

ENGINEERING A HOMOGENEOUS ALKANE CONVERSION CATALYST: A
PORPHYRIN BASED APPROACH TO ALKANE ACTIVATION AND
FUNCTIONALIZATION

by

Andrew P. Nelson

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Under the Supervision of Professor Stephen G. DiMagno

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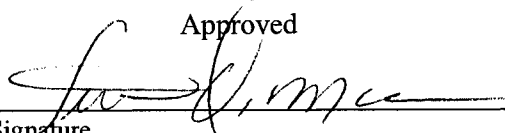
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Engineering a Homogeneous Alkane Conversion Catalyst: A Porphyrin Based Approach to
Alkane Activation and Functionalization

BY

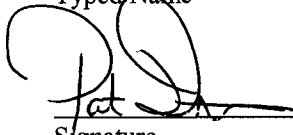
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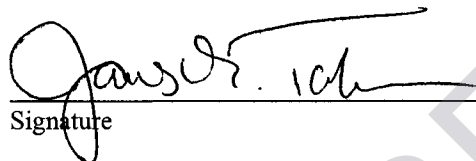
Date
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Stephen G. DiMagno
Typed Name


Signature


11/1/04

Patrick H. Dussault
Typed Name


Signature

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James M. Takacs
Typed Name


Signature

11/1/04

T. Adrian George
Typed Name


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Stephen W. Ragsdale
Typed Name

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ENGINEERING A HOMOGENEOUS ALKANE CONVERSION CATALYST: A
PORPHYRIN BASED APPROACH TO ALKANE ACTIVATION AND
FUNCTIONALIZATION

Andrew P. Nelson, Ph.D.

University of Nebraska, 2004

Advisor: Stephen G. DiMagno

The design of a metal mediated catalytic system capable of carrying out both alkane C-H bond activation and functionalization depends critically upon engineering the appropriate ligand environment. The rationale for the synthesis of 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato rhodium [(F₂₈TPP)Rh, Chapter 1] relies upon differential effects on the homolytic and heterolytic bond cleavage processes central to alkane conversion. Here we report that increasing the effective electronegativity of the rhodium metal by placing it at the center of a perfluorinated porphyrin ligand has little effect on the metal's ability to activate carbon-hydrogen (C-H) and hydrogen-hydrogen (H-H) bonds.

We hypothesized that increasing the metal's effective electronegativity would stabilize the Rh(I) oxidation state and allow the nucleophilic removal of the methyl group bound to the rhodium center following the C-H activation reactions. To verify this hypothesis (Chapter 2), we subjected the (F₂₈TPP)RhCH₃ complex to a variety of nucleophiles, and found that triphenylphosphine (PPh₃) reacts with (F₂₈TPP)RhCH₃ to

cleanly produce the methyl triphenylphosphonium salt of the Rh(I) porphyrin $[(F_{28}TPP)Rh]^- [CH_3PPh_3]^+$ as the sole isolatable product.

The electrochemical behavior of $Rh(F_{28}TPP)$ was explored to provide a thermodynamically more efficient pathway for the regeneration of the Rh(II) catalyst (Chapter 3). We show here the first unambiguous reversible one electron redox couple for four coordinate Rh(II) porphyrins. These studies have also shown that the disproportionation of Rh(II) porphyrins is facilitated by coordination and ion pairing events, and that the ability to maintain a stable Rh(II) complex relies on a careful choice of reaction environment.

In an effort to accelerate C-H activation, we prepared a series of heavily fluorinated diporphyrin dimers (Chapter 4). By tethering the two rhodium centers necessary for C-H activation, we hoped to improve upon the reaction rates observed for the monomeric, termolecular activation step. These new fluorinated rhodium(II) porphyrin dimers exhibit 200 fold rate enhancements for the activation of methane C-H bonds when compared to $(F_{28}TPP)Rh$, while maintaining the electronic properties necessary for alkane conversion.

Acknowledgement

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Lastly I am forever grateful to my wife Amanda. I will perpetually thank you for the sacrifices that you have made these last few years. I would not have completed this work without you by my side. Thank you for being my constant source of reassurance, my biggest fan, and my best friend.

I dedicate this work to the memory of my mother-in-law Cynthia K. Robison who showed me that, regardless of the circumstances you find yourself in, you must strive to live well the life God has given you.

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Chapter 1

Synthesis and Reactivity of [2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-Tetrakis(Pentafluorophenyl)-Porphinato]Rhodium(II) [(F₂₈TPP)Rh]

Introduction

Porphyrins constitute a well-known class of aromatic ligands capable of coordinating multitudinous transition and main group metal ions. The use of metalloporphyrins as catalysts for important organic transformations has been studied for many years.¹⁻⁴ One reason the porphyrin ligand is an attractive platform for study is that it is possible to vary systematically the electronic properties of the ligand system while maintaining a stable coordination geometry for a desired metal ion.^{5,6} As a result, a large number of metal ions in a host of different oxidation states can be studied within a single ligand environment. The DiMaggio laboratory has developed two new classes of heavily fluorinated porphyrins, β -octafluorinated porphyrins such as (F₈TPP)H₂ and (F₂₈TPP)H₂⁷ as well as 5,10,15,20-tetrakis[perfluoroalkylporphyrins].^{8,9} We have demonstrated that the weak field ligand environment provided by these porphyrins gives access to chemical behavior never before seen in porphyrin chemistry.^{5,7} In our quest to develop new catalysts based on the porphyrin framework, a variety of early and late transition metal and lanthanide ions have been successfully inserted into these fluorinated porphyrins. This dissertation will detail the behavior of fluorinated rhodium porphyrins.

