CHAPTER 8

Catalytic, Thermal, Regioselective Functionalization of Alkanes and Arenes with Borane Reagents

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Work in the author's group that has led to a regioselective catalytic borylation of alkanes at the terminal position is summarized. Early findings on the photochemical, stoichiometric functionalization of arenes and alkanes and the successful extension of this work to a catalytic functionalization of alkanes under photochemical conditions is presented first. The discovery of complexes that catalyze the functionalization of alkanes to terminal alkylboronate esters is then presented, along with mechanistic studies on these system and computational work on the stoichiometric reactions of isolated metal-boryl compounds with alkanes. Parallel results on the development of catalysts and a mechanistic understanding of the borylation of arenes under mild conditions to form arylboronate esters are also presented.

1. Introduction

Although alkanes are considered among the least reactive organic molecules, alkanes do react with simple elemental reagents such as halogens and oxygen.[1,2] Thus, the conversion of alkanes to functionalized molecules at low temperatures with control of selectivity and at low temperatures is a focus for development of catalytic processes.[3] In particular the conversion of an alkane to a product with a functional group at the terminal position has been a longstanding goal (eq. 1). Terminal alcohols such as *n*-butanol and terminal amines, such as hexamethylene diamine, are major commodity chemicals[4] that are produced from reactants several steps downstream from alkane feedstocks.

$$\text{(structure)} + \text{X-Y} \xrightarrow{\text{catalyst}} \text{(structure)-X} + \text{Y-H} \qquad (1)$$
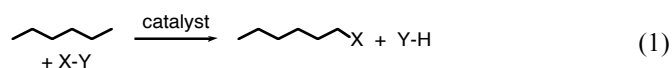
The conversion of alkanes to functionalized products with terminal regioselectivity must confront several challenges outlined in Scheme 1. The internal C-H bond of an alkane is weaker than the terminal C-H bond,[5] and so reactions that are selective for one position over the other are typically selective for the internal C-H bond.[1] Second, the products formed by functionalization are generally more reactive than the alkane starting material. Thus, alcohol products are ultimately converted to ketones, aldehydes or even CO_2, and water, while monohalo alkanes tend to undergo reaction to produce geminal dihalo alkanes.[6] In addition to problems of selectivity are problems of conversion. Many of the desired transformations of alkanes are thermodynamically disfavored. The dehydrogenation of an alkane is, of course, uphill; hydrogenation is a well-known catalytic reaction. The carbonylation of an alkane is also uphill;[7] decarbonylation is a known catalytic reaction.[8,9] And a reaction related to results presented later in this manuscript – the dehydrogenative coupling of water with an alkane to form dihydrogen and a terminal alcohol – would be spectacular, but it is again thermononamically uphill[5].
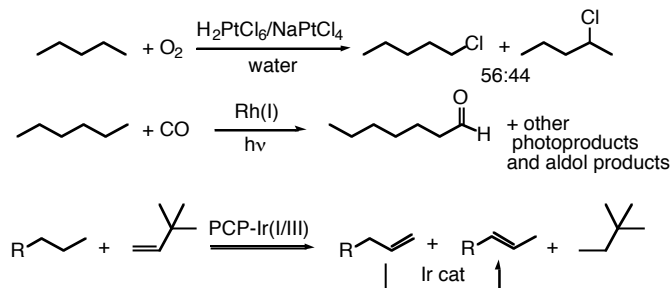
Scheme 1
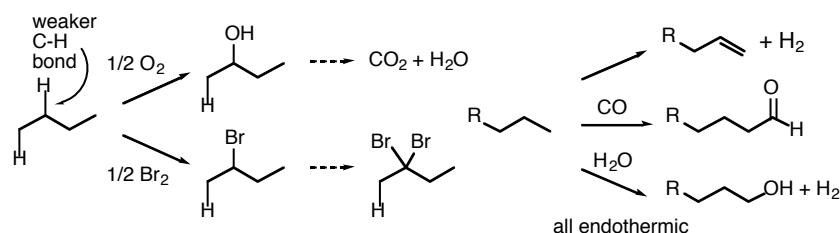
Many transition metal complexes are now known to react selectively at the terminal position of an alkane (Scheme 2). Bergman and Jones have shown that rhodium complexes will react at the terminal position of linear alkanes to generate 1-substituted rhodium alkyl products.(*10,11,12,13*) In a much different type of C-H activation, Wolczanski has shown that a titanium imido complex reacts with alkanes to generate terminal titanium alkyl products.(*14*) Thus, non-radical reactions of transition metal complexes with alkanes often generate the desired product from terminal activation.

