

A physical organic road to organometallic C–H oxidative addition reactions

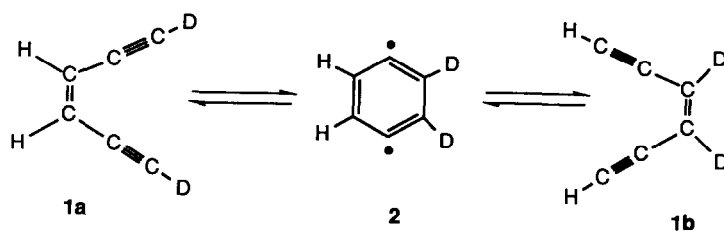
Robert G. Bergman

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley CA 94720 (USA)

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My participation in this anniversary issue of the *Journal of Organometallic Chemistry* is somewhat ironic, because at the time I began my independent research at the California Institute of Technology in 1967 I had barely even heard of the journal. I was trained as a physical organic chemist (my graduate work even included an attempt to solve the nonclassical norbornyl cation problem [1]), and in the 1960s chemistry was quite a compartmentalized field. Exciting things were going on in many chemical sub-disciplines, but with a few important exceptions, cross-talk between these areas occurred less frequently than it does today.

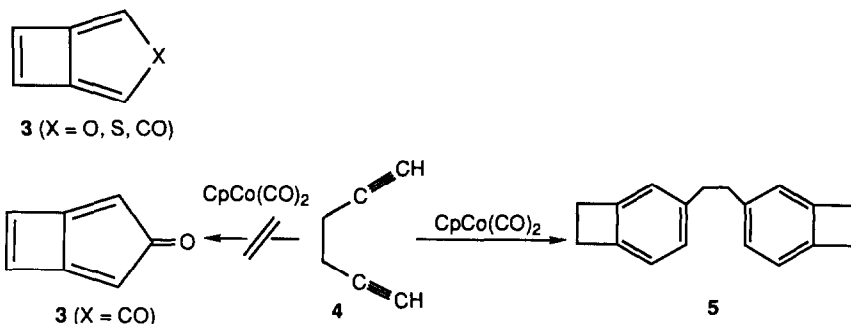
During my early years at Caltech, true to my training with Jerome Berson [1] and Ronald Breslow [2], my group began synthesizing and exploring reactions of unusual new organic molecules and examining the mechanisms of their reactions. William Carter looked at the mechanism of isomerization of optically active cyclopropanes [3], Shelby Sherrod and Donald Kelsey uncovered the first cyclopropyl-substituted vinyl cations [4], and Richard Jones found an interesting thermal rearrangement of 1,5-hexadiyne-3-enes (**1a** / **1b**) that proceeded through a symmetrical “1,4-dehydrobenzene” intermediate with a 1,4-diradical structure (**2**) [5].



On leave at Stanford in 1973, I taught a catalysis course that led me to look at some of the interesting and provocative science that was being published in journals such as *Journal of Organometallic Chemistry*. In addition, John Bercaw joined the Caltech faculty in 1972, and began his intriguing work that eventually led to new organometallic methods for N_2 and CO reduction using early transition metal complexes. From my initial reading and talks with Bercaw, it seemed clear that organometallic chemistry was filled with interesting and unprecedented transforma-

tions whose mechanisms were little understood. This was an insight that a few other individuals, such as Whitesides, Halpern, Collman and Kochi, had already had. However, most of the field seemed still to be virgin territory waiting for someone interested in exploratory and reaction mechanisms chemistry to plow it.

This background, combined with my group's general interest in reactive dehydroaromatic molecules [6] (i.e., aromatic systems such as benzene and cycloheptatrienyl that have two additional hydrogens removed), led Peter Vollhardt to do the first experiments with organotransition metal complexes in my laboratory. After first coming to Caltech Peter had worked out thermal rearrangement syntheses of dehydro-oxepin and -thiepin (3, X=O, S) [7]. We were looking for a method to make dehydrotropone (3, X=CO), and decided to try a simple extension of the well known metal-induced alkyne-plus-CO cocyclization reaction, which had been applied to a tetrasubstituted 1,5-diyne by Macomber [8]. We were unable to extend this reaction to simple diynes (e.g., 4) and ene-diynes, but an intriguing synthesis of benzo-cyclobutenes such as 5 resulted instead. Further studies of this reaction led to our first contribution to mechanistic organometallic chemistry [9].