Rhodium porphyrins have been reported to react with dihydrogen (H_2) as well as saturated carbon-hydrogen (C-H) bonds in light alkanes, including methane, by cleaving H-H and C-H bonds homolytically.¹⁰⁻¹² The homolytic cleavage or "activation" of alkanes under these conditions results in the formation of the new rhodium-carbon (Rh-C) bond as well as a new rhodium-hydrogen bond. It is our hypothesis that placing rhodium metal in an extremely electron deficient environment will allow nucleophilic cleavage of the Rh-C bond by stabilizing the resulting Rh(I) oxidation state. Combining the ability of rhodium porphyrins to activate saturated C-H bonds with the ability to cleave the resulting Rh-C bonds nucleophilically, would allow us to catalytically convert unreactive alkanes into functionalized products.

The chemical inertness of saturated alkanes is well known. In fact, the historical naming of these compounds as "paraffins" (from the Latin *parum affin* - "without affinity") speaks to their inability to enter into common chemical reactions. Their chemical inertness arises as a consequence of their extremely high carbon-hydrogen (C-H) bond energies. These values range from 90 to 98 kilocalories per mole (kcal/mole) in primary and secondary C-H bonds. For methane, the major constituent in natural gas, the bond energy is even greater, 105 kcal/mole. However, as one of the most abundant classes of organic compounds, alkanes represent an enormous potential feedstock for the production of chemical energy as well as precursor compounds for chemical synthesis. Conversion of these plentiful hydrocarbons to more valuable products such as alcohols has the potential to alter the industrial landscape by providing new and economically viable resources for energy and manufacturing.¹³ From the intellectual prospective, the selective functionalization of otherwise unreactive hydrocarbons is a long sought goal,

and would have a tremendous impact on the field of chemistry. Accomplishing such a goal would allow the scientific community to view the ubiquitous alkyl chain as a useful, well-defined functional group possessing its own set of accessible chemical reactions.

Background

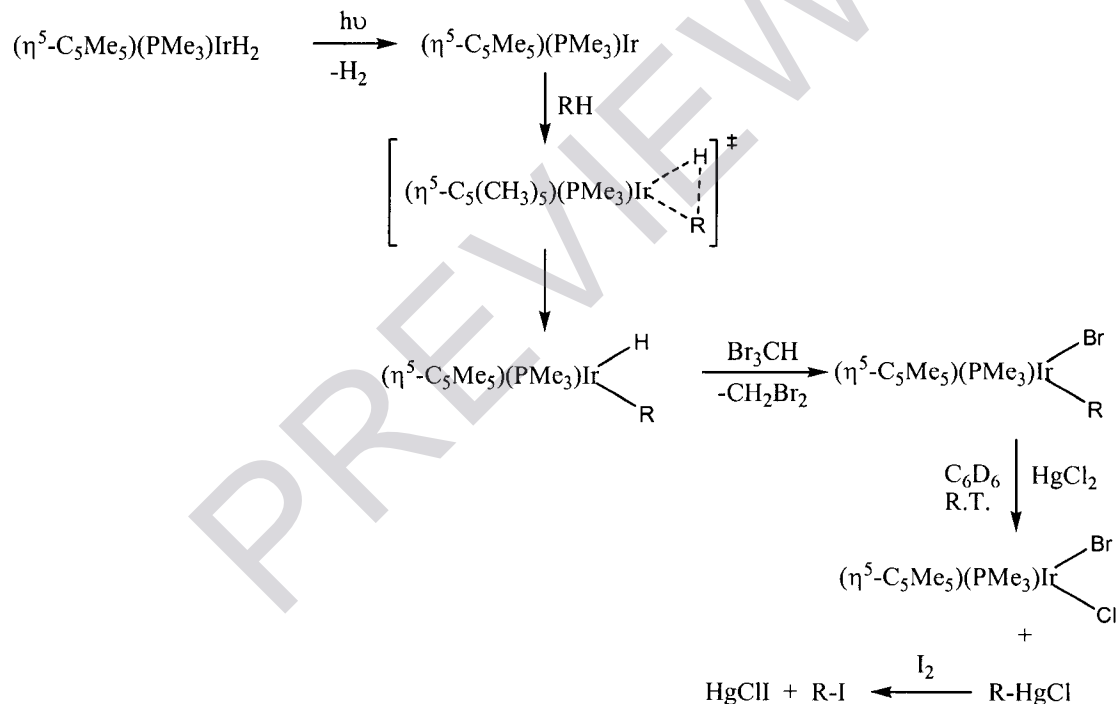
Facile C-H bond activation occurring at the surface of metals and oxides was observed as early as the 1930's.¹⁴ Despite these early reports, serious consideration was not given to the possibility of a homogeneous alkane activation catalyst until the 1960's. In 1968, when mechanistic theory in organometallic chemistry was developing, J. Halpern, one of the leaders in the field, described the task as "to develop a successful approach for activation of C-H bonds, particularly saturated hydrocarbons, this problem being at present one of the most important and challenging in the entire field of homogeneous catalysis".¹⁵ This feeling, shared by many researchers in the field, prompted an explosion of ideas aimed at the goal of developing soluble transition metal systems with which alkanes can be observed to react. To date, numerous systems employing a variety of metals and ligands have been developed. Complexes of platinum, mercury, iridium, rhenium and rhodium have been shown to catalyze the C-H activation of alkanes and in some cases their functionalization.^{14,16,17}

The difference between activation and functionalization is an important one. Breaking an unactivated C-H bond usually resulting in the formation of new metal-carbon bonds (M-C) and a new metal hydrogen (M-H) bonds is termed activation. Converting the M-C bond to a C-X bond, where X is another functional group, by chemical transformation is termed functionalization. While there are many systems capable of C-H activation and many more reports of organometallic functionalization (M-