Scheme 2
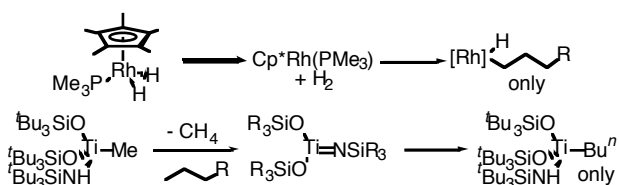
However, the reactions just described are stoichiometric. Catalytic reactions of alkanes that make use of this terminal selectivity are rare. A few examples are summarized in Scheme 3. Before any of the directly observed oxidative additions of alkanes were observed, Shilov had shown that platinum chemistry can provide more terminal product than radical chemistry does, but the selectivity for the terminal product remained lower than would be needed for synthetic purposes.(*15,16*) Tanaka and Goldman studied the carbonylation of alkanes.(*17,18*) Although this chemistry shows good terminal selectivity, the reaction yields are low. Products from secondary photochemistry and condensation dominate. Dehydrogenation has recently been shown by Goldman and Jensen to provide α−olefin as the kinetic product.(*19*) However, the catalyst for this dehydrogenation is also a catalyst for isomerization, and a thermodynamic mixture of internal and terminal olefins is ultimately produced. This thermodynamic mixture favors the internal olefin.

Scheme 3

Scheme 4
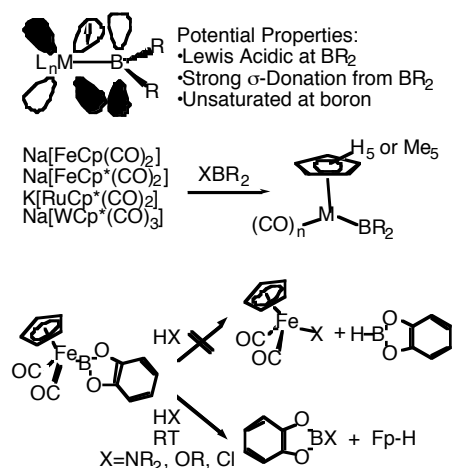
2. Development of a Catalytic Functionalization of Alkanes

## 2.1 Stoichiometric Studies of Metal-Boryl Complexes

Our studies on the functionalization of alkanes originated from studies of transition metal boryl complexes.(*20-22*) We anticipated that the unoccupied p-orbital on boron would affect both structures and reactions of this class of molecule (Scheme 4, top). The boryl complexes would be strong sigma donors because of the high basicity of an anionic boryl fragment, but their unsaturation would lead to some back-donation from the metal.

We initially prepared these complexes by the reaction of classic metal carbonyl and Cp metal carbonyl anions with haloboranes (Scheme 4, middle). By this route we prepared a family of metal boryl complexes with catecholate, pinacolate, dithiocatecholate and dialkyl substituents boron.(*23-25*)

Several years ago we found that these metal boryl complexes reacted with XH bonds in a process that placed the hydrogen on the metal and X at boron (Scheme 4, bottom).(*26*) Most striking, this regiochemstry was also observed from C-H activation processes. Irradiation of CpFe(CO)$_2$Bcat (Fp-Bcat, **1**) in benzene solvent generated the phenyl boronate ester PhBcat in quantitative yields, as shown at the top of Scheme 5.(*24,27*) Fp dimer was the transition metal product, and H$_2$ presumably formed. Because Fp complexes had shown no

previous intermolecular C-H activation chemistry of hydrocarbons, this reaction demonstrated the unusual ability of a boryl ligand to trigger C-H activation.

Scheme 5
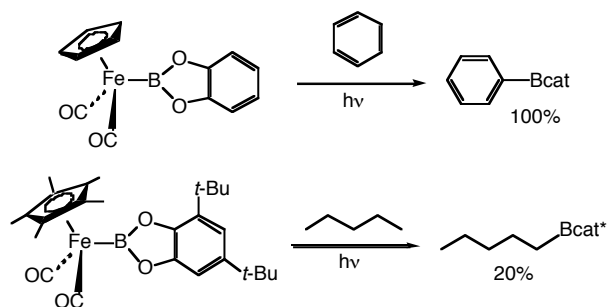
Starting with this complex that functionalized arenes, we sought to create boryl complexes that would undergo analogous reactions of alkanes to replace the hydrogen with the boryl group. If such a complex is to be generated, the reactive arene C-H bonds must be absent from the system. Thus, we made two changes to the boryl complex to observe the borylation of alkanes. First, the simple catecholboryl group was replaced by the 3,5-di-*tert*-butyl catecholboryl group to eliminate and sterically block the aromatic C-H bonds. Second, the Cp ligand was replaced with Cp* to eliminate the pseudo aromatic C-H bonds on this part of the molecule. With these two changes to the metal complex, the modified Fp boryl complex reacted with alkanes to produce functionalized products, albeit in a modest 20% yield (Scheme 5, bottom).(*28*) Yet the regiochemistry for this reaction of an alkane was perfect for placing a boryl group at the terminal position. This result indicated that even simple, classic metal fragments were capable of terminal alkane CH activation and functionalization when ligated by a boryl group.