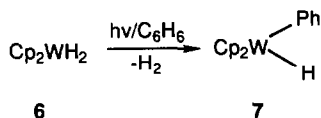
With our interest in the field stimulated, other people who joined my group began to explore related organometallic problems. Although at the time we had no expectations of being able to make a contribution to the alkane C–H activation field, in hindsight it is interesting to see threads of interest among some of my coworkers that eventually led to contributions to the area. Neil Schore and Mary Ann White, for example, initiated some of our early studies of alkyl complexes in the cobalt series, and were the first to utilize crossover experiments to help elucidate organometallic reaction mechanisms in the group [10]. Although Patricia Watson's postdoctoral work was aimed at cationic alkyne complexes, she was astute enough to recognize the significance of one of the C–H bond-breaking processes occurring in her systems [11]. Her interest in this type of chemistry later paid off handsomely in her discovery of lanthanide methane activation reactions at DuPont [12].

Our interest in metal hydrides was stimulated by the efforts of Robert Kinney and William Jones, who looked at reactions of hydridovanadium anions with organic halides [13]. When I decided to move to Berkeley in 1977, Jones moved with me. Among colleagues in the new laboratory were Henry Bryndza and Andrew Janowicz, two of my early Berkeley coworkers, who were carrying on our studies of the chemistry of cobalt alkyls and hydrides. With Frank Feher, one of his early students at Rochester, Jones' interest in hydrides later led him to carry out the first alkane C–H oxidative addition reactions at rhodium [14].

Andy Janowicz was responsible for the first alkane oxidative addition reactions we observed, but we were led to these observations by a circuitous route. Janowicz

had worked out the mechanism of hydrogenolysis of $\text{CpCo}(\text{PPh}_3)_2\text{Me}_2$, which turned out to proceed by a complicated autocatalytic process [15]. We believed that the organometallic product of this reaction—which also served as the autocatalyst—was $\text{CpCo}(\text{PPh}_3)_2\text{H}_2$, but this compound was too unstable to isolate. By then we had learned two things, from John Bercaw and other good organometallic chemists, about how to make stable analogues of unstable molecules: first, change from the parent Cp to the substituted Cp^* ($\eta^5\text{-C}_5\text{Me}_5$) ligand, and second, “go down”—down the periodic table, that is. Andy proceeded to work out syntheses of the three cobalt triad $\text{Cp}^*(\text{PPh}_3)_2\text{MH}_2$ complexes. These were in fact more stable than their cyclopentadienylcobalt relatives, and we were able to fully characterize the rhodium and iridium members of this series.

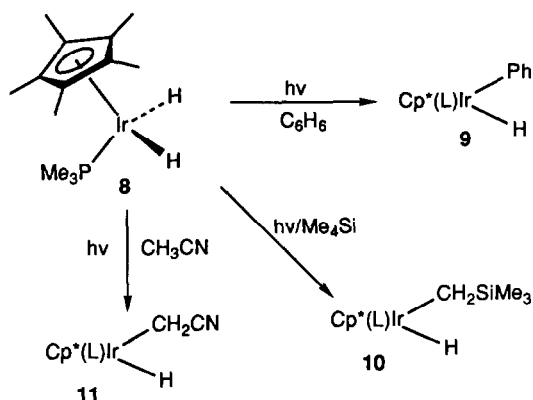
In his excellent retrospective article on iridium C–H activation published in the 300th issue of this journal [16], William Graham mentions his awareness of Malcolm Green’s earlier investigations of the photochemistry of tungstenocene dihydride **6**, leading to products formed by C–H activation of arenes (**7**) and even tetramethylsilane [17]. Graham notes that Green’s observations stimulated his discovery of C–H oxidative addition using $\text{Cp}^*\text{Ir}(\text{CO})_2$, which were carried out independently of and at essentially the same time as ours. We, too, were aware of Green’s work, and the similarity between his tungstenocene complex and our dihydrides did not escape us. Many intramolecular C–H oxidative addition reactions had been observed by then, but examples of intermolecular arene C–H oxidative addition were still rather rare at the time, and alkane C–H activation was of course unknown.



