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OXIDATIVE ADDITION OF ORGANOTRANSITION METAL COMPLEXES TO THE C-H BONDS IN ORGANIC MOLECULES

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Presented at the Catalytica, Inc. Workshop on  
Carbon-Hydrogen Activation, Sanibel Island, FL,  
April 27-28, 1985

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COMPLEXES TO THE C-H BONDS IN ORGANIC MOLECULES

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April 1985

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**Oxidative Addition of Organotransition Metal Complexes  
to the C-H Bonds in Organic Molecules**

By Robert G. Bergman

Presented at the Catalytica, Inc. Workshop on Carbon Hydrogen Activation  
Sanibel Island, Florida - April 27-28, 1985

**MATERIALS & MOLECULAR  
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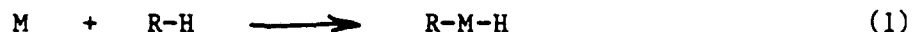
By Robert G. Bergman

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Presented at the Catalytica, Inc., Workshop on Carbon-Hydrogen Activation  
Sanibel Island, Florida, April 27-28, 1985

I. Initial Results

Early in 1982 the first examples of direct intermolecular oxidative addition of a transition metal into the C-H bonds of alkanes (eq. (1)) were reported<sup>1,2</sup>. In our group, Cp\*(L)IrH<sub>2</sub> (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; L = PMe<sub>3</sub>) was irradiated with ultraviolet light, extruding H<sub>2</sub> and leading to an



intermediate which we formulated as the reactive, coordinatively unsaturated species Cp\*Ir(L). This transient species reacts rapidly with all solvents (R-H) to which it has so far been exposed, leading to oxidative addition products Cp\*(L)Ir(R)(H).

II. Mechanistic Studies

Since this discovery, extensive work has been done aimed at examining the characteristics, scope and mechanism of this reaction.<sup>3,4</sup> After much effort, purification and full characterization of several of the very sensitive oxidative addition products have been achieved by chromatography at low temperatures (-60 to -100 °C). In one case (the cyclohexane addition product), good crystals have been obtained, and an X-ray structure completed.<sup>5</sup> This has demonstrated that the hydrocarbon C-H bond is fully broken, and new M-C and M-H bonds formed in the oxidative addition.

Mechanistic studies suggest a concerted, three-center transition state for the oxidative addition, rather than a more complicated stepwise process (e.g., one involving free radicals). In support of this mechanism, crossover experiments have been used to demonstrate that the R and H groups connected in the substrate molecule remain associated with one another in the final product. In addition, the C-H oxidative addition proceeds with a small but finite isotope effect ( $k_H/k_D = 1.4$ ), similar to that observed for carbene insertion into C-H bonds.

III. Selectivity

The oxidative addition reaction shows unexpected selectivity. Under no

circumstances are products derived from intramolecular C-H insertion (cyclometallation) formed; i.e., in contrast to most other known C-H insertion systems, the inter-/intramolecular selectivity is quite high. In addition, insertion into tertiary C-H bonds is not observed, indicating that secondary/tertiary and primary/tertiary selectivity is also high. Discrimination between different types of C-H bonds which do undergo insertion is weaker, although the trends observed are interesting. Thus, the most reactive C-H bond so far examined is that in benzene; it undergoes insertion about 50 times more rapidly than the least reactive bond, which is in cyclooctane. Within the series of organic compounds whose selectivity we have studied, no correlation of relative rates with the homolytic C-H bond energies exists, further supporting the postulate that organic radicals are not involved as intermediates in these reactions.

#### IV. Other Metals

Subsequent to the discovery of these iridium-based reactions, intermolecular insertions involving rhodium<sup>6,7</sup> and rhenium<sup>8</sup> have been uncovered. Work on the rhodium system  $Cp^*(L)RhH_2$ <sup>9</sup> has also been carried out independently in Prof. William Jones' laboratory. Both groups have found that the intermediate generated on irradiation of this dihydride,  $Cp^*Rh(L)$ , mimics the iridium system in its oxidative addition reaction with arenes and alkanes. It differs, however, in that the products of oxidative addition  $Cp^*(L)Rh(R)(H)$  are considerably less stable, undergoing reductive elimination of alkane at temperatures below ambient. The rhodium system parallels the iridium system in its selectivity, but the rate constant ratios measured relative to cyclohexane are larger, consistent with the lower exothermicity of the rhodium reactions.