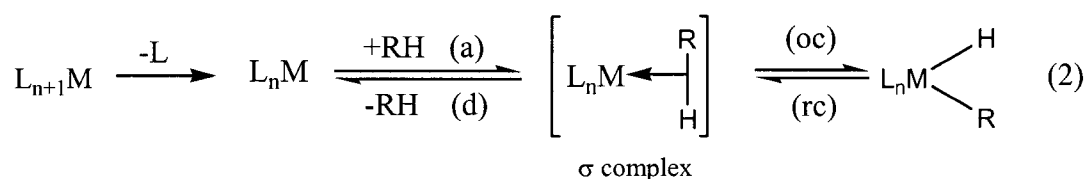
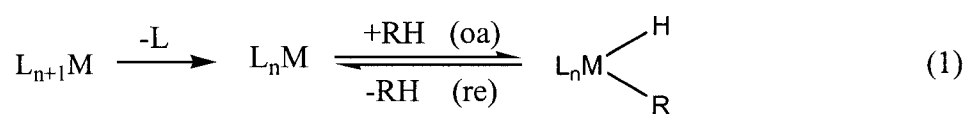
C used to make C-X), there are few systems that can carry out both activation and functionalization at the same transition metal site. Consequently there are few catalytic systems capable of converting alkanes into functionalized products.

A recently published ACS symposium entitled “Activation and Functionalization of C-H Bonds”¹⁸ takes an in-depth look at systems designed to combat this difficult chemical transformation. Central to the discussion of C-H bond activation and functionalization is the pioneering work of Bergman *et al.* on extremely reactive iridium(I) complexes of the type $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}$.^{19,20} The irradiation of the iridium(III) dihydride complex promoted the loss of hydrogen (H_2) and produced the coordinatively unsaturated $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}$ complex which was shown to produce alkyl hydride complexes $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrR(H)}$ when added to a variety of alkane solvents. These results were published nearly simultaneously with similar communication by Hoyano and Graham,²¹ in which a similar iridium(I) complex was generated by photo-dissociation of CO from the starting $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Ir}$ complex and resulted in the first spectroscopic evidence for the oxidative addition product derived from unactivated, saturated alkanes. In addition to showing the ability of these reactive metal complexes to oxidatively cleave the alkane C-H bonds, those workers also demonstrated further alkane functionalization in which the newly formed alkyl iridium hydride complex was converted to an alkyl halide (Scheme 1). The initial studies by Bergman and coworkers included linear, branched, and cyclic alkanes. Methane was targeted immediately thereafter²² when it was discovered that the active iridium complex could be generated thermally under 20 atm of methane in an cyclohexane solution. Over time the coordinatively unsaturated $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}$ complex gave the

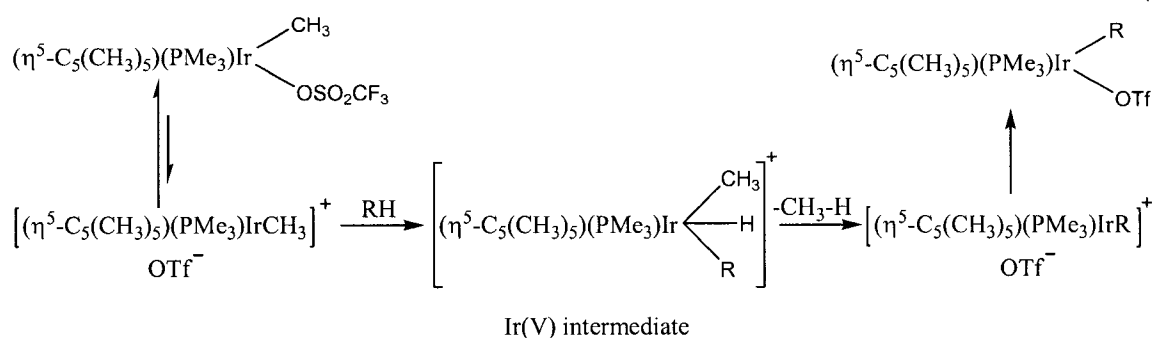
thermodynamically more stable $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrCH}_3(\text{H})$ as the sole observable product in the reaction. Although it was not the first²³ example of methane C-H activation by a homogeneous metal complex, this study provided the first definitive evidence of methane activation via the desired oxidative addition pathway exemplified by Equation 1. Subsequent studies would lend support for the proposed alkane coordination (Scheme 1, step 1) prior to oxidative cleavage of the C-H bond. The more detailed Equation 2 reflects this precoordination equilibrium. The main drawback to these initial studies was the inability to regenerate the active Ir complex after one turnover.



Scheme 1. Proposed mechanism for alkane activation and functionalization by a coordinatively unsaturated iridium(I) complex adapted from ref²² (Figure 2 and Eq. 16 & 17).



More recently, Bergman and coworkers have prepared a series of higher valent $(\eta^5C_5Me_5)(PMe_3)(OTf)Ir^{III}CH_3$ complexes that also activate C-H bonds by simply replacing the initial iridium bound methyl group with the alkyl group of the activated hydrocarbon.²⁴⁻²⁶ In addition to the CH_3 group, a reactive trifluoromethane sulfonate (triflate) ligand has been added. These iridium(III) complexes do not exhibit the same reactivity of their Ir(I) counterparts, however, the corresponding cationic complexes $(\eta^5C_5Me_5)Ir^+CH_3(BAr)_f$ (where $(BAr)_f$ is the tetrakis(pentafluorophenyl)borate counter ion) attack the same range of C-H bonds as those reported for the Ir(I) complexes. The mechanism of activation for these Ir(III) complexes has been investigated, and the preponderance of evidence indicates an oxidative addition pathway through a very high oxidation state Ir(V) intermediate followed by the loss of methane (Scheme 2). The most convincing evidence for the oxidative addition pathway came from the unexpected formation of a cyclometalated Ir(V) hydroarylcenter formed from an initial Si-H activation followed by intramolecular C-H activation (Figure 1).²⁷ Treatment of this Ir(V) complex with acetonitrile produced the C-H reductive elimination product, illustrating the feasibility of Ir(III)/Ir(V) interconversion in the system.



