

Activation of carbon–hydrogen bonds in alkanes and other organic molecules by Ir(I), Rh(I) and Ir(III) complexes

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ABSTRACT: Pentamethylcyclopentadienyliridium(I) complexes are now known to undergo rapid and general oxidative addition reactions with a wide range of carbon-hydrogen bonds, including those in alkanes and isolated alkyl groups. The first part of this paper describes flash kinetic experiments carried out on pentamethylcyclopentadienylrhodium carbonyl complexes in liquid krypton and liquid xenon solvents at low temperature. These studies have established that noble gas complexes and alkane complexes (intermediates involving weak complexation of the noble gas or alkane C-H bonds to the metal center) are generated as precursors to the final oxidative addition products in these reactions. Information about the relative binding constants of alkanes of different sizes and isotopic substitution to the metal center has been obtained, and activation energies and entropies for the conversion of the alkane complexes to the final C-H oxidative addition products have been determined. In the second part of the study, a new alkane C-H activation process involving reactions of Ir(III) trifluoromethanesulfonates with alkanes and arenes is reported. Preliminary investigations indicate that cationic Ir(III) intermediates are involved in these reactions.

INTRODUCTION

Alkanes make up a significant fraction of the world's petroleum and natural gas resources and are therefore a potentially useful source of carbon in large-scale synthesis. Standing in the way of this potential is the fact that alkane carbon-hydrogen and carbon-carbon bonds are unreactive toward most organic reagents. As a result there has been a long-standing interest in finding ways to "activate" C-H bonds in alkanes and alkyl groups so that they might be converted into more readily usable functional groups (1).

The possibility of using transition metal complexes to activate C-H bonds has been considered viable since Shilov first discovered that certain platinum compounds could be employed to convert alkanes into alkyl halides and acetates (2). Although it was often assumed that these reactions proceed by initial oxidative addition of the C-H bonds to the platinum center, it was not until 1982 that our group and W. A. G. Graham's first observed direct photochemical reaction of the metal complexes $\text{Cp}^*\text{Ir}(\text{CO})_2$ and $\text{Cp}^*(\text{PMe}_3)_3\text{IrH}_2$ (1; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with alkanes (R-H) to give hydridometal alkyl complexes $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{H})$ (3) (3, 4). Extensive experimentation since that time has provided strong evidence that irradiation of 1 leads to loss of H_2 , generating a reactive intermediate that has traditionally been written as the coordinatively unsaturated (16-electron) intermediate $\text{Cp}^*\text{Ir}(\text{PMe}_3)$ (2). This complex then undergoes oxidative addition to a C-H bond of the alkane solvent R-H, presumably through a simple three-center transition state (Fig. 1).

There are several unique features of the photochemistry of 1 in organic solvents. Chief among these is its unusual selectivity properties. The reactions of intermediate 2 are exclusively intermolecular: no cyclometalation products resulting from oxidative addition of Cp^* or PMe_3 C-H bonds to the Ir center (Fig. 1) have ever been observed. In that sense, it seems very selective. However, if one focuses only on intermolecular reactions of 2, it often seems much less selective. Thus, the intermediate has so far been observed to react with every organic solvent in which 1 is soluble. Furthermore, only modest differences are seen between the rates of reaction of C-H bonds of different structural type (with the exception that ordinary tertiary C-H bonds are substantially less reactive than primary or secondary C-H bonds). The latter observation provides one of the