To improve the yields of this process, we investigated second- and third-row analogs of these iron boryl complexes.(*28*) The ruthenium analogs produced 40% yield of the terminal, pentylboronate ester. After a brief study with osmium analogs, we investigated the more synthetically accessible Cp*W(CO)$_3$-boryl complexes. These tungsten complexes were remarkably reactive toward borylation of terminal, alkane C-H bonds, as summarized in Scheme 6.(*28*) Irradiation of this complex in pentane for 20 min generated 85% yield of the 1-pentylboronate ester without formation of any detectable quantities of internal isomers. These metal fragments displayed low reactivity toward any hydrocarbon secondary C-H bond. For example, the analogous reaction of the tungsten complex in cyclohexane solvent generated only 22% yield of the cyclohexyl boronate ester. Reaction with ethylcyclohexane produced only the product from functionalization at the terminal position of the ethyl sidechain in

74% yield. Finally, isopentane, which contains two sterically different methyl groups, reacted in 55% yield to produce an 11:1 ratio of the product from the functionalization of the less hindered methyl group to the product from functionalization of the more hindered methyl group.

Scheme 6
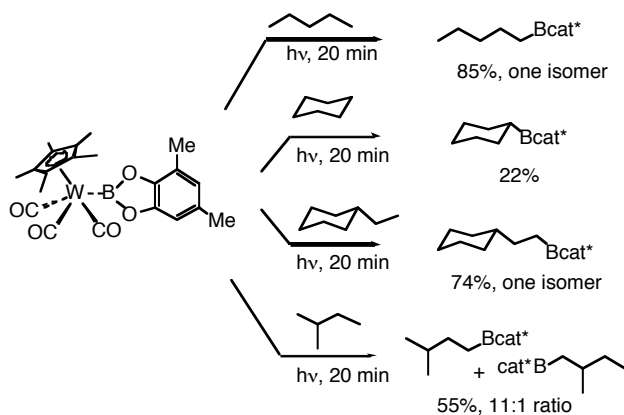
2.2. Development of a Photochemical Catalytic Functionalization of Alkanes

These results implied that boryl complexes could be used as intermediates in a catalytic functionalization of alkanes and arenes. However, a catalytic cycle involving the $Cp*M(CO)_n$-boryl complexes was difficult to imagine because these complexes were generated by substitution reactions with metal anions. Thus, we sought to use diboron compounds such as bis-pinacoldiborane(4) (B_2pin_2, pin=pinacolate) as reagents to generate the required boryl intermediates. We envisioned that oxidative addition of these diboron reagents would occur to a 16-electron $Cp*M(CO)_n$ fragment in a similar fashion to the additions to other unsaturated fragments published previously by Marder and Baker,(*29-31*) Miyaura,(*32*) Smith,(*33*) and us.(*31*) Subsequent reaction of this $Cp*M(CO)_n$ bis-boryl intermediate with an alkane or arene could generate functionalized product, borane side product, and the same 16-electron fragment that added the diboron compound. If we started his process with $Cp*M(CO)_3$ (M=Mn,Re), then this reaction would occur through intermediates that are isoelectronic and nearly isostructural with the $Cp*M(CO)_n$-boryl complexes that functionalized alkanes stoichiometrically. This reaction occurred as planned.(*34*) As shown in Scheme 7, the reaction of bis-pinacolato diboron with pentane in the presence of 2.5 mol% of the rhenium catalyst under photochemical conditions generated 95% yield of the 1-pentylboronate ester. This reaction was slow – It required 56 h for

complete conversion – but the yield of functionalized product was high. This result demonstrated the potential to conduct catalytic borylation of alkanes.

Scheme 7

pin=pinacolate
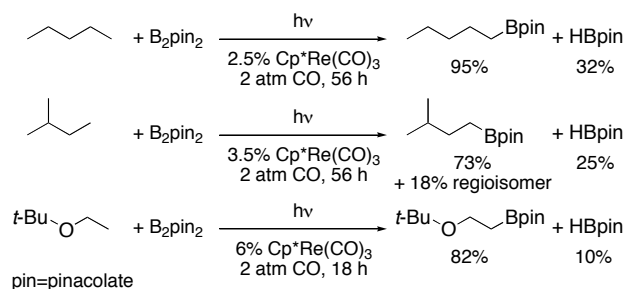
2.3. Development of a Thermal Catalytic Functionalization of Alkanes