Scheme 2. Proposed mechanism for alkane activation by cationic iridium(III) complexes.

The cationic hydrido-iridium(III) complexes $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrH}]^+$ synthesized by hydrogenolysis of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{CH}_2\text{Cl}_2)\text{IrCH}_3]^+$ were also studied.²⁸ In contrast to the cationic methyl iridium complexes, these hydrido complexes underwent hydrogen-deuterium exchange as a result of R-H over H-H reductive elimination from the Ir(V) intermediate. The ability of these complexes to promote rapid H/D exchange under mild conditions (-50 °C) has prompted their use as deuteration catalysts from readily available deuterium sources like C_6D_6 . A brief summary of the compounds that have been deuterated by this method are listed in Table 1. In the studies described above, a regioselective preference for terminal C-H activation is observed. This selectivity is in direct contrast to the trends observed for radical cleavage ($3^\circ > 2^\circ > 1^\circ$) of C-H bonds. C-H activation studies have indicated that this metal-mediated selectivity arises as a consequence of the steric environment around the substrate C-H bonds.

Figure 1

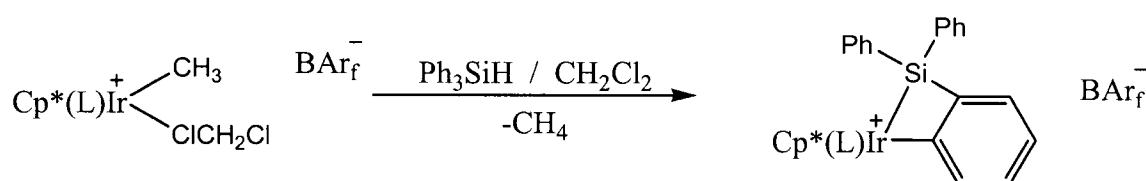


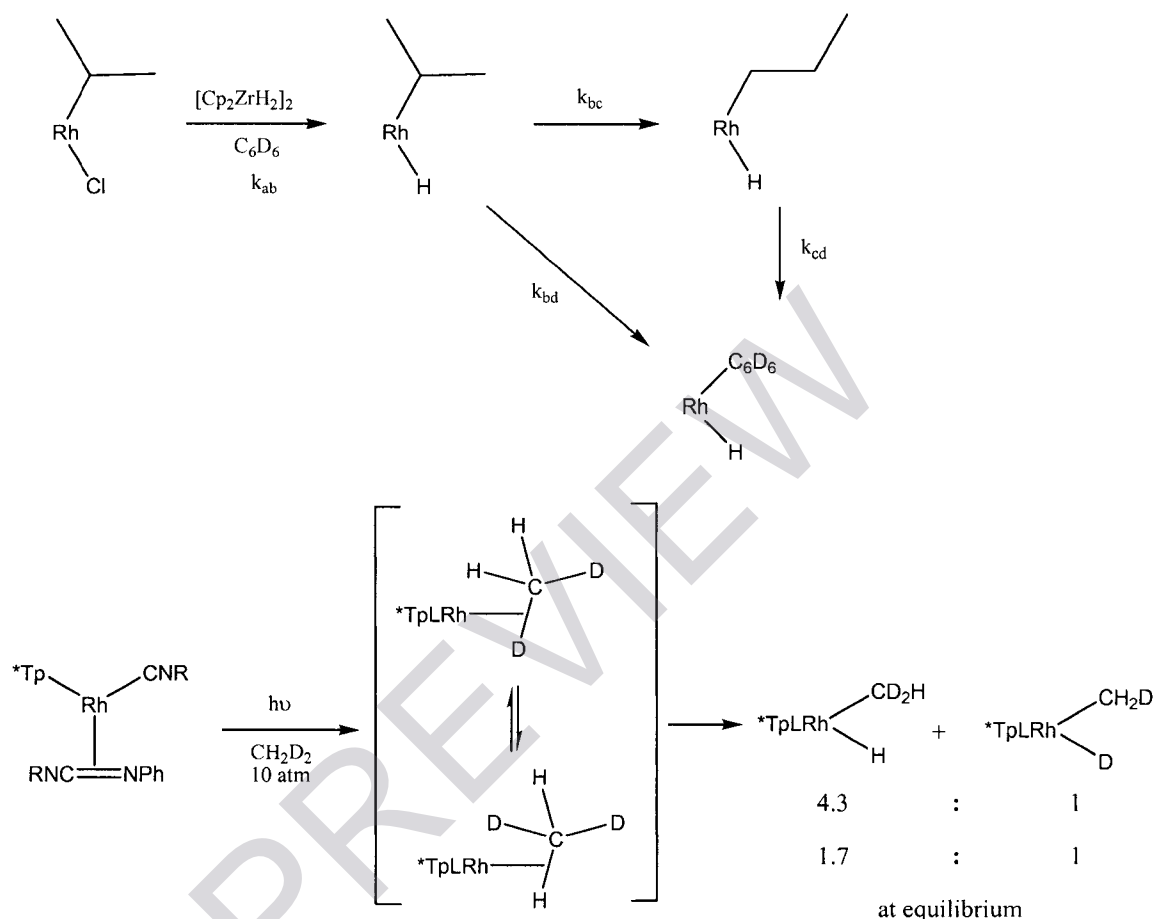


Table 1. Deuteration of alkanes by H/D exchange catalyzed by cationic hydrido-iridium(III) complexes (C_6D_6 as the deuterium source).