In the case of rhenium we have found that reactive 16-electron intermediates of general type  $Cp^*ReL_1L_2$  can be generated from appropriate 18-electron cyclopentadienylrhenium precursors.<sup>8</sup> As in the iridium and rhodium series, these species undergo intermolecular oxidative addition into alkane and arene C-H bonds. However, in this case insertion into secondary, as well as tertiary, C-H bonds is not observed. This provides a method for selective activation of the terminal methyl hydrogens in linear alkanes such as hexane. It also has allowed us to utilize cyclic alkanes such as cyclohexane as inert solvents, a situation which was impossible with the more reactive rhodium and iridium systems. Also in contrast to the earlier-studied systems, generation of  $Cp^*ReL_2$  in unreactive solvents leads to cyclometallation of the L ligand. This intramolecular insertion is reversible at room temperature, and so the cyclometallation product can be used to regenerate the reactive intermediates. This proves to be a useful method for generating methane and ethylene C-H activation products in the Re system.

#### V. Current and Future Studies

A number of important questions have been raised by the results summarized in the above paragraphs, and work currently in progress is aimed at addressing them. The most important issues are the following.

1. Factors controlling attack at primary, secondary and tertiary C-H bonds. The factors which control primary/secondary and primary/tertiary selectivity, especially in cases in which one of these processes does not

occur at all (i.e., tertiary attack in the Ir and Rh systems; both secondary and tertiary attack by Re) are not understood. In addressing this problem, it is essential to distinguish kinetic and thermodynamic products. For example, for Ir and Rh we do not yet know whether attack at tertiary C-H bonds is inherently slow, or whether these products are formed and simply undergo the reverse reaction (reductive elimination) so rapidly that they cannot be detected. In order to test this possibility, independent syntheses of the undetected hydrido(alkyl)metal complexes must be developed, so that their stability to the C-H insertion reaction conditions can be examined.

2. Intra- vs. intermolecular selectivity. The physical causes which underlie the relative propensity for intra- and intermolecular oxidative addition in a given system are not understood. It is unclear why certain complexes, such as the Ir system described in this work, undergo intermolecular insertion so readily, whereas other rather similar systems (especially those based on platinum, the metal known to undergo heterogeneous reaction with alkanes) do not. Halpern has suggested that the stability of the oxidative addition products  $M(R)(H)$  may be a critical factor.<sup>10</sup> Apparently unreactive systems may undergo intermolecular insertion, but the products may be unstable relative to cyclometallation products, and simply undergo reductive elimination too rapidly for detection. Similarly, in our Ir system, it is possible that the reverse is true--undetected cyclometallation products may for some reason (perhaps steric, as Halpern has proposed) be the less stable species, and if formed, undergo rapid reductive elimination under the reaction conditions. In order to test these possibilities, as discussed in paragraph (1) above it is essential to develop independent syntheses of the undetected complexes, and subject them to the reaction conditions. In our Ir and Rh systems, we are searching for good routes to the complexes in which the  $PMe_3$  and  $Cp^*$  ligands are cyclometallated. Similarly, in systems where intermolecular addition is not observed, it is critical to prepare independently and test the stability of the undetected intermolecular products (e.g.,  $L_2Pt(R)(H)$ ;  $(CO)_4Os(R)(H)$ ;  $Cp^*(CO)_2Re(R)(H)$ ). The  $Cp^*ReL_2$  system provides a particular advantage, since it is one of the very few in which both intra- and intermolecular alkane C-H bond activation occur at similar rates. It is hoped that further studies of this system will provide insight into the intra-/intermolecular selectivity problem.

3. Relationship of acidity to the nature of the C-H bond attacked. The factors which control the relative rates of attack on different types of C-H bonds which do lead to insertion products are also not well understood. As mentioned above, no correlation between relative rates of attack and homolytic C-H bond dissociation energy exists. A better correlation may exist with acidities of the reacting hydrogens, but this will only be clear when data on insertion into organic compounds with more accurately known  $pK_a$ 's are available.