This success with a photochemical, catalytic functionalization suggested that we could develop a thermal process for the conversion of alkanes to alkylboronate esters. To observe catalytic chemistry under such conditions, the carbonyl ligands must be replaced with ligands that undergo thermal dissociation more readily. We initially investigated iridium complexes because of their history of success in alkane transformations.(*35-37*) We envisioned that the boron reagent would abstract hydrides from Cp*IrH$_4$ and ethylene from Cp*Ir(C$_2$H$_4$)$_2$ to generate an unsaturated intermediate. Indeed, early results with these complexes, albeit modest, suggested that a catalytic process could be developed. With 10 mol % iridium over 4 d at 170 °C, the bis-ethylene complex generated 16% yield of functionalized product (eq. 2).(*38*)

$$(2)$$
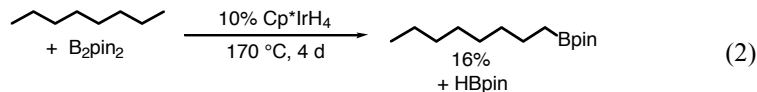
Second-row metal complexes typically react with faster rates than first-row complexes. For this reason we hoped to increase the rates of these iridium-catalyzed reactions by studying the analogous rhodium complexes. Some results from this study are shown in Scheme 8. Cp*RhH$_4$ is not known, but Cp*Rh(C$_2$H$_4$)$_2$ is well known.(*39*) Thus, we tested Cp*Rh(C$_2$H$_4$)$_2$ for the borylation of alkanes with B$_2$pin$_2$ and found that the alkyl boronate ester was formed in yields over 80%. C$_2$-boryl products, however, were generated from the two ethylene ligands, and the generation of these products reduced reaction yields. To generate a catalyst without forming such organoborane byproducts,

we tested the related η^4-hexamethyl benzene complex whose synthesis had been published,(*40,41*) but whose reaction chemistry had not been studied. Reaction of octane with B_2pin_2 in the presence of 0.5 mol% of $Cp*Rh(\eta^4\text{-}C_6Me_6)_2$ with respect to Bpin units formed 1-octylBpin in 72% yield, which corresponds to 144 turnovers.(*38*) Reaction with 5 mol% $Cp*Rh(\eta^4\text{-}C_6Me_6)_2$ gave 88% yield of the 1-alkylboronate ester. The catalyst can also be generated from the air-stable and commercially available $[Cp*RhCl_2]_2$.(*42,43*) Abstraction of chloride by B_2pin_2 generates ClBpin and the active catalyst. Thus, reaction of octane with 1.25 mol% $[Cp*RhCl_2]_2$ gave 80% yield of the 1-octylboronate ester. Thus, regiospecific functionalization of an alkane can be conducted with a catalyst and reagent that are air-stable and commercially available.
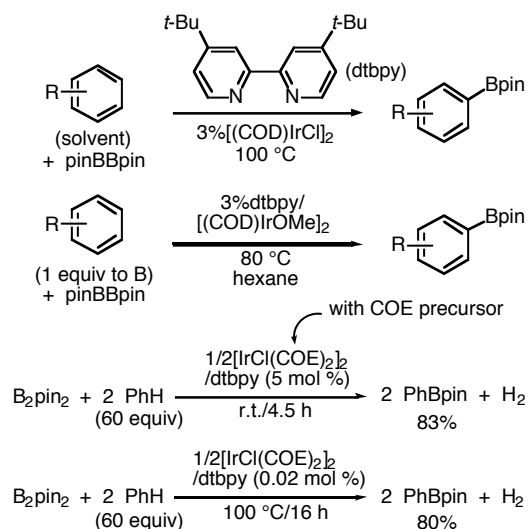
Scheme 8
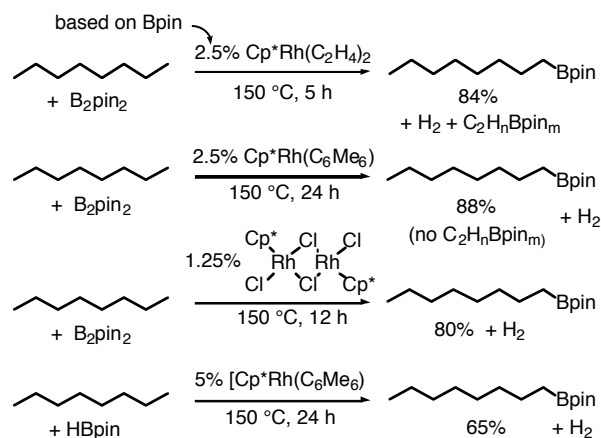
In addition to reactions of diboron reagents with alkanes to form alkylboronate esters, reactions of pinacolborane with alkanes occurred in the presence of $Cp*Rh(\eta^4\text{-}C_6Me_6)$. Octane reacted with pinacolborane to form 1-octylboronate ester in 80% yield in the presence of 5 mol% $Cp*Rh(\eta^4\text{-}C_6Me_6)$. This process is simply the second stage of the reactions of B_2pin_2 with alkanes. The first stage of the catalytic reaction of B_2pin_2 with an alkane generates one equivalent of alkyl boronate ester and one equivalent of pinacol borane. The second stage leads to the dehydrogenative coupling of pinacolborane with the alkane to form the second equivalent of alkyl boronate ester.