R-H		CH ₄		Cp ₂ Fe	Cp ₂ *Fe
T(°C)	-30	-50	-30	-80	-80
%D	10	>80	$\alpha : 80$ $\beta : 20$	>95	>95

To provide further understanding of the mechanism of C-H bond activation in transition metal complexes, Jones has studied C-H bond activation by $[Tp^*Rh(CNR)]$ ($Tp^* = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$, $CNR = \text{neopentylisocyanide}$).^{29,30} These studies have focused on isotope effects for both the oxidative addition and reductive elimination portions of the activation mechanism and sought an understanding of the behavior of the elusive alkane σ -complexes formed as a result of alkane coordination. Evidence for these alkane σ -complexes include the scrambling of metal deuteride into the α position of the metal bound alkyl group,³¹⁻³⁹ temperature dependent line width variations,⁴⁰ and direct observation via low temperature NMR⁴¹ and fast IR studies.⁴² It is important to note that for the activation of linear alkanes by $Tp^*Rh(CNR)$, only the n-alkyl products were isolated, but the ability to activate secondary C-H bonds is manifested in the activation of the cyclic alkane substrates. To measure the isotope effect on the reductive elimination process, a series of rhodium alkyl hydride and alkyl deuteride complexes $Tp^*Rh(CNR)(R)X$ ($X = H, D$) were prepared by the metathesis reaction of the rhodium chloride complex $Tp^*Rh(CNR)RCl$ with Cp_2ZrH_2 or Cp_2ZrD_2 .²⁹ The isopropyl hydride complex was formed by this method and found to rearrange to form the n-propyl derivative. The rearrangement occurred at a similar rate as propane loss, and was

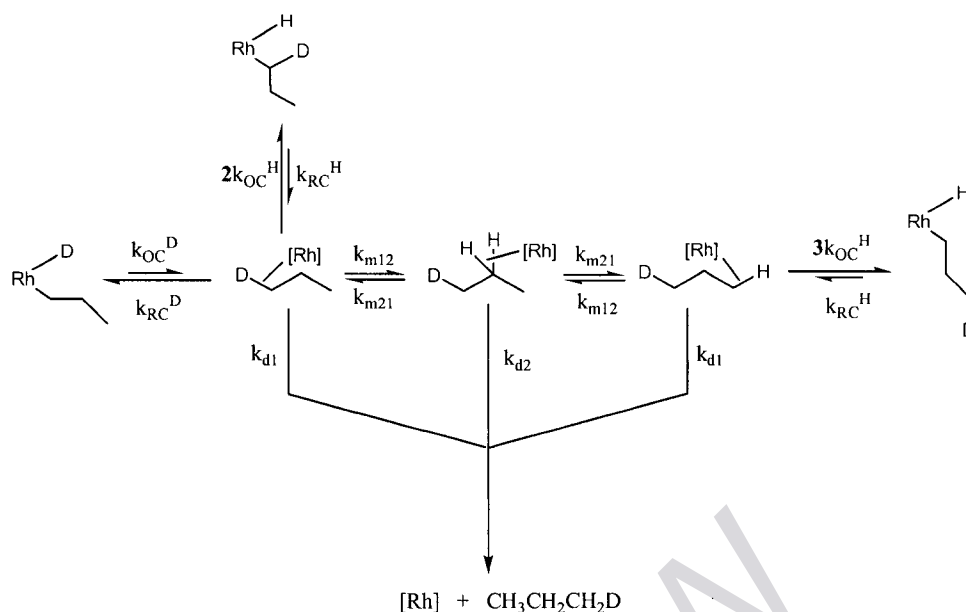
determined by trapping with benzene (Scheme 3, top). The observation of a stable secondary alkyl complex provided evidence that the selectivity for primary positions in n-propane was of kinetic origin.



Scheme 3. (top) rearrangement of isopropyl hydride complex used to determine $k_{\text{RC}}^{\text{H}}/k_{\text{RC}}^{\text{D}}$. (bottom) activation of dideuteromethane used to determine $k_{\text{OC}}^{\text{H}}/k_{\text{OC}}^{\text{D}}$ and $K_{\text{H/D}}$. Adapted from ref.¹⁸ (Chp. 3 Fig. 1 and Eq. 6).

Of more interest, when the corresponding isopropyl deuteride complex was synthesized, similar reactivity was observed. In this case, the rearrangement to the n-propyl derivative was observed in competition with overall reductive elimination but without deuterium scrambling. This reaction indicated that the reductive elimination of the secondary alkyl hydride complex is irreversible. The irreversible nature of the

secondary reductive elimination reaction simplified the overall reductive elimination reaction so that the rate of disappearance of isopropyl deuteride or hydride could be used to determine the rate of reductive coupling. From the separate hydride and deuteride reactions the isotope effect $k_H/k_D = 2.1$ was observed. The rate of oxidative cleavage (the reverse reaction) had already been determined when the carbodiimide complex $\text{Tp}^*\text{Rh}(\text{CNR})$ complex was placed under 10 atm of CH_2D_2 at 5 °C. The kinetic products formed were a 4.3:1 ratio of the $\text{Tp}^*\text{Rh}(\text{CNR})(\text{CHD}_2)\text{H}$ and $\text{Tp}^*\text{Rh}(\text{CNR})(\text{CH}_2\text{D})\text{D}$ indicating a kinetic isotope effect for oxidative cleavage of $k_H/k_D = 4.3$. The experiment has been explained as initial formation of a σ -complex which exchanges between two statistically equivalent C-H or C-D bonds followed by oxidative cleavage to give the kinetic product ratio observed and a normal KIE as was previously observed for the reductive coupling reaction (Scheme 3 bottom). Following the formation of the kinetic products the mixture equilibrates prior to the loss of CH_2CD_2 to a 1.7 : 1 ratio. The new equilibrium ratio (1.7 : 1) for the reaction $\text{Tp}^*(\text{CNR})\text{Rh}(\text{CHD}_2)\text{H} = \text{Tp}^*(\text{CNR})\text{Rh}(\text{CH}_2\text{D})\text{D}$ indicates an inverse equilibrium isotope effect (EIE) $K_{H/D} = 0.59$. The inverse nature of the EIE was confirmed by comparing the previously reported KIE's for the reductive coupling and oxidative cleavage reactions in which $K_{H/D} = (k_{\text{RC}}^{\text{H}}/k_{\text{RC}}^{\text{D}}/k_{\text{OC}}^{\text{H}}/k_{\text{OC}}^{\text{D}}) = 2.1/4.3 = 0.49$. Experimental and computational (DFT) studies on the reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ reported by Parkin provided similar evidence for the existence of a σ -complex.^{43,44} The evidence was again manifested as this type of inverse EIE while the KIE's for the reductive coupling and oxidative cleavage remain normal.



