our system; the reactions are exclusively intermolecular. Another question concerns whether the photochemical and thermal reactions proceed by analogous mechanisms. As shown in Scheme 4, it is possible that **1***, the excited state of dihydride **1**, when produced photochemically simply extrudes H_2, leading to the same 16-electron complex Cp*ML that is generated in the thermal reaction. Alternatively, the hydrocarbon substrate might attack the excited state **1*** directly, giving an intermediate (e.g., **5**) that would subsequently lose H_2 in a second step. We are attempting to distinguish these possibilities by developing methods to carefully examine the selectivity of the photochemical and thermal iridium reactions under precisely identical conditions. If the photochemical and thermal reactions proceed by different mechanisms, this should be reflected in different selectivities for attack of intermediates **1*** and **5** on different types of C-H bonds.

<u>Scheme 4</u>



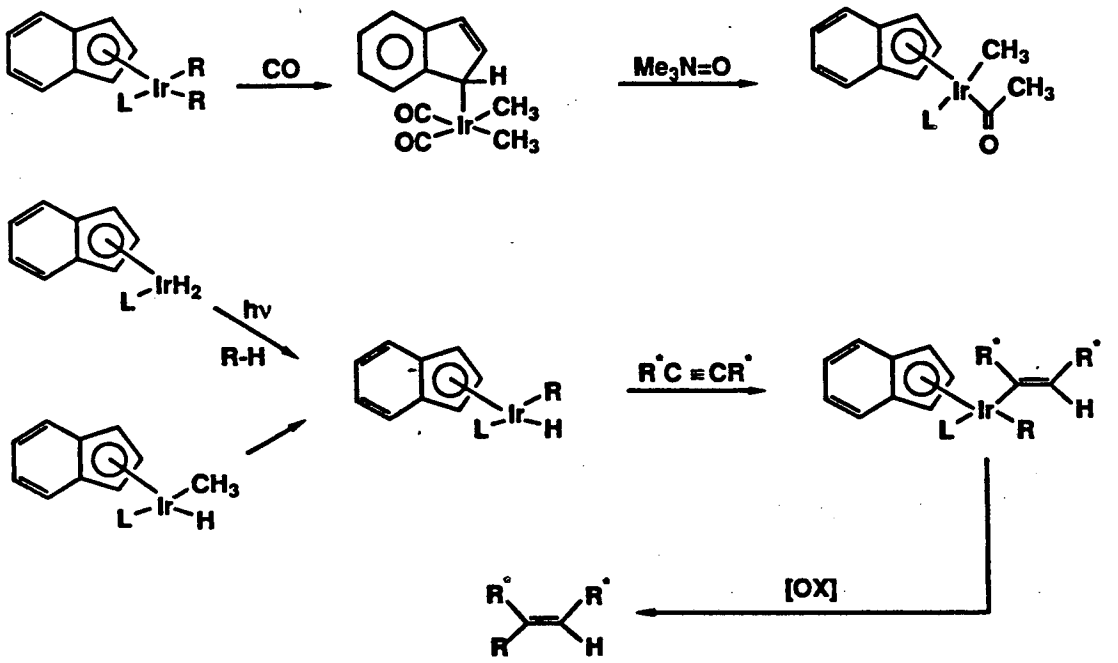
We are also working on the development of methods for the conversion of alkane oxidative addition products to functionalized organic molecules. We have found it possible to convert alkylmetal hydrides to organic halides using the sequences outlined in Scheme 5.[3b, 9]

<u>Scheme 5</u>



However, it would be substantially more useful to generate functionalized molecules by a combination of C-H oxidative addition and migratory insertion to a second coordinated 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 6).[10]

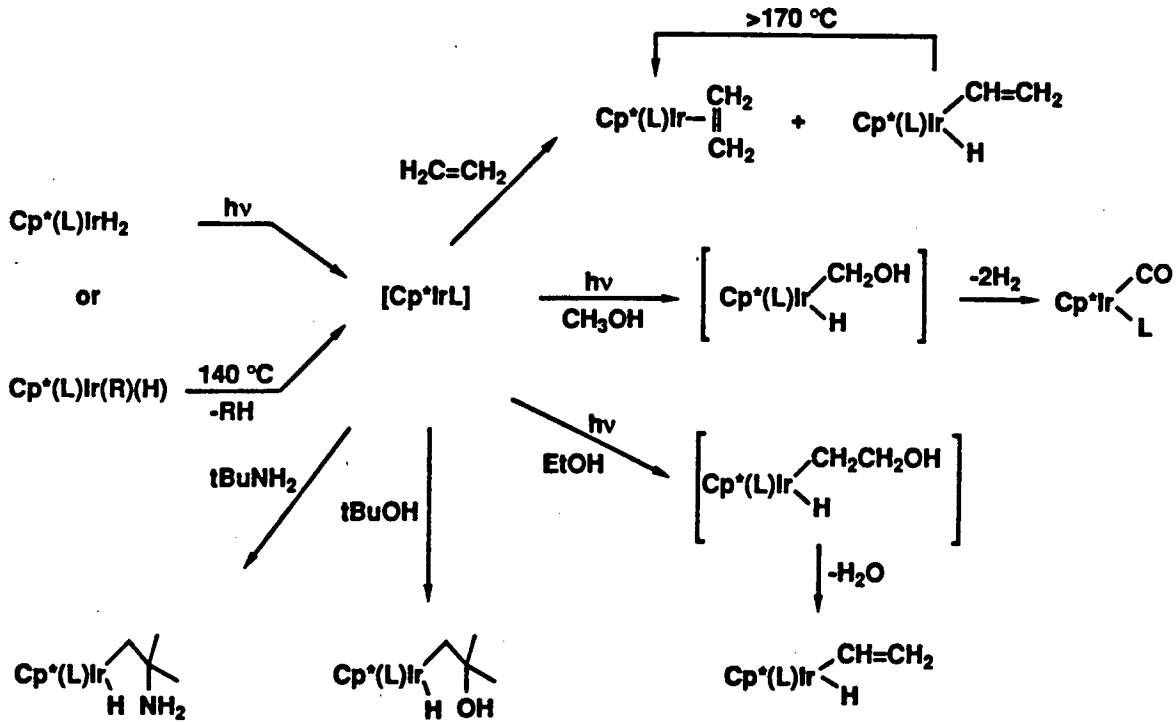
Scheme 6



Most of our initial studies were directed toward the investigation of C-H oxidative addition in alkanes. We have recently began 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 7 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.[11] When the reaction is carried out in alcohol or amine solvents, C-H insertion appears to occur in preference to O-H insertion,[12] although with methanol and ethanol surprising products are produced by subsequent transformation of the proposed initially formed insertion products.

As mentioned earlier, we have not yet found an organic liquid that is unreactive toward Cp*ML, 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.

Scheme 7



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. Initial experiments have demonstrated that xenon liquified at -70 °C and 10 atm pressure does, in fact, serve as an inert solvent for the C-H oxidative addition reaction. This has allowed us to directly examine the reactivity of gaseous substrates such as methane, and solid materials such as naphthalene, adamantane, and even cubane.[13] In addition to these preparative studies, we have utilized liquified noble gases as inert solvents for carrying out flash kinetic studies designed to generate transient coordinatively unsaturated C-H activating intermediates, and directly measure the rates of their reactions with C-H bonds.[14]

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