Scheme 9
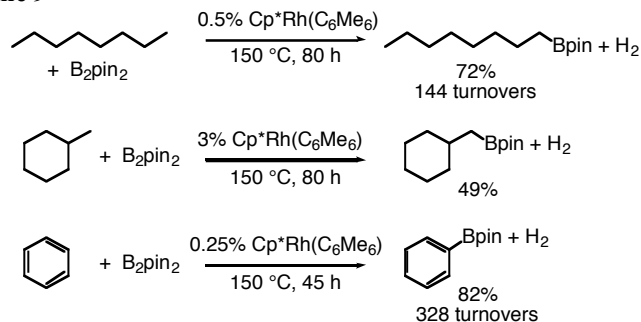
The thermal, catalytic borylation of alkanes is sensitive to the steric properties of the alkane (Scheme 9). Reactions of linear alkanes, such as octane, occurred in the highest yields. Reactions of alkanes containing more hindered methyl groups, such as methylcyclohexane, required longer times, higher catalyst loadings, and occurred in lower yields. However aromatic hydrocarbons, such as benzene, generated the products in high yields. Reactions of benzene with B_2pin_2 in the presence of $Cp*Rh(\eta^4\text{-}C_6Me_6)$ generated the phenylboronate ester in 82% yield with only 0.25 mol% catalyst, corresponding to 328 turnovers.

Scheme 10

2.4. Development of an Efficient Functionalization of Arenes

In addition to developing catalysts for the regioselective functionalization of alkanes, we have developed efficient catalysts for the functionalization of arenes (Scheme 10). Aryl boronate esters are common reagents for Suzuki cross-coupling (*44-46*) and for oxidation to phenols. These reagents are typically prepared by halogenation of an arene, generation of the corresponding Grignard reagent, quenching of the Grignard reagent with a trialkylborate and either hydrolysis or alcoholysis with a diol. Thus, a route to aryl boronate esters directly from arenes would be much more efficient. Synthetic studies by Ishiyama and Miyaura, along with mechanistic studies by our group, led to the development of a room-temperature process for the borylation of arenes.(*47-49*) The combination of 4,4'-di-*tert*-butyl bipyridine and [(COE)$_2$IrCl]$_2$ generated a species that converted arenes, including various substituted arenes, to aryl boronate esters in excellent yields. Reactions of monosubstituted arenes gave a mixture of 3-, and 4-aryl boronate esters while reactions of 1,3-disubstituted arenes gave 5-aryl boronate esters, and reactions of symmetric 1,2-disubstituted arenes generated 4-aryl boronate esters. In addition, the complex that is generated *in situ* catalyzed the borylation of arenes with remarkably high turnover numbers at elevated temperatures. Reaction of benzene with B$_2$pin$_2$ at 100 °C generated 80% yield of arylboronate ester with only 0.01 mol% catalyst, corresponding to 8,000 turnovers.(*47*) This value surpasses most, if not all, turnover numbers reported for homogeneous functionalization of hydrocarbons.

$$\text{(3)}$$
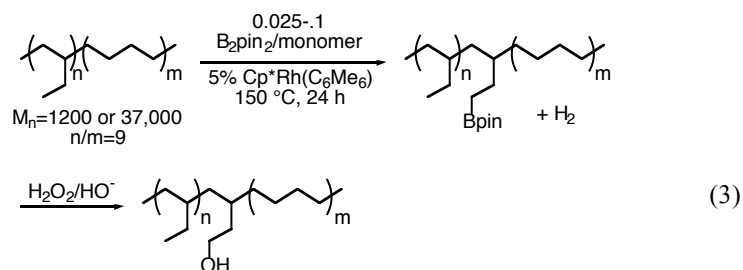
2.5. Functionalization of Polyolefins

Polyolefins are alkanes, and selective functionalization of these high molecular weight alkanes would generate particularly valuable products. Polyolefins containing hydroxyl groups display higher glass transition temperatures, improved barrier properties, improved miscibility with polar phases, and the potential to generate graft copolymers.(*50-55*) To demonstrate that polyolefins undergo selective borylation, we conducted catalytic reactions of boron reagents with hydrogenated polybutadiene (polyethyl ethylene, PEE,

see eq. 1),(*56*) which contains relatively unhindered methyl groups on the polymer sidechain and which can be prepared with narrow polydispersities.(*57*) The narrow polydispersities would allow the identification of chain coupling or chain scission processes that are characteristic of radical oxidation chemistry. Indeed, reaction of diboron compounds with these polyolefins in the presence of a Cp* rhodium catalyst generated PEE with boryl groups at the termini of the sidechains (eq. 1)(*58*) Subsequent standard oxidation generated the analogous hydroxylated polymer. ^{1}H NMR, ^{13}C NMR and IR spectroscopy demonstrated that hydroxylation of the termini of the ethyl sidechains had occurred. The amount of functionalization was dictated by the ratio of diboron compound to ethyl sidechains. Functionalization of up to 20% of the ethyl groups was achieved.