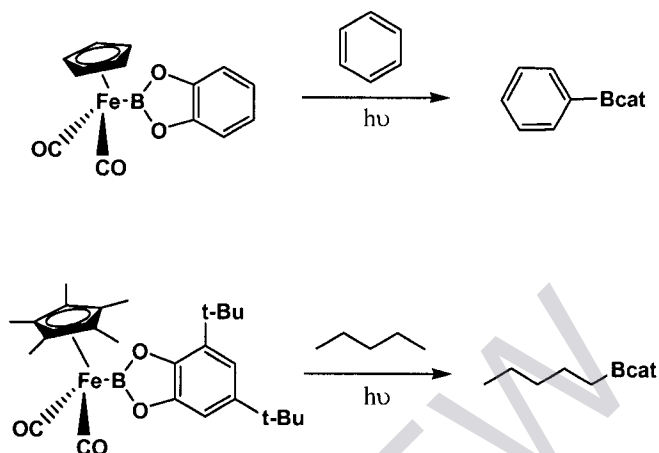
Scheme 4. Kinetic model for the deuterium migration and reductive elimination of $\text{CH}_3\text{CH}_2\text{CH}_2\text{D}$ from the n-propyl rhodium complex

To provide evidence for the regioselectivity observed in linear alkanes, deuterium migration studies were undertaken on the ethyl, n-propyl, n-butyl, n-pentyl, and n-hexyl deuteride complexes. In each case the alkyl deuteride complex was generated in-situ from the rhodium chloride complex and Cp_2ZrD_2 . Migration of the deuterium into the α -position was observed to be the same in all of the alkyl complexes ($\sim 20\%$). Migration to the end of the alkyl chain was also observed in all cases excluding the n-hexyl derivative but was diminished as the length of the alkyl chain is increased. This result argued against a direct end-to-end migration that would be expected to increase for n-hexyl over the shorter alkyl groups. Kinetic simulations of these reactions were used to fit the data and obtain the relative rate constants for each individual step. The kinetic model employed for the n-propyl complex is illustrated in Scheme 4. Since the energies of the σ -complexes cannot be determined, the rate constants for the oxidative cleavage (k_{oc}),

migration (k_m) and dissociation (k_d) were determined relative to one another. The results indicated a ratio of $\approx 4:2:1$ ($k_{oc}:k_m:k_d$) for the ethyl complex and a similar $\approx 5:3:1$ ratio for the n-propyl complex. The relative rate constants for the n-propyl derivative were assumed to be the same for the n-butyl, n-pentyl and n-hexyl derivatives with good agreement. However, for the longer alkyl groups a second migration term had to be inserted for the migration from one 2° carbon to the next along the alkyl chain. The rate constant for the migration from the 1° to 2° (k_{m12}) remains the same, however the rate of migration up and down the alkyl chain (k_{m22}) was found to be quite fast with ratio of 7 : 1 for migration vs. dissociation. This result explained why even if an alkane coordinates to the metal at one of the secondary C-H positions it rapidly runs to the end of the chain and once there, the rate of oxidative cleavage exceeds all other processes leading to the selective activation of terminal C-H bond in linear alkanes.

Hartwig *et al.* have developed the most successful system to date for the catalytic conversion of alkanes as well as arenes to the corresponding alkyl and aryl borane reagents. A number of different metals and ligand systems have been employed to discover both photochemical and thermal routes to the catalytic conversion of alkanes to terminal alkyl boranes. Their work in the field of alkane functionalization began when their studies of transition metal boryl complexes revealed that the irradiation of the cyclopentadienyliron dicarbonyl catecholborane ($\text{CpFe}(\text{CO})_2\text{Bcat}$) complex in a benzene solution yielded the phenylboronate ester in quantitative yield (Scheme 5).^{45,46} Modifications made to the iron complex to eliminate aryl activation produced the pentylboronate ester as the pentane activation product (Scheme 5). The scope of this original system was quickly expanded to include ruthenium and tungsten complexes all

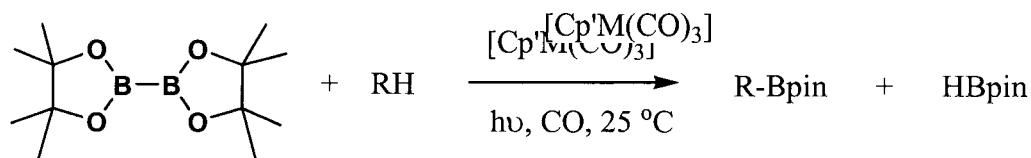
capable of high yield stoichiometric conversion of linear alkanes to terminal alkylboronate esters.⁴⁷ These initial successes suggested that these metal boryl species could be intermediates in a catalytic functionalization cycle.