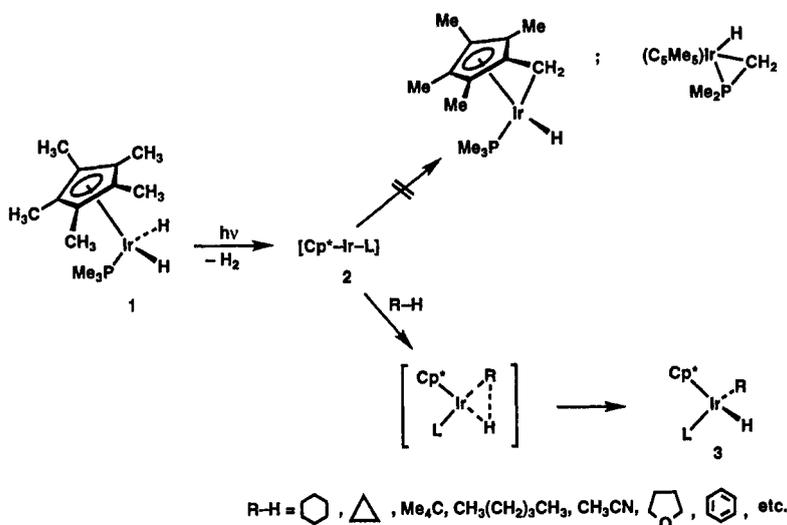


Fig. 1. Intermolecular alkane C-H activation at an Ir(I) center

strongest arguments against a free radical mechanism for the C-H oxidative addition reaction (5, 6).

FLASH KINETIC STUDIES OF THE C-H OXIDATIVE ADDITION REACTION

Our early studies provided substantial information about the kinetics and thermodynamics of the alkane C-H oxidative addition reaction. However, until recently little information has been available about one of the most important properties of the postulated intermediate 2: the absolute rate at which it reacts with C-H bonds. In order to address this question, we established a program aimed at detecting and measuring the rates of reaction of transient C-H activating metal complexes with alkanes. To maximize our ability to identify the reactive species involved, we wished to monitor these reactions by infra-red (IR) rather than uv-visible spectroscopy. We therefore utilized a spectrometer that employs a xenon chloride excimer laser to irradiate the sample and a diode laser (an earlier version of this instrument employed a CO laser) to monitor the IR spectra of starting materials, reactive intermediates and products (7, 8).

To take advantage of the strong IR signals characteristic of the M-CO linkage, we decided to investigate C-H activating systems having ancillary CO rather than phosphine ligands. We chose to investigate $\text{CpRh}(\text{CO})_2$ and $\text{Cp}^*\text{Rh}(\text{CO})_2$ complexes ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) because earlier workers had demonstrated that complexes in this series undergo C-H activation reactions in analogy to the iridium complexes discussed above, although the products of the rhodium reactions are relatively unstable (9, 10). Significantly, irradiation of $\text{CpRh}(\text{CO})_2$ under matrix isolation conditions had been shown to give a reactive intermediate absorbing at 1968 cm^{-1} (presumed to be CpRhCO) which reacted in a methane matrix to give a new species with a band at 2025 cm^{-1} , assigned as $\text{Cp}(\text{CO})\text{Rh}(\text{CH}_3)(\text{H})$ (11).

Irradiation of $\text{Cp}^*\text{Rh}(\text{CO})_2$ (4) in cyclohexane solution in our spectrometer did lead to a band in the metal carbonyl region assignable to $\text{Cp}^*(\text{CO})\text{Rh}(\text{Cyclohexyl})(\text{H})$ (6). However, the monocarbonyl precursor to this C-H oxidative addition product apparently had reacted too rapidly for us to observe it at room temperature in hydrocarbon solution. Aware of the finding that metal carbonyl photochemistry can be carried out in liquefied noble gas solvents (12), we decided to try our experiments in liquid xenon (LXe) and liquid krypton (LKr) at low temperatures.

Under these conditions, photolysis of $\text{Cp}^*\text{Rh}(\text{CO})_2$ produced a detectable transient monocarbonyl species absorbing near 1946 cm^{-1} with a lifetime long enough for us to monitor with the flash kinetics spectrometer and observe its conversion to the C-H activated product **6** in the presence of dissolved cyclohexane. Surprisingly, however (in view of its rapid decay in cyclohexane solvent), the transient disappeared very slowly in LXe at $-80\text{ }^\circ\text{C}$ but much more rapidly in LKr. We conclude from this that the transients are in fact noble gas solvates (12) $\text{Cp}^*(\text{CO})\text{Rh}(\text{Xe})$ and $\text{Cp}^*(\text{CO})\text{Rh}(\text{Kr})$ (**5**), the former having a stronger noble gas-metal bond and thus a slower rate of reaction with C-H bonds. Shown in Figure 2 are sample plots for the conversion of the 1946 cm^{-1} transient in LKr to the cyclohexane C-H activation product that absorbs at 2003 cm^{-1} in this solvent.