3. Mechanistic Studies of Alkane Borylation

3.1 Stoichiometric Alkane Borylation

Our mechanistic studies on the borylation of alkanes include stoichiometric reactions of isolated Cp*M(CO)$_n$BR$_2$ complexes and single-turnover experiments of potential intermediates in the catalytic process. To probe whether photochemical dissociation of CO occurred during reactions of the Cp* metal carbonyl complexes, we irradiated these complexes in the presence of ^{13}CO, 2 atm of CO, and PMe$_3$.(*25*) Irradiation of these complexes in the presence of ^{13}CO did not lead to incorporation of label into the starting complex. Moreover, reactions in the presence of 2 atm of CO did not occur more slowly than those conducted in the absence of added CO. Thus, dissociation of carbon monoxide either does not occur or occurs irreversibly. Reactions of the tungsten complex in the presence of PMe$_3$ demonstrated that dissociation of carbon monoxide occurred irreversibly.(*25*) Irradiation of Cp*W(CO)$_3$Bcat* in the presence of 2 equiv of PMe$_3$ generated the mixture of phosphine-ligated tungsten boryl and the alkyl boronate ester in Scheme 11. Irradiation of Cp*W(CO)$_3$Bcat* with 4 equiv of PMe$_3$ generated roughly twice as much of the phosphine ligated boryl product as irradiation with 2 equiv of PMe$_3$. Thus we propose that generation of a 16-electron intermediate occurs by initial photochemical dissociation of carbon monoxide and that reaction of the 16-electron intermediate with alkane occurs faster than reassociation of the released carbon monoxide.

Scheme 11
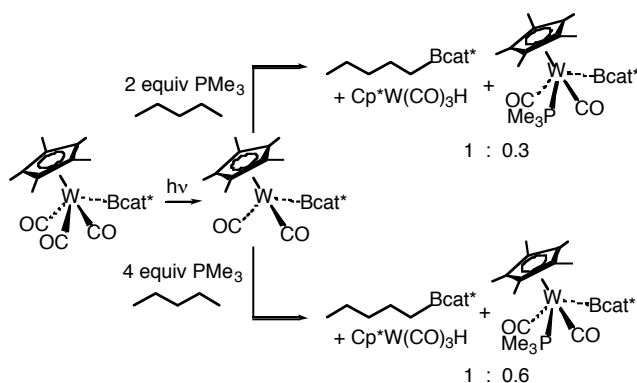
Scheme 12
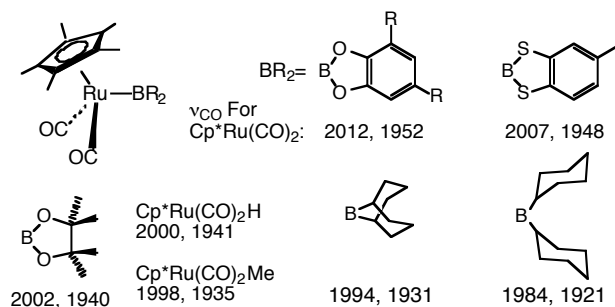
One might propose that the boryl ligand imparts onto the transition metal unusual electronic properties and that this unusual electronic property triggers the C-H activation chemistry. To determine if the overall electron density of the metal center was unusually high becuase of strong sigma donation of the boryl ligand or unusually low because of back donation from the metal, we prepared several Cp*Ru(CO)$_2$-boryl complexes and obtained infrared data (Scheme 12).(*25*) The catecholboryl complexes displayed ν_{CO} values that were 10-20 wavenumbers higher than those of the classic Cp*Ru(CO)$_2$H(*59*) and Cp*Ru(CO)$_2$Me(*59*) analogues. The dialkylboryl complexes displayed stretching frequencies that were 5-15 wavenumbers lower than those of the hydride and methyl analogues. Yet the ruthenium complex of the pinacolboryl group, which is the most effective boryl group for the catalytic transformations and reacts as cleanly as the catecholboryl groups in the stoichiometric chemistry, showed ν_{CO} values that were nearly identical to those of the hydride and methyl compounds.

Therefore, the overall electron density of the metal center is not the driving force for the unusual C-H activation chemistry.