Scheme 5. Stoichiometric functionalization of benzene and pentane following arene and alkane C-H activation

In order to make the system catalytic a method for regenerating the metal boryl complex had to be discovered. For this reason bis-pinacoldiborane was employed in hopes that it would add oxidatively to a 16-electron $\text{Cp}^*\text{M}(\text{CO})_n$ fragment whose subsequent reactions with an alkane would produce the alkylboronate ester, and regenerate the 16-electron fragment. When $\text{Cp}^*\text{Re}(\text{CO})_3$ (2.5 mol %) was added to bis-pinacoldiborane and pentane under photochemical conditions, the pentylboronate ester was produced in 95 % yield (Scheme 6).⁴⁸ Under similar conditions utilizing several catalysts, a variety of alkanes were converted into terminal alkylboronate esters (Table 2).

Scheme 6



The success of this reaction under photochemical conditions prompted the development of a catalyst that would produce the same catalytic activity under thermal conditions. For a catalyst of this type it was necessary to replace the thermally stable CO ligands with ligands that are more thermally labile. They examined a series of hydride, ethylene, benzene and chloride complexes of iridium and rhodium.⁴⁹ To generate the active catalyst in this study, the new ligands were chosen to be susceptible to thermal dissociation or to be abstracted by diborane. At elevated temperatures (150 °C to 170 °C) all of the metal complexes show excellent catalytic activity and all give the terminal alkylboronate ester as the sole functionalized alkane product (Scheme 7). These results also illustrated that pinacol borane can be used as the borane reagent without loss of catalytic activity. Perhaps the most spectacular of these results is the reaction which employs pentamethylcyclopentadienylrhodium dichloride dimer ($[\text{Cp}^*\text{RhCl}_2]_2$) as the catalyst. This reaction illustrated the power of this system to functionalize alkanes catalytically starting with air stable, commercially available reagents.

Table 2. Regiospecific, catalytic functionalization of alkanes, alkyl ethers, and benzene. Adapted from ref⁴⁸

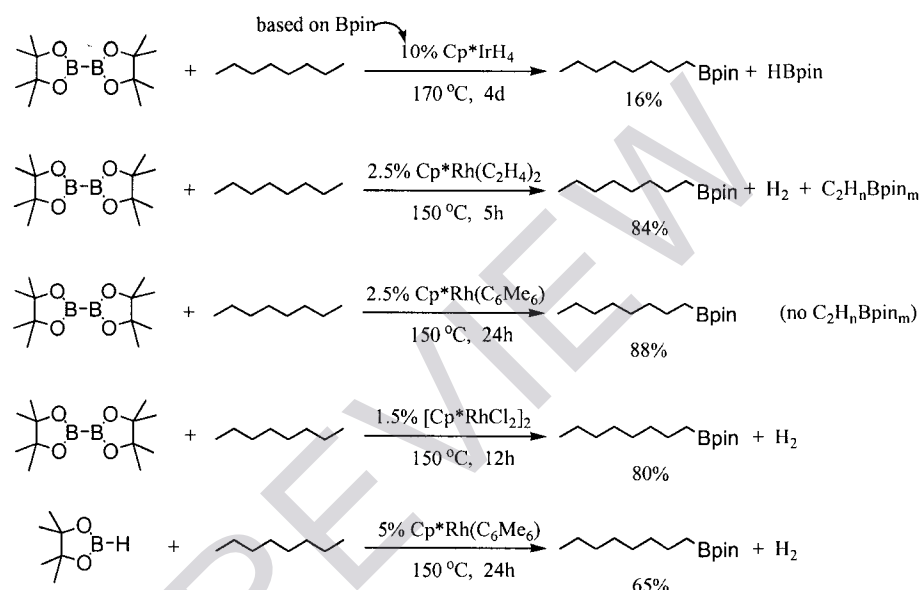
Substrate	Catalyst	Catalyst Amt. [%]	t[h]	Conv. of B_2pin_2	Yield [%]	
					Rbpin	HBpin
n-pentane	$\text{Cp}^*\text{Re}(\text{CO})_3$	2.4	56	94	95	32
2-methylbutane	$\text{Cp}^*\text{Re}(\text{CO})_3$	3.4	55	89	83 ^a	24
methylcyclohexane	$\text{Cp}^*\text{Re}(\text{CO})_3$	5.0	60	88	75	27
di-n-butyl ether	$\text{Cp}^*\text{Re}(\text{CO})_3$	5.0	45	100	100	23
<i>tert</i> -butyl ethyl ether	$\text{Cp}^*\text{Re}(\text{CO})_3$	4.9	46	100	82	26
benzene	$\text{CpMn}(\text{CO})_3$	10	36	97	76	23
n-pentane	$\text{Cp}^*\text{Re}(\text{CO})_2(\text{Bpin})_2$	2.5	56	92	97	31

^aThe two terminal regioisomers were obtained in a 3.6 : 1 ratio.

The synthetic utility of these catalytic transformations has also been expanded to include efficient catalysts for the functionalization of arenes⁵⁰⁻⁵² and polyolefins.⁵³

Phenylboronate esters are important synthetic reagents for Suzuki couplings and the oxidation to phenols. The ability to produce arylboronate esters catalytically from both simple and complex arenes provides an alternative to the more standard methods of quenching the previously prepared Grignard reagent with trialkylborate followed by hydrolysis.