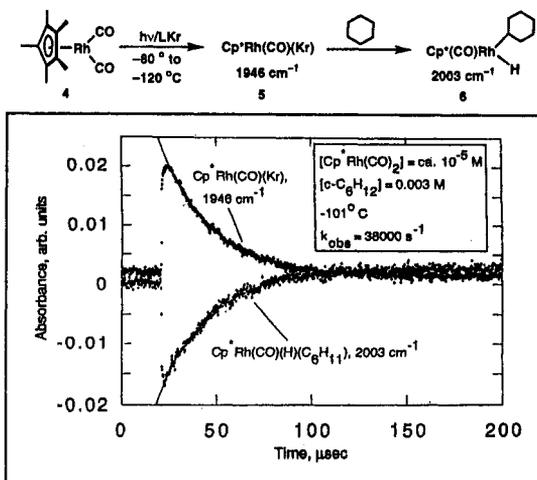


Fig. 2. Plots of absorbance vs. time for disappearance of **4** and appearance of **6** in liquid Kr containing 0.003 M cyclohexane at $-101\text{ }^\circ\text{C}$.

In the presence of excess cyclohexane pseudo-first order (exponential) conversion of the transient to the product is observed, demonstrating that the rate law is first order in $\text{Cp}^*(\text{CO})\text{Rh}(\text{Kr})$. Repetition of this experiment using different concentrations of excess cyclohexane showed a more complicated dependence on this reaction partner. As shown in Fig. 3, a plot of the pseudo first order rate constants k_{obs} vs. cyclohexane concentration demonstrates that the rate constant exhibits saturation in the concentration of hydrocarbon. One possible mechanism that might explain this observation involves dissociation of Kr from the krypton complex **5** to give Cp^*RhCO , followed

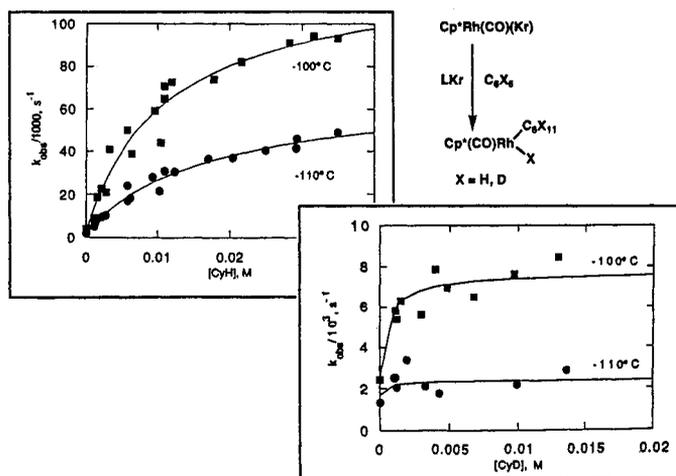


Fig. 3. Comparison of k_{obs} vs. concentration of alkane for C_6H_{12} and C_6D_{12}

by reaction of the latter species with alkane. However, this mechanism would require that the saturation rate constant be equal to the rate constant for dissociation of Kr from the krypton complex. This should be independent of the hydrocarbon involved in the subsequent oxidative addition. As shown in Fig. 3, which illustrates the saturation kinetic curves for both cyclohexane and cyclohexane- d_{12} at two temperatures, quite the opposite is observed--the saturation value of k_{obs} for cyclohexane and for its deuterated analogue are very different, the latter being substantially lower. The saturation kinetics can therefore not be explained by a dissociative mechanism. A more likely mechanism is that illustrated in Fig. 4, which postulates an initial preequilibrium between the krypton complex **5** and a new intermediate, the alkane complex **7** (analogous intermediates have been postulated earlier and detected in non-C-H activating systems; they have also been referred to as " σ -complexes" or "agostic" species) (13, 14, 15). This is followed by a second unimolecular step in which the alkane complex