With the simple hope that we might be able to generate a 16-electron intermediate that would mimic Green’s arene C–H activation chemistry, Andy began to study the solution photochemistry of $\text{Cp}^*(\text{PPh}_3)_2\text{IrH}_2$. Graham makes some important points about how his initial Si–H and C–H activation experiments were done, and about the value of isolating and fully characterizing the products of organometallic reactions [16]. Graham notes that he (and Marvin Rausch, who looked at the reaction of $\text{Cp}^*\text{Ir}(\text{CO})_2$ in benzene [18] in 1977) probably carried out the iridium/benzene C–H oxidative addition reaction in 1970. However, pinning down the primary products of the reactions was difficult because of the great sensitivity of the product molecules, a characteristic known to be typical of many hydrido(alkyl) complexes.

We shared Graham’s feeling that the products of reactions should be isolated and identified properly. However, in our laboratory we had adopted the organic chemist’s habit of monitoring exploratory reactions by NMR spectrometry (an easier thing to do in 1981 than 1970). We ran some of our experiments in sealed NMR tubes and observed the results directly (another technique learned from John Bercaw and his coworkers), and some were carried out by irradiation of reaction solutions in stopcock-sealed flasks, followed by removal of the reaction solvent, replacement with deuterated solvent and examination of the crude product by NMR before attempted purification.

Because of the unique position of hydride absorptions in the proton NMR



spectra, this technique provided intriguing results in Janowicz's first C–H oxidative addition experiments [19]. Irradiation of $\text{Cp}^*(\text{PPh}_3)\text{IrH}_2$ in benzene and other liquid hydrocarbons gave new hydride absorptions, due (as we later established) to the formation of both intra- and intermolecular C–H oxidative addition products. We therefore turned to the corresponding trimethylphosphine complex $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ (**8**) in the hope that cyclometallation would be disfavored in this material [20]. The dihydride exhibits a doublet (due to coupling to the iridium-bound phosphorus atom) at -17.38 ppm in its ^1H NMR spectrum in benzene solution. Irradiation in benzene led to cleaner results in this case, leading to loss of H_2 and the observation of one new hydride signal at -16.36 ppm.

From this simple observation we could only conclude that a new hydride had been formed. In order to quickly assess whether we were observing an intra- or intermolecular process, we carried out the reaction in tetramethylsilane and acetonitrile. In these solvents irradiation led to new doublets at -17.23 and -17.08 ppm, indicating that a hydrogen atom from the solvent, rather than one located initially in the starting molecule, had been transferred to the iridium center. The mixtures also exhibited new Cp^* resonances that corresponded to the new hydride absorptions, indicating that the Cp^* rings were intact in the product molecules. It seemed very likely that these reactions had led cleanly to the intermolecular C–H oxidative addition products **9**, **10** and **11**.

Andy Janowicz recently recalled the following in a letter: "At this point, I decided to test the ultimate in reactivity and irradiated the complex in the presence of cyclohexane. It worked!" In cyclohexane, irradiation of $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ proceeded just as it did with other solvents—except that a completely new (and much higher-field) hydride doublet was observed at $\delta -18.67$, as shown in Fig. 1.