4. Alkane functionalization and oligomerization. Successful functionalization of alkanes requires C-H activation as a first step, followed by conversion of the activation product  $Cp^*(L)Ir(R)(H)$  into a functionalized organic molecule R-X. We have achieved one stoichiometric method for conversion of  $Cp^*(L)Ir(R)(H)$  into organic halides. However, much more direct and efficient methods must be developed. Ultimately, it would be most useful if these methods result in regeneration of the reactive intermediate  $Cp^*Ir(L)$ , so that the functionalization process could be made catalytic. A related and

equally important goal is the development of methods for the conversion of light alkanes, such as methane, into higher alkanes of the type which are more easily transportable and can still be used as efficient fuels.

5. Reactions with functionalized organic molecules. Conventional oxidative addition reactions occur most readily at carbon-heteroatom bonds, especially those involving halogen. At present very little information is available on the propensity for insertion of intermediates such as  $\text{Cp}^*\text{M}(\text{L})$  ( $\text{M} = \text{Ir}, \text{Rh}$ ) and  $\text{Cp}^*\text{ReL}_2$  into bonds other than C-H. In order to examine this question, the reaction of the intermediate  $\text{Cp}^*\text{Ir}(\text{L})$  in alkenes and functionalized organic solvents is being investigated. Reaction of  $\text{Cp}^*\text{Ir}(\text{L})$  with ethylene is particularly interesting.<sup>11</sup> Here, both the  $\pi$ -complex  $\text{Cp}^*(\text{L})\text{Ir}(\text{CH}_2=\text{CH}_2)$  and the C-H insertion product  $\text{Cp}^*(\text{L})(\text{H})(\text{CH}=\text{CH}_2)$  are formed. However, the  $\pi$ -complex is completely stable to the reaction conditions, and so cannot be an intermediate in the formation of the insertion product. How insertion occurs without the initial formation of the  $\pi$ -complex is an intriguing question. In some functionalized solvents, apparently straightforward chemistry is observed (e.g.,  $\text{CH}_3\text{Cl}$  gives  $\text{Cp}^*(\text{L})\text{Ir}(\text{CH}_3)(\text{Cl})$ ), but in other cases the results are very unexpected (e.g.,  $\text{tBu-Cl}$  gives  $\text{Cp}^*(\text{L})\text{Ir}(\text{Cl})[\text{CH}_2-\text{CH}(\text{CH}_3)_2]$ ; irradiation of  $\text{Cp}^*(\text{L})\text{IrH}_2$  in ethanol gives  $\text{Cp}^*(\text{L})\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)$ ,<sup>11,12</sup> the same complex observed in the ethylene reaction). The mechanisms of these processes are being investigated.

6. Identification and direct study of reactive intermediates. We have been working under the assumption that the reactive intermediates in these systems are  $\text{Cp}^*\text{M}(\text{L})$  ( $\text{M} = \text{Ir}, \text{Rh}$ ) and  $\text{Cp}^*\text{ReL}_2$ . Kinetic studies carried out on the thermal decomposition of  $\text{Cp}^*(\text{L})\text{Ir}(\text{R})(\text{H})$  are consistent with the unimolecular conversion of this species to R-H and a transient intermediate such as  $\text{Cp}^*\text{Ir}(\text{L})$ , which reacts rapidly with a second alkane R'H. However, the precise structure of this intermediate is not known, nor do we yet have information on the absolute rate of its insertion reactions. Approaches to this problem require the generation of the reactive intermediates under conditions where they can be observed directly. With appropriate precursors, we hope this will be possible using matrix isolation and fast kinetics techniques.

7. Carbon-carbon bond activation. In view of the successful observation of intermolecular C-H insertion, it seems reasonable to consider the possibility of C-C insertion. Since the rate of C-H insertion in any given system is likely always to be faster than C-C insertion, a feasible system may require a complex which undergoes C-H insertion reversibly, but leads to a C-C insertion product which is thermodynamically more stable than the C-H product.

8. Relationship between homogeneous and heterogeneous chemistry. A particularly intriguing problem in this field is the relationship between homogeneous and heterogeneous C-H activation. Alkanes have been known for some time to react easily with metal surfaces, especially platinum.<sup>13</sup> In view of this, the difficulty associated with unearthing homogeneous complexes which mimic these heterogeneous reactions, at least historically, is perplexing. There are many heterogeneous C-H activation reactions which still have no homogeneous models; one of the most intriguing is dehydrocyclization. Ideas for devising accurate homogeneous models for known heterogeneous C-H activation reactions, and for understanding the relationship between homo- and heterogeneous systems, would be extremely useful.



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