

Intermolecular Alkane C-H Bond Activation  
by Oxidative Addition to Organometallic Compounds

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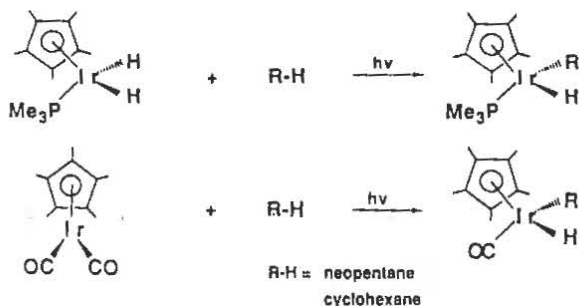
Literature Seminar

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Alkanes constitute a large portion of naturally occurring fossil fuels such as petroleum and natural gas and play a major role in the chemical industry as several heterogeneous processes are producing large amounts of important petrochemical products using alkanes as feedstocks. But it has been a long standing challenge to organometallic chemists to discover a plausible approach to selectively and catalytically activate and functionalize paraffin C-H bonds under relatively mild conditions using discrete organometallic compounds [1].

In contrast to the success of C-H bond activation in hydrocarbonyl ligands incorporated in organometallic molecules (intramolecular C-H activation or cyclometallation) reported in the 1960's and 1970's, attempts to activate C-H bonds in external alkanes using soluble transition metal complexes generally failed, although there have been reports that H/D exchange in light aliphatic alkanes can be achieved using platinum salts as catalysts [2]. The mechanism of this process is not well established and the debate over the involvement of a heterogeneous catalyst (colloidal Pt) is not settled. Another prevalent category of reactions involves the cleavage of activated C-H bonds, such as those in arenes, olefins and other functionalized organic molecules. One postulate holds that the lack of progress in intermolecular alkane C-H bond activation could be mainly for thermodynamic reasons [3]. Metal-carbon bonds are normally weak (18-25 kcal/mol for cobalt and manganese), while the C-H bonds in alkanes are strong and the overall C-H bond oxidative addition to a first row organometallic moiety is considered to be a thermodynamically unfavorable process.

The earliest reports of successful syntheses of cis-alkyl hydrido organometallic compounds directly from alkanes came from Bergman's [4a] and Graham's groups [6a] in 1982. The compound used in Bergman's study is  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)_2\text{H}_2$ , which was irradiated at room temperature in saturated hydrocarbon solvents. Products  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)(\text{R})(\text{H})$  were characterized and deuterium labelling studies ruled out a radical process. The elimination of  $\text{H}_2$  to give a  $16 e^-$  intermediate followed by alkane oxidative addition is consistent with experimental observations [4b]. An  $\eta^2\text{-}\sigma$  complex is suggested as the transition state for the alkane oxidative addition, based on results from the microscopic reverse reaction, reductive elimination of alkanes from  $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{R})(\text{H})$  [5]. The complex  $\text{Cp}^*\text{Ir}(\text{CO})_2$ , as shown by Graham and coworkers, also reacts with various alkanes under photolysis [6a-b]. It is believed that the initial step in generating a  $16 e^-$  intermediate is CO loss, as confirmed by a low temperature methane matrix experiment [7a]. There is, however, evidence that the presence of CO does not reduce the benzene C-H bond oxidative addition rate, as reflected by photochemical quantum yield [7b]. Subsequent reports describing the activation of saturated alkanes by analogous rhodium [4c-d] and rhenium [4e] systems have appeared.



To understand the thermodynamic driving force of these seemingly exceptional systems, bond disruption enthalpies of Ir-C and Ir-H in  $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{R})(\text{H})$  were measured. It was found that iridium has much stronger Ir-C and Ir-H bonds than those formed by its lighter congeners, cobalt and rhodium. The reaction of  $[\text{Ir}] + \text{R-H} \rightarrow \text{R}-[\text{Ir}]-\text{H}$  [ $\text{Ir}] = \text{Cp}^*(\text{PMe})\text{Ir}$ ] is an exothermic process [8].