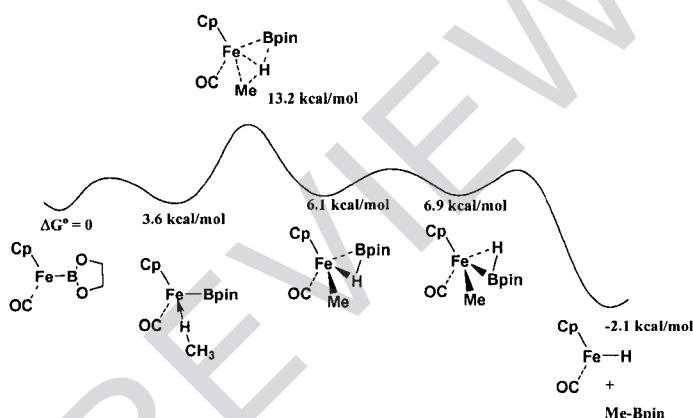
Scheme 7



Mechanistic studies that include stoichiometric reactions of isolated $\text{Cp}^*(\text{CO})_n\text{BR}_2$ complexes reveal that the generation of the catalytically active 16-electron complex was facilitated by photochemical dissociation of CO.⁴⁵ This dissociation was thought to be irreversible because there was no isotopic incorporation when the complex was irradiated under an atmosphere of ^{13}CO . However, when the tungsten complex is irradiated in the presence of trimethylphosphine (PMe_3) and alkane substrate, a new phosphine ligated tungsten complex is formed along with the alkylboronate ester.⁵⁴ These studies suggested that while the catalytically active 16-electron complex is generated by photochemical dissociation of a ligand, the activation of the alkane occurs faster than ligand

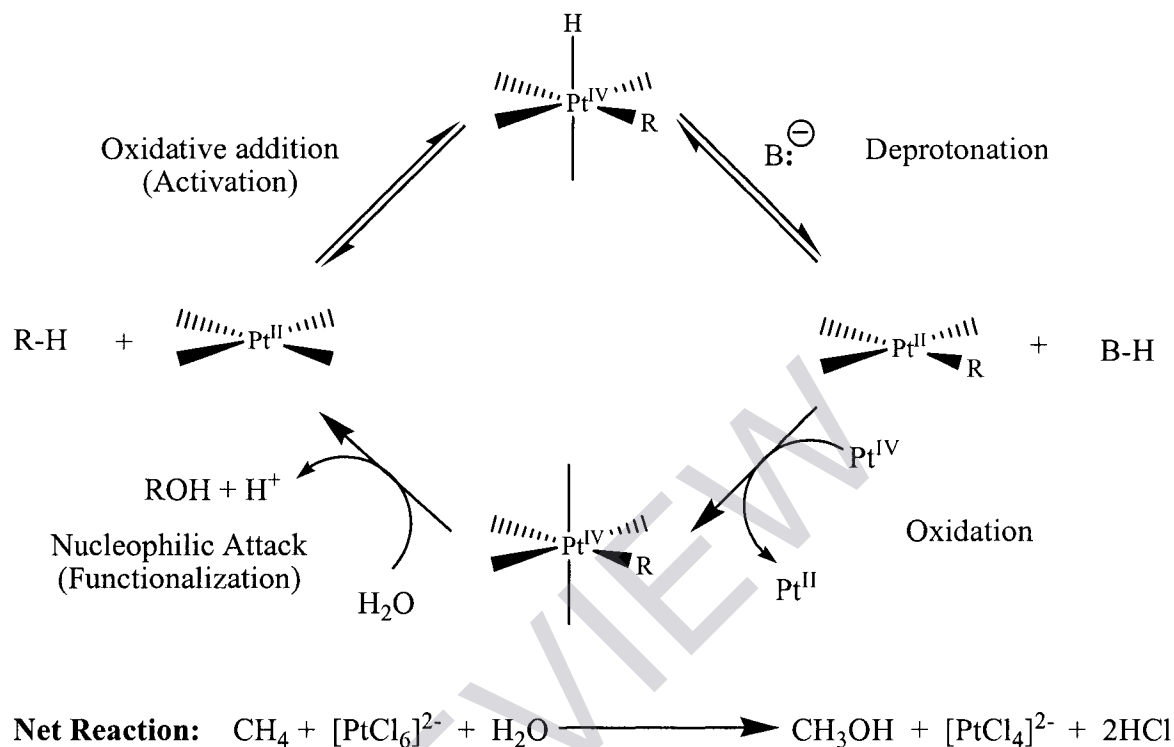
reassociation. Computational analysis performed in collaboration with Hall and coworkers indicated that the unoccupied p-orbital on boron serves to trigger the C-H activation step in the reaction.⁵⁵ Their calculations suggested that the initial addition of the alkane to the metal catalyst proceeds by way of a σ -bond metathesis reaction in which a transient alkane-boryl σ -complex is formed. Rearrangement of this σ -complex to place the boryl and alkyl group in a *cis* orientation is followed by reductive elimination of the alkylborane product (Scheme 8).

Scheme 8



The oldest successful transition metal systems for alkane activation and functionalization are based on the platinum system discovered by Alexander Shilov in 1968.^{16,17} Bercaw and Labinger have done the most extensive study of the Shilov system, and most of the mechanistic detail for this reaction can be credited to their work.⁵⁶ The proposed mechanism, illustrated in Scheme 9, reveals a catalytic cycle consisting of four steps. 1) oxidative addition of Pt(II) to a C-H bond, 2) deprotonation of the resulting Pt(IV) alkyl hydride to generate a Pt(II) alkyl species, 3) Oxidation of the Pt(II) alkyl complex to a Pt(IV) alkyl complex, and 4) nucleophilic attack at the carbon atom of the

Pt(IV) alkyl complex resulting in a functionalized alkane and regeneration of the Pt(II) starting material.



Scheme 9. A mechanistic illustration of the catalytic Shilov alkane hydroxylation cycle

While this system shows catalytic activity with regard to the Pt(II) starting material, the main drawback is the use of a stoichiometric amount of expensive oxidant, usually platinum, to complete Step 3. Because the use of hexachloroplatinate remains cost prohibitive, much attention has been paid developing cheaper oxidants to perform this key step. Additional drawbacks to this approach include slow reaction rates and a propensity for the catalytic species to precipitate out as metallic platinum. This would at first appear to present only the minor problem of decreased catalytic turnover as the