We hoped, but would hardly let ourselves believe, that this was the simple oxidative addition product $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{C}_6\text{H}_{11})$ (**12**). A strong indication that this conclusion was correct (and one of the most dramatic characteristics of these early experiments) was the generality of the C–H insertion: every simple organic C–H containing molecule we investigated (including, as we learned later, methane [21]) led to new hydrido(alkyl) complexes, each one exhibiting a different hydride resonance or set of resonances in the high-field region of the proton NMR spectrum. Even changing the phosphine ligand did not prevent intermolecular C–H

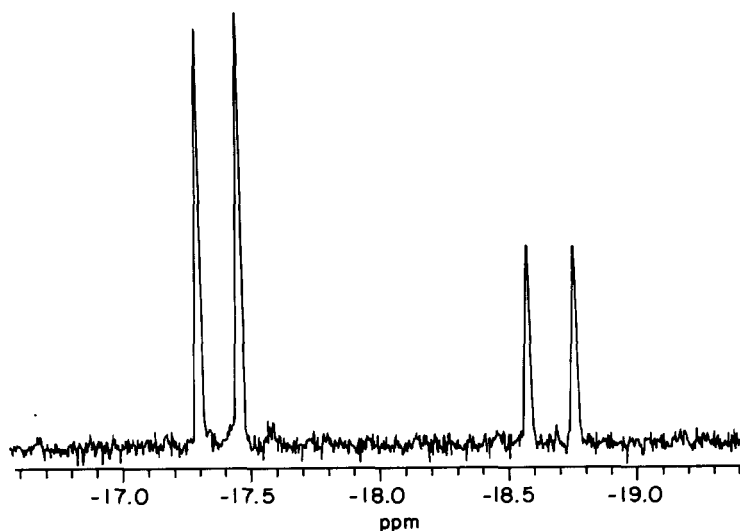


Fig. 1. High-field region of the ^1H NMR spectrum of the mixture formed on irradiation of $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ in cyclohexane, showing the doublet due to starting dihydride at -17.38 ppm and that due to product $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{cyclohexyl})$ at -18.67 ppm.

activation—Fig. 2 illustrates graphically the hydride chemical shifts that were observed for several different complexes of general structure $\text{Cp}^*(\text{L})\text{Ir}(\text{R})(\text{H})$ formed by irradiation of the corresponding dihydride in the appropriate solvents [22]. In only the PPh_3 and $\text{P}(\text{n-Pr})_3$ complexes was competitive cyclometallation to the

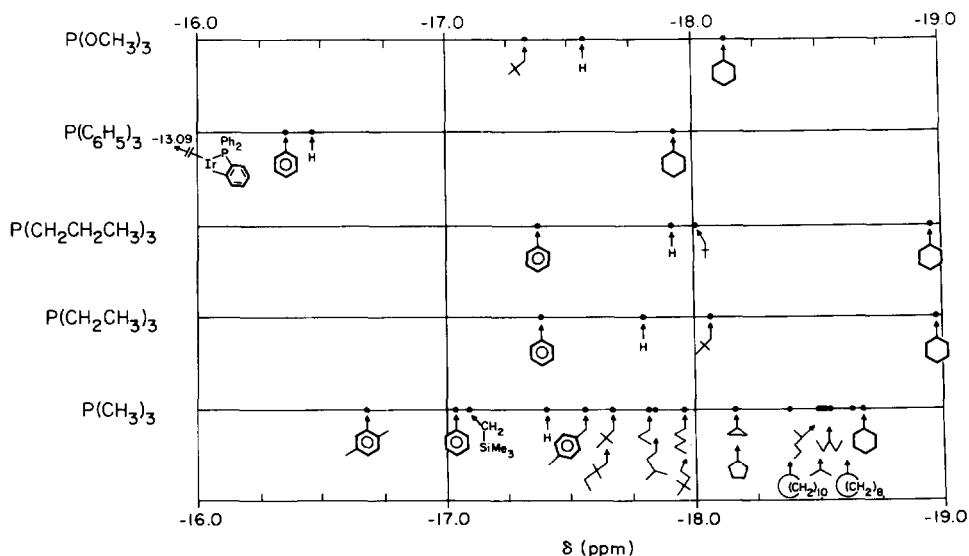
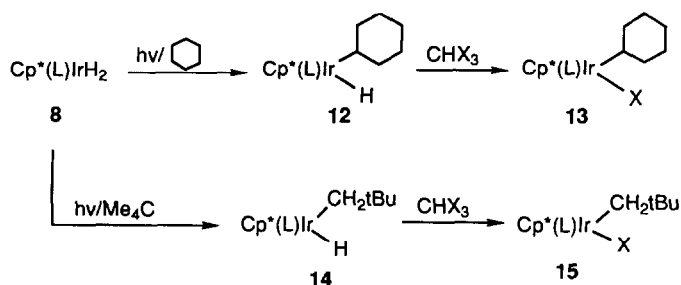