A molecular orbital study was carried out using the extended Huckel method to calculate the potential energy surface of  $\text{CH}_4$  approaching unsaturated organo-metallic fragment [9]. The approach of  $\text{CH}_4$  to a bent  $d^8 \text{Rh}(\text{CO})_4^+$  is energetically favored over approach to a square planar molecule. This is attributed to the energy level of the HOMO  $d_{yz}$  orbital which controls the oxidative addition activation barrier. The higher the energy of the  $d_{yz}$  orbital is, the lower the activation energy. An example of a bent  $\text{ML}_4$  C-H activating molecule is carbonyl[tris(3,5-dimethylpyrazolyl)borato]rhodium(I) which shows enhanced photochemical efficiency [10]. It is also predicted that the  $d^{10}$  trigonal  $\text{ML}_3$  and bent  $\text{ML}_2$  intermediates should insert into C-H bonds. This is confirmed by the report that a (diphos)platinum(0) intermediate can activate saturated C-H bonds at mild temperatures in dilute solutions [11].

An important goal has also been the control of the selectivity of alkane C-H bond activation. This includes the selective activation of external C-H bonds without cyclometallation of the ligand, activation of saturated C-H bonds, and the activation of primary C-H bonds. Since cyclometallation is always favored thermodynamically (by entropy arguments) over the intermolecular process provided no ring strain is involved, it is fundamental to know what makes the aforementioned systems special in choosing external C-H bonds. Crabtree concluded, after studying various complexes known to have an agostic C-H interaction [12a-b] and summarizing previous works concerning intramolecular C-H activation [13a-b], that there is a delicate balance between the conformational change needed to reach the transition state and the steric crowding around the metal that governs the inter- vs. intramolecular selectivity. Intermolecular reaction is favored by the former factor but the latter factor acts against it. Jones shows that  $\text{Cp}^*(\text{PMe}_2\text{Pr}^n)\text{Rh}$  can react with both n-propane (intermolecular C-H bond activation) and the phosphine n-propyl substituent (cyclometallation). The latter process is more exothermic, but needs to overcome a larger activation barrier [14]. The more sterically encumbered  $\text{Cp}^*\text{Re}(\text{PMe}_3)_3$  also shows reduced reactivity towards external C-H bonds [15].

The working hypothesis concerning the generally more facile arene or olefin C-H bond activation is that arenes can precoordinate to the metal center through  $\pi$ -electrons so that they have lower energy access to the transition states of oxidative addition. This is found to be the case in arene C-H bond activation by

$\text{Cp}^*(\text{PMe}_3)\text{Rh}$  [16a-c] but not for the reaction between ethylene and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}$ . The authors of the Ir work proposed a  $\sigma$ -ethylene complex to be the intermediate [17a-b].

The preference for primary C-H bonds in both the iridium and rhodium systems seems to be the results of the steric requirements of the transition states and the bond energies of the products. A carbon atom with bulkier substituents forms a less stable metal-carbon bond. Rhodium is observed to have better selectivity than iridium, presumably because of the strength of the metal-carbon bonds [18a-b].

All the above systems give only stoichiometric C-H bond activation. Although cis-alkyl hydrido complexes can be transformed into alkyl halides, which can then reductively eliminate RX in the presence of  $\text{Br}_2$  or  $\text{HgCl}_2$ , the yields are far from satisfactory. It was observed several years before the first isolation of the cis-alkyl hydrido complexes that certain iridium and rhenium polyhydrides can catalyze dehydrogenation of cycloalkanes with the help of a hydrogen acceptor such as t-butylethylene, and incorporate the product diene as a ligand. By varying the phosphine ligand and the reaction conditions, catalytic dehydrogenation of cycloalkanes was achieved with moderate turnover numbers [19a-d]. The catalytic cycle is proposed to contain a step in which the alkane C-H bond oxidatively adds to the metal.

Further investigation is underway in the discovery of complexes that facilitate catalytic alkane C-H bond functionalization as well as systems that can shed more light on the fundamentals of this process.

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