Instead, recent computational work in collaboration with Hall's group at Texas A&M suggests that the unoccupied p-orbital on boron triggers the C-H activation process.(*60*) These calculations indicate that reaction occurs by the sigma-bond metathesis mechanism in Scheme 13 in which the alkane C-H bond of a boryl σ-alkane complex adds across the M-B bond to generate an alkyl σ-borane complex. After an intramolecular rearrangement to place the boryl group of the coordinated borane cis to the alkyl group, reductive elimination of alkylborane occurs. This calculated pathway is roughly 10 kcal/mol lower in energy than the oxidative addition pathway.(*61*)
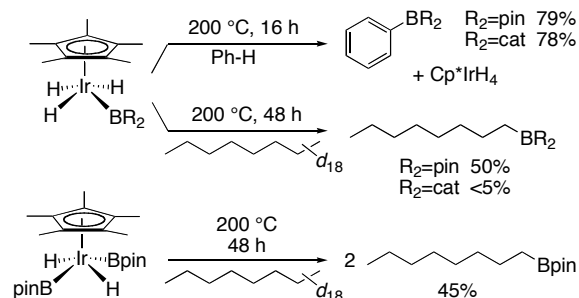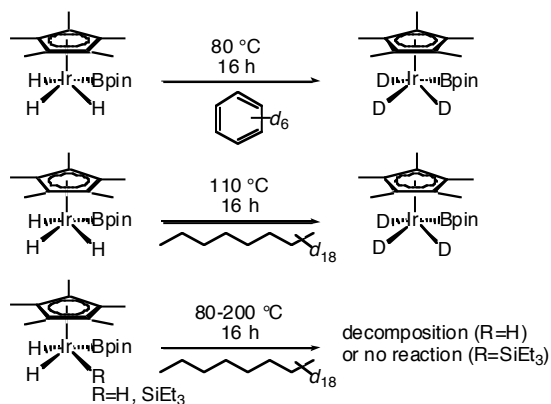
Scheme 13
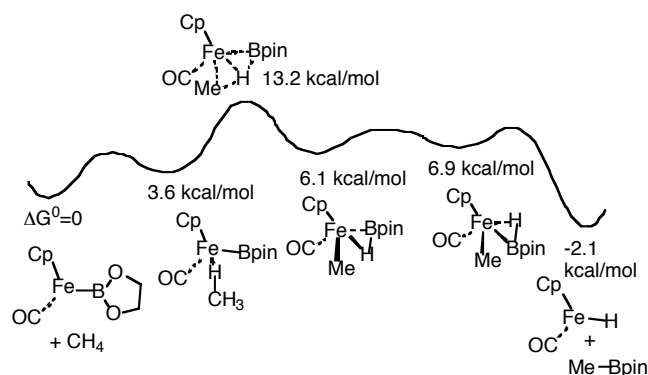
3.2 Single-Turnover Studies of the Borylation of Alkanes

Additional mechanistic studies have led to the generation of Cp*Ir(V)-boryl complexes that are potential intermediates in the iridium catalyzed borylation of alkanes and that are analogs of intermediates in the rhodium catalyzed borylation of alkanes.(*62*) Reaction of Cp*IrH$_4$ with excess pinacolborane generated Cp*IrH$_2$(Bpin)$_2$, and lithiation of Cp*IrH$_4$,(*63*) followed by quenching of the anion with ClBpin, generated Cp*IrH$_3$Bpin. These iridium boryl complexes reacted with alkanes, as shown in Scheme 14, to generate alkyl boronate esters in roughly 50% yield with the same regiospecificity as observed in the catalytic process. These complexes also reacted with benzene to generate the phenyl boronate ester. Related pinnacolboryl and 9-BBN complexes were also generated. The catecholboryl complexes did not react with alkanes but did react in good yields with arenes to generate aryl boronate esters. The 9-BBN complexes did not react with either alkanes or arenes.
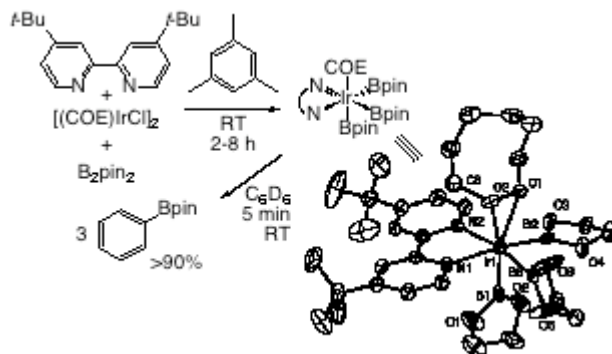
Scheme 14