Fig. 2. Proton NMR hydride chemical shifts (C_6D_6) of dihydrides, aryl hydrides, and alkyl hydrides formed on irradiation of $\text{Cp}^*(\text{L})\text{IrH}_2$ complexes in various alkane and arene solvents.

phosphine ligands observed, and to this day we have never observed cyclometallation involving methyl groups on the Cp* ring.



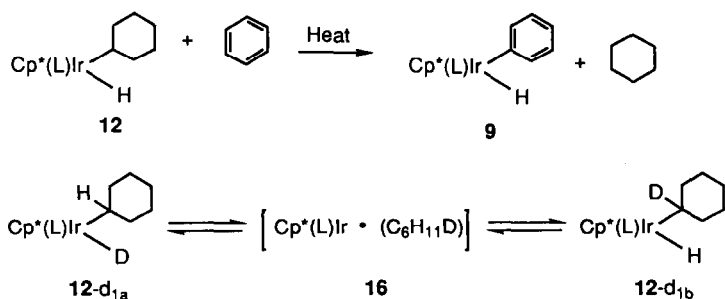
We were aware that many investigators had tried unsuccessfully to obtain intermolecular alkane C–H oxidative additions. We also knew of several instances in which claims of such reactions had been made that were later withdrawn, proven incorrect, or never substantiated. We were therefore infected with a strong case of paranoia (probably typical of physical organic chemists) that our observations might somehow be due to an artifact. As a result, we ran every control experiment we could think of to check our observations, and to make sure that the reagents and solvents we had used were completely pure. In a recent letter to me, Janowicz recently recalled of his initial observations: “I believe I ran the reaction three times before I took the results in to you. I wanted to have the proton and carbon NMRs, have isolated the compound and reproduced the results before venturing into your office. I had to be convinced myself, before I even attempted to convince you. I think I may have run the neopentane experiment [converting dihydride **8** to neopentyl hydride **14**] at that time to show that two hydrocarbons would have worked. It was an exciting time. I remember confiding in Bill Hersh [a postdoctoral coworker], because I couldn’t keep it to myself.”

Ultimately we were able to characterize the C–H activation products in several ways. First (as Graham had also done) we treated the new complexes with organic halides. This converted them to the corresponding halo(metal) complexes $\text{Cp}^*(\text{PMe}_3)_3\text{Ir}(\text{R})(\text{X})$ (e.g., **13** and **15**), where X = Br, Cl or I, and these materials were isolated by conventional crystallization techniques. Mindful of the importance of fully characterizing the C–H oxidative addition products themselves, we set about attempting to isolate them. We had difficulty purifying the alkyl hydrides by direct crystallization, and so we resorted to column chromatography inside our inert atmosphere box, followed by recrystallization. In this way the phenyl hydride **9** was purified and isolated. The cyclohexyl hydride was more sensitive, however. When Janowicz attempted to use benzene as a chromatography solvent, we were distressed to find that although the cyclohexyl complex **12** was loaded at the top of the column, the eluent contained only phenyl hydride **9**! Apparently a reductive elimination/oxidative addition exchange process (perhaps catalyzed by the alumina support) had occurred during the chromatography. To deal with this problem, Janowicz chromatographed the complex rapidly on alumina(III) under air-free conditions using a 4%THF/cyclohexane eluent, and forced the solution through the support quickly with pressure from a hand-held bulb. Eventually we learned how to purify these materials by low-temperature, air-free chromatography and subsequent

crystallization, and we were able to characterize the cyclohexyl hydride by X-ray diffraction [23].