is converted to the C-H activation product **6**. This model is analogous to the Michaelis-Menten mechanism used to understand simple enzyme kinetics, and it can be analyzed in a similar way. This leads to the expression for the rate constant k_{obs} shown in Fig. 4. A plot of k_{obs}^{-1} vs. $[\text{Kr}]/[\text{C}_6\text{H}_{12}]$ gives a straight line, from which can be extracted K_1 , which is essentially the pre-equilibrium constant for binding the alkane to the rhodium center with displacement of Kr, and k_2 , the saturation rate constant corresponding to insertion of the metal center into the C-H bond within the alkane complex **7**. In this picture saturation occurs because at high hydrocarbon concentration, the initial pre-equilibrium is shifted nearly completely from the krypton complex **5** to the cyclohexane complex **7**, and under these conditions one measures k_2 , the conversion of **7** to **6** directly. Because the hydrocarbon is present as a complexed ligand in **7**, k_2 should be dependent on the structure of the hydrocarbon, as we observe. By measuring k_2 over a range of temperatures from -120 to -80 °C, we have determined that $\Delta H^\ddagger = 4.6$ kcal/mole and $\log A = 10.9$ for the reaction that converts the cyclohexane complex to the cyclohexyl hydride.

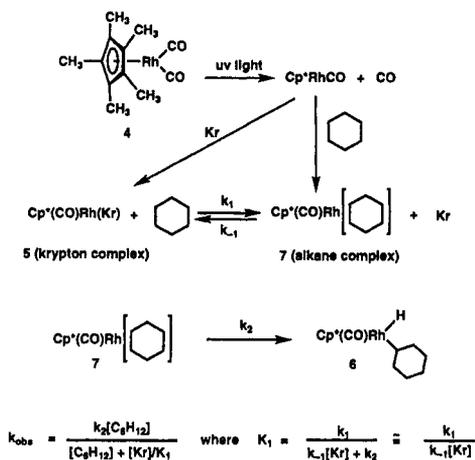


Fig. 4. Proposed mechanism and rate law for cyclohexane C-H activation by $\text{Cp}^*\text{Rh}(\text{CO})_2$

A critical, and initially somewhat worrisome, assumption of this mechanism results from the fact that we observe only one transient absorption, at 1946 cm^{-1} , and therefore if this model is correct intermediates **5** and **7** must have absorption frequencies that are within 1 cm^{-1} of one another. Recently we have obtained evidence supporting this assumption by experiments carried out with a second hydrocarbon, neopentane (2,2-dimethylpropane). In one specific set of experiments, carried out with neopentane- d_{12} at -108 °C, we observe two different transients at very similar spectrometer frequencies, 1946 and 1947 cm^{-1} . As shown in Fig. 5,

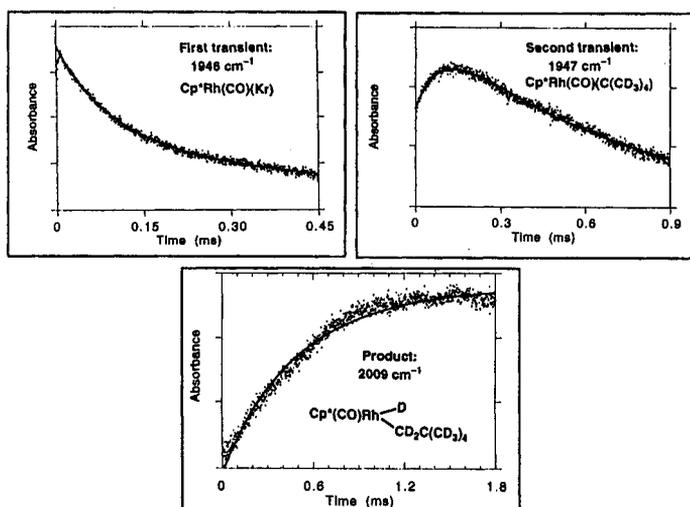


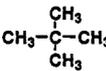
Fig. 5. C-D activation of neopentane- d_{12} : absorption vs. time plots that reveal two barely resolved transients at $T = 165\text{ K}$, $[\text{C}(\text{CD}_3)_4] = 0.04\text{ M}$

observe a bi-exponential decay. At the higher frequency, we observe a growth whose rate matches the fast decay at 1946 cm^{-1} , followed by a decay whose rate matches the slower decay at 1946 cm^{-1} . We assign the 1946 cm^{-1} absorption to the krypton complex **5** and the 1947 cm^{-1} absorption to $\text{Cp}^*(\text{CO})\text{Rh}(\text{neopentane-}\text{d}_{12})$, the alkane complex analogous to **7**. The fact that we are able to resolve the two species under these specific conditions is undoubtedly fortuitous, but it provides reassurance that a krypton complex and an alkane complex can have very similar IR absorptions in spite of their structural differences.