Scheme 15

Reactions of the mono- and bis-boryl complexes of iridium required long times, even at 200 °C, to undergo complete reaction. Yet, interaction of the hydrocarbons with the iridium complexes did occur at lower temperatures, as summarized in Scheme 15. For example, the mono pinacolboryl complex underwent H/D exchange at 80 °C with benzene-d_6 to place deuterium at the hydride position. It more slowly underwent exchange at the Cp* position, presumably by an intramolecular C-H activation process of the initially formed deuteride complex.(*64*) H/D exchange also occurred with alkanes at temperatures lower than those required for the functionalization process. Reaction of the mono pinacolboryl complex at 110 ° with octane-d_{18} also led to H/D exchange at the hydride position. This reactivity stands in contrast to the inertness of the iridium tetrahydride and iridium silyl hydride complexes toward alkanes.(*65*) We found that the tetrahydride simply undergoes decomposition at about 80 °C in octane-d_{18}, while the triethylsilyl complex does not undergo decomposition or H/D exchange after 20 h at 200 °C in octane-d_{18}.

3.3. Single Turnover Experiments on the Borylation of Arenes

Iridium boryl complexes that are potential intermediates in the rapid and high-turnover borylation of arenes have also been prepared.(*47*) Reaction of bis-cyclooctadiene iridium dichloro dimer with di-*tert*-butylbipyridine in the presence of excess of the B_2pin_2 reagent generated a tris-boryl complex (Scheme 16). Yields for the generation and isolation of this complex were only 15-30%, but a sample suitable for X-ray diffraction and samples suitable for preliminary studies on reactivity were obtained. This tris-boryl complex reacted at room temperature with neat benzene to generate in high yield 3 equiv of the phenyl boronate ester. The role of this complex in the major catalytic pathway is not yet clear, and the mechanism by which this complex reacts with benzene has not yet been determined, but the selectivity of this complex for reaction with benzene vs benzene-d_6 and for trifluorotoluene vs toluene was indistinguisable from that of the catalytic process.

Scheme 16

Scheme 17
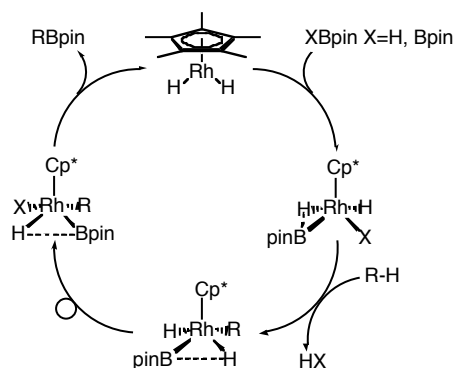
3.4 Proposed Catalytic Cycle

Based on the isolation of Cp*Ir(V)-boryl complexes and the participation of the boron p-orbital in the C-H bond cleavage process deduced by theory, we propose the mechanism in Scheme 17 as one pathway followed during the catalytic functionalization of alkanes. Clearly, further work must be conducted to test this hypothesis, but the proposal is consistent with the current data. In this mechanism, a $Cp*RhH_2$ intermediate undergoes oxidative addition of the diboron or pinacolborane reagent to generate a dihydride bis-boryl or trihydride mono-boryl intermediate. These boryl complexes would then undergo dissociation of borane or H_2 to generate a mono hydride, mono boryl intermediate. This 16-electron intermediate would then undergo reaction with alkane to generate an alkyl σ-borane complex that would form the alkyl boronate ester product and the starting dihydride. Several other mechanisms containing other monomeric hydride or boryl complexes as intermediates can also be drawn and may be occuring in parallel. Yet, a Rh(III)-boryl complex should be the intermediate that reacts with the alkane in any mechanism.

4. Conclusions

The first process by which alkanes are transformed regiospecifically into terminal functionalized products has been developed. Enzymes called omega-hydroxylases are also capable of terminal functionalization of alkanes. These enzymes generate alcohol with preferential reactivity at the terminal position, but the regioselectivity of the oxidation varies with alkane chain length and is much lower than the regioselectivity of the process described here.(*66*) Moreover, these hydroxylases are membrane-bound and are, therefore, difficult to study and to use synthetically.(*67*) Other transition metal complexes noted in the Introduction are capable of cleaving the terminal C-H bond of an alkane, but catalytic processes that involve this regioselective elementary reaction and that form functionalized product in good yield are rare.

Boranes and metal boryl complexes undergo this C-H functionalization chemistry for several reasons. First, the B-C bond is a strong 111-113 kcal/mol in $MeB(OR)_2$,(*68,69*) which makes the C-H bond of the alkane appear weak. Second, the boryl group contains no β-hydrogens, and the pinacolboryl group is remarkably stable. Finally, the unoccupied p-orbital at boron appears to assist in the C-H bond cleavage event and may also facilitate the B-C coupling. Perhaps these concepts can be used to find additional reagents and metal complexes that create similarly selective functionalization processes.

Acknowledgement

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