Andy Janowicz' experiments opened up a field of research that was tailor-made for physical organic chemists who had "seen the light" of organometallic chemistry. Accordingly, much of our research since that period has been aimed at understanding the mechanism and structure–reactivity characteristics of the C–H oxidative addition process, and at identifying relationships between the C–H activating intermediates involved in this reaction and reactive intermediates that are important in organic reactions. We assumed initially that irradiation of $\text{Cp}^*(\text{L})\text{IrH}_2$ resulted initially in loss of H_2 and generation of the 16-electron or "carbene-like" species Cp^*IrL . The oxidative addition reactions observed with Cp^*IrL are reminiscent of so-called "insertion" reactions that the highly reactive fragment CH_2 (methylene) undergoes with C–H bonds. One of our initial priorities was to utilize competition experiments to investigate the selectivity of Cp^*IrL , in much the same way that carbene insertion selectivities had been determined many years earlier [19b]. We also later learned that Cp^*IrL adds to both the C=C and C–H bonds of alkenes. As in the carbene case, the π -complex or "metallacyclopropane" $\text{Cp}^*(\text{L})\text{Ir}(\text{H}_2\text{C}=\text{CH}_2)$ is not an intermediate in the formation of the C–H oxidative addition product $\text{Cp}^*(\text{L})\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)$ [24].

Taking another leaf from the physical organic chemist's handbook, we decided that important information about the C–H oxidative addition transition state could be obtained by studying its microscopic reverse reaction, reductive elimination of hydrocarbon R–H from the oxidative addition products $\text{Cp}^*(\text{L})\text{Ir}(\text{R})(\text{H})$ [23]. We learned in these studies that if electrophilic catalysts such as alumina were not present, the alkyl hydrides were surprisingly stable thermally, undergoing reductive elimination only at temperatures well above 100°C . At this temperature in benzene solution, cyclohexyl hydride **12** was converted to phenyl hydride **9** in a clean first-order reaction. It seemed likely at the time that the intermediate was the simple coordinatively unsaturated species Cp^*IrL , as we had postulated for the "forward" C–H oxidative addition reaction. However, we did "one experiment too many"—in an attempt to examine isotope effects in the reductive elimination, we prepared **12-d_{1a}** which had the metal-bound hydrogen replaced with deuterium. The kinetic isotope study was frustrated by our observation that at about the same temperature that reductive elimination occurred, the deuterium and hydrogen located at the α -carbon of the ring underwent exchange. This was our first hint that weakly bound alkane complexes (in this case, $\text{Cp}^*(\text{L})\text{Ir}(\text{C}_6\text{H}_{11}\text{D})$, **16**)—sometimes referred to as η^2 -alkane complexes, σ -complexes [25] or "agostic" complexes [26]—might be involved as intermediates in the alkane oxidative addition reaction.



The relatively high temperature required for reductive elimination of alkane suggested that the Ir–C and Ir–H bonds in these (hydrido)(alkyl)iridium complexes were unusually strong. With the help of Carl Hoff and Steven Nolan at the University of Miami, and Kevin Peters and Gilbert Yang at Colorado, we were able to quantify these bond energies and make a contribution to the growing field of organometallic thermochemistry [27]. All the relatively unhindered Ir–C bonds we examined are in fact unusually strong for transition metal systems, with the iridium–phenyl bond having the exceptionally high dissociation energy of 81 kcal/mol. These strong bonds M–H and M–C are clearly responsible for the high thermodynamic driving force for C–H activation in this system.