The reversible formation of alkane complexes, as revealed by the flash kinetic studies summarized above, make the "selectivities" obtained by competition studies at room temperature in mixtures of hydrocarbon solvents (5) difficult to interpret. Hopefully extension of the flash experiments to other organic substrates will provide more direct information about the rates of reaction of C-H activating metal complexes with different types of C-H bonds. Some information of this type has already been obtained in the experiments described above with cyclohexane and neopentane and their perdeuterated isomers, as well as with propane and methane. A summary of the results obtained so far are given in Tables 1 and 2.

Two unusual results have come out of this work. First, as shown in Table 1 it appears that the larger hydrocarbons cyclohexane and neopentane undergo oxidative addition more rapidly than the smaller ones. Analysis of the saturation kinetics observed with the C₆, C₅ and C₃ hydrocarbons reveal that the k₂ step that converts the alkane complex to oxidative addition product does not change very much as the alkane structure changes; rather, the retardation in rate is due to the poorer metal-alkane binding constants (K₁'s) characteristic of the smaller hydrocarbons. This is consistent with earlier work on the dependence of the binding of alkanes to W(CO)₅ centers observed by Rayner and coworkers (13), but it is quite opposite to the dependence one might

TABLE 1. K₁ and k₂ Values for Alkanes of Different Sizes

			CH ₃ CH ₂ CH ₃	CH ₄
k _{obs} (x 10 ⁻⁵ s ⁻¹) ^a	3.5	1.3	0.61	< 0.01
K ₁	909 ± 300	1040 ± 300	84 ± 30	?
k ₂ (x 10 ⁻⁵ s ⁻¹)	7.02 ± 0.84	2.8 ± 0.4	15 ± 2	?

^aAt 0.03 M conc. of hydrocarbon in LK₁; T = 193K

TABLE 2. Isotope Effects on the Rhodium-Alkane Binding (K₁) and C-H Activation (k₂) Steps

T, K	Alkane	k ₂ (s ⁻¹)	k ₂ ^H /k ₂ ^D	K ₁ ≡ k ₁ /k ₋₁	K ₁ ^H /K ₁ ^D
163		6.85 x 10 ⁴	26.3	1.4 x 10 ³	0.039
163		2.6 x 10 ³	-	3.7 x 10 ⁴	
165	(CH ₃) ₄ C	3.9 x 10 ⁴	15.6	1.2 x 10 ³	0.067
165	(CD ₃) ₄ C	2.5 x 10 ³	-	1.8 x 10 ⁴	

expect on the basis of simple steric effects. Another unusual binding phenomenon discerned from these studies arises from a comparison of the protiated and deuterated isomers of the C₆ and C₅ hydrocarbons (Table 2). Here the k₂ step experiences an expected "normal" isotope effect; i.e., the C-D cleavage in the perdeuteroalkane complex (k₂^D) occurs substantially more slowly than the corresponding step in the perprotioalkane complex (k₂^H). However, the pre-equilibrium binding constant K₁ shows an inverse isotope effect. That is, cyclohexane-d₁₂ and neopentane-d₁₂ bind to rhodium substantially more strongly than do the corresponding protiated alkanes. At present we do not have a completely solid explanation for these observations, although the size effect may be caused by the higher polarizability of the larger alkanes, and the inverse isotope effect may result from bending modes in the alkane complexes that are not present (or are present only as free rotations) in the separated reactants.

C-H ACTIVATION REACTIONS OF Ir(III) COMPLEXES

In the course of exploring ways to convert C-H activation products in the phosphineiridium series Cp*(PMe₃)Ir(R)(H) into functionalized organic compounds, we developed synthetic routes for converting these materials to the corresponding alkyl triflates Cp*(PMe)Ir(R)(OTf) (Tf = SO₂CF₃).⁽¹⁶⁾ Dissolution of the methyl complex Cp*(PMe)Ir(CH₃)(OTf) (**8**; characterized by X-ray dif-fraction) in benzene produced a surprising result: it was converted at room temperature into the corresponding phenyl triflate Cp*(PMe)Ir(C₆H₅)(OTf) (**9**). To determine whether this transformation would occur with saturated C-H bonds, we carried out the reaction of the methyl triflate **8** with ¹³CH₄. Once again C-H activation was observed; as illustrated in Fig. 6, monitoring by ¹H NMR showed the appearance of Cp*(PMe)Ir(¹³CH₃)(OTf) (**8**-¹³C) and unlabeled CH₄ at 45 °C in CH₂Cl₂ solution (17).