Once C–H oxidative addition had been observed in iridium complexes, similar reactions at a number of other metal centers were uncovered [28]. Early indications that alkane complexes might be involved in these reactions, as mentioned above, were strengthened by similar rearrangements observed by Roy Periana in rhodium systems at much lower temperature [25]. Our inability to find a solvent that is inert to reaction with the intermediate generated by irradiating $\text{Cp}^*(\text{L})\text{IrH}_2$ (including fluorocarbons, which can be used in Graham's $\text{Cp}^*\text{Ir}(\text{CO})_2$ system [29] but give complex mixtures in ours) led us finally to examine liquified noble gases, such as xenon and krypton, as solvents for the oxidative addition reaction. These solvents were the first we found to be inert to overall reaction with the metal, providing a means to activate solids and other materials that are difficult to liquify or utilize as solvents themselves [30]. In addition, in collaboration with C.B. Moore, G.C. Pimentel, and their coworkers we have used noble gas solvents to carry out flash kinetics experiments on C–H oxidative addition reactions. These have provided direct evidence for existence of transient metal–alkane and metal–noble gas complexes [31].

Research in C–H activation carried out by us and others over the past decade has resolved some of the questions raised by early work in this area, but many of the insights gained have also raised new questions. Finding effective methods for utilizing C–H oxidative addition chemistry to achieve efficient thermal catalytic conversion of alkanes into functionalized organic compounds remains a high priority. Many descriptive and mechanistic questions also remain unanswered. For example, we still do not fully understand why some systems undergo only intramolecular C–H oxidative additions, but Cp^*IrL (or its solvate) shows such a strong propensity for intermolecular reaction. We also lack understanding of the factors that determine why some metal centers undergo the oxidative addition reaction but others do not, and whether this difference is controlled by thermodynamic or kinetic factors. The role played by alkane complexes and other solvates in determining the relative rates of reaction of metals at various types of C–H bonds needs to be worked out; similarly, we know little so far about the factors that control the oxidative addition of metal centers to C–H vs. other types of X–H bonds.

In closing, I would like to echo some of Bill Graham's comments about the "sociological" aspects of C–H activation. First, we too have benefited from the willingness of funding agencies (in this case, the Department of Energy) to support our research without demanding adherence to a master plan. Frequently we have found that our major discoveries—especially those that are most surprising or unprecedented—have had little to do with the goals we were working toward when we made them. As I have noted above, our finding that irradiation of $\text{Cp}^*(\text{L})\text{IrH}_2$

complexes results in C–H activation occurred in a project directed toward a very different goal by a student who was willing to try reactions whose outcome was not very predictable. Another example has occurred recently: the rearrangement mentioned at the beginning of this article that interconverts 1,5-hexadiyne-3-ene (**1**) and diradical **2** has recently been found to be the critical step by which certain anti-tumor antibiotics (the calicheamicin and esperamicin classes) induce double-stranded cleavage of DNA. I think it is fair to say that no one could have predicted this when we were working on the chemistry of diradical **2** in the 1970s. Such events provide a strong argument against attempts to guide the flow of research funding in predetermined directions.

Finally, I would like to support Graham's remark about the positive interactions that have existed between people working in this area. For several years Bill's group and mine used our related systems to address very similar questions, and the competitiveness inherent in this situation could have easily generated hard feelings. However, I have been continually impressed by Bill's willingness to share both his insights and information, and we have tried to respond in kind. We have had similar positive interactions with many other people working the area, such as Bill Jones, Bob Crabtree, Les Field, and John Bercaw. When this type of generosity and respect exists between investigators working on closely related problems, science progresses much more efficiently and students learn that trust, rather than mistrust, can be an inherent part of the scientific endeavor.

Acknowledgement

I am greatly indebted to the students and postdoctoral fellows who have worked on the C–H activation project in my group, many of whom are listed in the references to this paper. None of the research results I have described would have been possible without their hard work and intellectual insights. Special thanks go to Andrew H. Janowicz, both for his initial discovery of the iridium C–H oxidative addition reaction in our laboratory and for his assistance during the writing of this article. This work also benefitted from loans of iridium and rhodium from the Johnson Matthey Corporation. Finally, the research was supported financially by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract no. DE-AC03-76SF00098.

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