Although there is some precedent for reaction of arene C-H bonds with Ir(III) centers (18, 19, 20, 21), to our knowledge this is the first observation of reaction of a saturated C-H bond with Ir(III). To explore the potential scope of this reaction, we have carried out preliminary investigations of the reaction of iridium triflate **8** with other saturated hydrocarbons. Our preliminary studies

indicate that reactions of this system may be much more sensitive to steric inhibition than the reactions at Ir(I) centers discussed above. Thus, as illustrated in Fig. 7, cyclohexane and neopentane do not react. C-H bonds in the smaller hydrocarbons cyclopropane and ethane do react, although as shown they lead to rearranged products. Toluene gives only attack on the *para*-arene-C-H bonds; in contrast *p*-xylene (not illustrated in the figure) leads exclusively to attack at the methyl group, presumably because all the aryl hydrogens in this molecule are in sterically hindered environments. Diethyl ether does not react, but dissolving **8** in dimethyl ether leads to the novel cationic carbene hydride **9**.

Several important mechanistic questions present themselves as a result of our initial observations. One important question is whether the reaction is initiated by heterolytic cleavage of the iridium-triflate bond, generating a transient $[\text{Cp}^*(\text{PMe}_3)\text{Ir-CH}_3]^+$ cation that would be electrophilic enough to react rapidly with C-H bonds (Fig. 8). As shown in the Figure, a second important question is how this cation, once generated, reacts with C-H bonds. One possibility is that it induces oxidative addition of the C-H bond to give an Ir(V) intermediate (22, 23), followed by reductive elimination of methane to give the substituted cation $[\text{Cp}^*(\text{PMe}_3)\text{Ir-R}]^+$ and rapid reaction of this species with OTf^- to give the final product. Another option is that the second cationic intermediate $[\text{Cp}^*(\text{PMe}_3)\text{Ir-R}]^+$ is formed in a one-step "σ-bond metathesis" reaction.

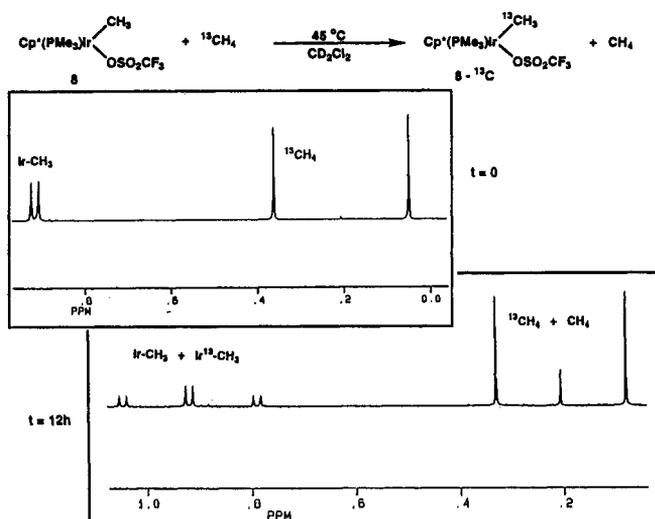


Fig. 6. Reaction of methyliridium triflate **8** with $^{13}\text{CH}_4$ monitored by ^1H NMR spectrometry

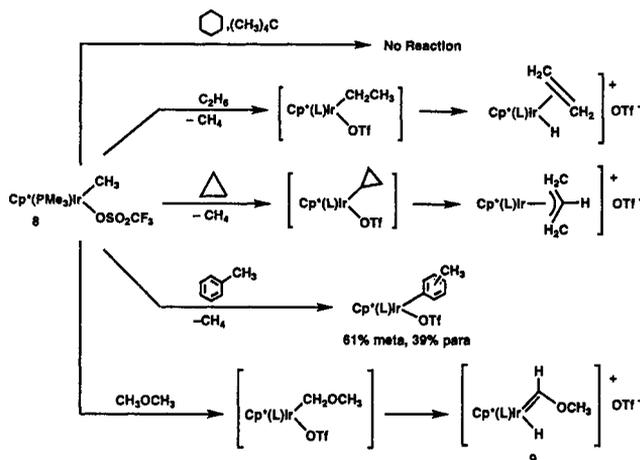


Fig. 7. Reactions of **8** with other hydrocarbons (CD_2Cl_2 solution, 45°C)

Although we have not yet investigated the mechanism of this new C-H activation reaction extensively, we have obtained qualitative information that bears on the first question. One observation, for example, is that triflate is critical to the reactions; the corresponding chloride $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_3)\text{Cl}$ does not react with benzene even at temperatures near 100°C . A second recent result is that we have treated the methyl triflate **8** with the sodium salt of the non-coordinating anion (**24**) $[\text{B}(3,5\text{-di}(\text{CF}_3)\text{C}_6\text{H}_3)_4]^-$ in methylene chloride solution. This precipitates NaOTf and generates the tetraarylborate salt of $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_3)(\text{ClCH}_2\text{Cl})]^+$, which has been characterized by X-ray diffraction. This material is substantially more reactive than the triflate, reacting with benzene at -35°C to give the corresponding phenyl-substituted solvate. The methyl-substituted methylene chloride solvate also reacts with diethyl ether (unlike methyl triflate **8**), leading to rearranged product $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{H}_2\text{C}=\text{CH}(\text{OEt}))]^+$, presumably

by a C-H activation/ β -elimination sequence. These observations support ionization as the first step in the reaction of the methyl triflate **8** with C-H bonds.

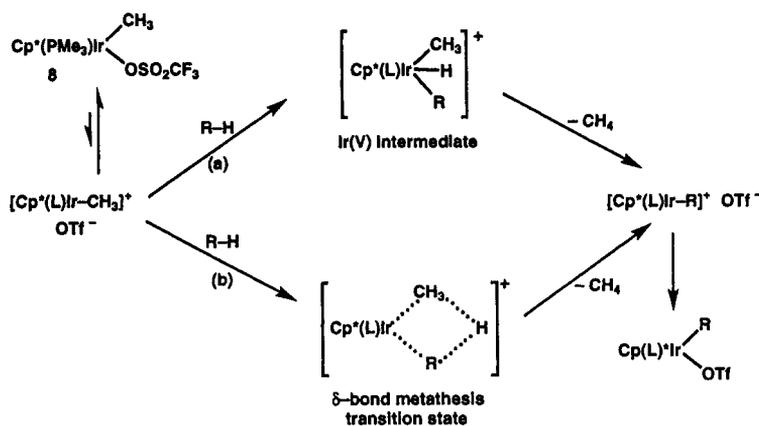


Fig. 8. Possible mechanisms for the Ir(III) C-H activation reaction

CONCLUSIONS

It is now well established that appropriately substituted Ir(I) complexes can undergo oxidative addition with a wide range of carbon-hydrogen bonds, including the so-called "unactivated" C-H bonds present in alkane or isolated alkyl groups, to give hydrido(alkyl)iridium complexes. Extensive mechanistic studies strongly implicate, as intermediates in these reactions, alkane complexes in which the C-H bond is weakly complexed to the metal center. These intermediates go on to the oxidative addition product in a second step. The alkane complexes have been directly detected in flash kinetic spectroscopic experiments in liquefied noble gas solvents and the rates and activation energies associated with their conversion to the final oxidative addition products have been measured. The rhodium centers in these alkane complexes have some surprising (and as yet not well understood) properties, such as the ability to bind large hydrocarbons more strongly than smaller ones, and the tendency to bind deuterated hydrocarbons more strongly than their undeuterated analogues.

More recently complexes having cationic Ir(III) centers have also been shown to react with unactivated C-H bonds. These transformations are more sensitive to steric effects than the Ir(I) reactions, but their lower reactivity may be due to the difficulty of generating truly free Ir(III) cations in solution. The reactivity of these species appears to increase as the anions associated with them become less coordinating. Efforts to increase the reactivity of the Ir(III) systems, and to further understand the mechanisms of the Ir(I) and Ir(III) C-H activation reactions, are continuing in our laboratory.

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