Iridium complexes of *N*-heterocyclic carbenes in C–H borylation using energy efficient microwave technology: influence of structure, ligand donor strength and counter ion on catalytic activity†

Christoph F. Rentzsch, Evangeline Tosh, Wolfgang A. Herrmann* and Fritz E. Kühn*

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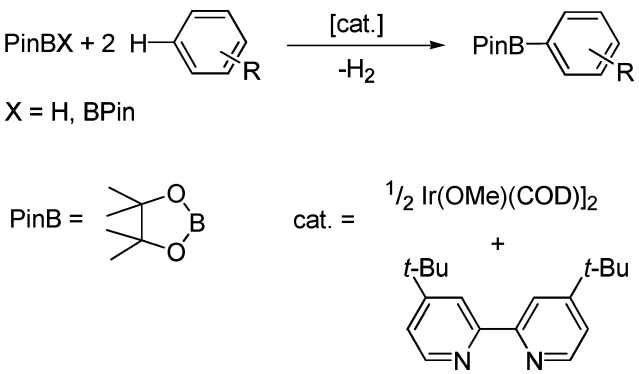
Bridged and unbridged *N*-heterocyclic carbene (NHC) ligands were metalated with $[Ir(COD)Cl]_2$ to give iridium(I) mono- and biscarbene substituted catalysts [Ir(COD)NHC(Cl)] and $[Ir(COD)(NHC)_2][X]$ (X: I, PF_6, BF_4, CF_3COO, OTf). The prepared NHC-complexes were tested in the C–H borylation reaction of aromatic carbons with bis(pinacolato)diboron (B_2pin_2) and pinacolborane (HBpin). The use of microwave technology in this study not only facilitates a time efficient screening of a wide range of influences such as ligand σ-donor strength and structural motif as well as the effects of the complex counter ion, but also provides an energy efficient heating source. Catalyst $\mathbf{6}^{TFA}$, which features a chelating NHC ligand, proved to be most effective catalyst and further investigations with this complex in the borylation of mono- and disubstituted benzene derivatives exploring chemo- and regioselectivity were undertaken.

Introduction

The selective transition metal catalyzed functionalization of "unreactive" C–H bonds remains a challenge in present day organometallic chemistry.[1] Since first reports by Chatt and Davidson[2] in 1965 on the C–H activation of aliphatic and aromatic hydrocarbons mediated by ruthenium complexes, various transition metal complexes have been tested for activity in this reaction.[1–7]

Among catalytic transformations, the C–H borylation reaction proves to be a powerful tool for the direct synthesis of valuable alkyl or aryl boronic acid esters.[7] Boronic acid esters are employed as starting materials for the Suzuki–Miyaura reaction[8] and are readily transformed into functionalized amines or hydrocarbons such as alkenes and alcohols.[9] As a result, boronic acid ester derivatives are of high interest for synthetic organic chemistry and recently several research groups have investigated rhenium, iridium, rhodium and ruthenium catalyzed C–H borylation of aliphatic and aromatic hydrocarbons.[10–22] The most active catalyst system reported for the C–H borylation of aromatic compounds with B_2pin_2 and HBpin is derived from $[Ir(COD)(OMe)]_2$ and 4,4′di-*tert*.-butyl-2,2′-bipyridine which can proceed in inert solvents (Scheme 1)[14] and is tolerant to a wide range of functional groups.[13,15] In contrast, catalysts derived from iridium precursors $[Ir(COD)(X)]_2$ (X = Cl, OAc) displayed a significantly lower activity.[13a] Intramolecular C–H activation with iridium–NHC complexes has already been documented[23]



Scheme 1 C–H borylation of hydrocarbons.

and encouraged us to explore iridium biscarbene complexes as catalysts for catalytic C–H borylation.

For over 15 years the use of *N*-heterocyclic carbenes as ligands for catalysts has brought about a renaissance in organometallic chemistry.[13b,13c] These ligands have proven to be far more than simple well bound phosphine replacements, and substitution within and about the ring have resulted in a wide range of complexes that are not only highly stable but also catalytically active.[24] In recent years we[23,25,26] and others[27,28] have prepared a wide variety of iridium NHC complexes, and investigated the catalytic utility of these systems. Herein a comparative study of various NHC iridium catalysts in the C–H borylation reaction is presented. By studying complexes which vary in ligand steric and electronic properties as well as complex counter ion, the influence in catalysis of alterations on the basic motif were elucidated. Microwave conditions are known to accelerate the reaction progress through rapid heating. Moreover the reaction media is heated directly, reducing decomposition *via* wall effects, and as such we decided to employ microwave technology for our investigations.[29] To the best of our knowledge this is the

Chair of Inorganic Chemistry and Molecular Catalysis, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, D-85747, Garching, Germany

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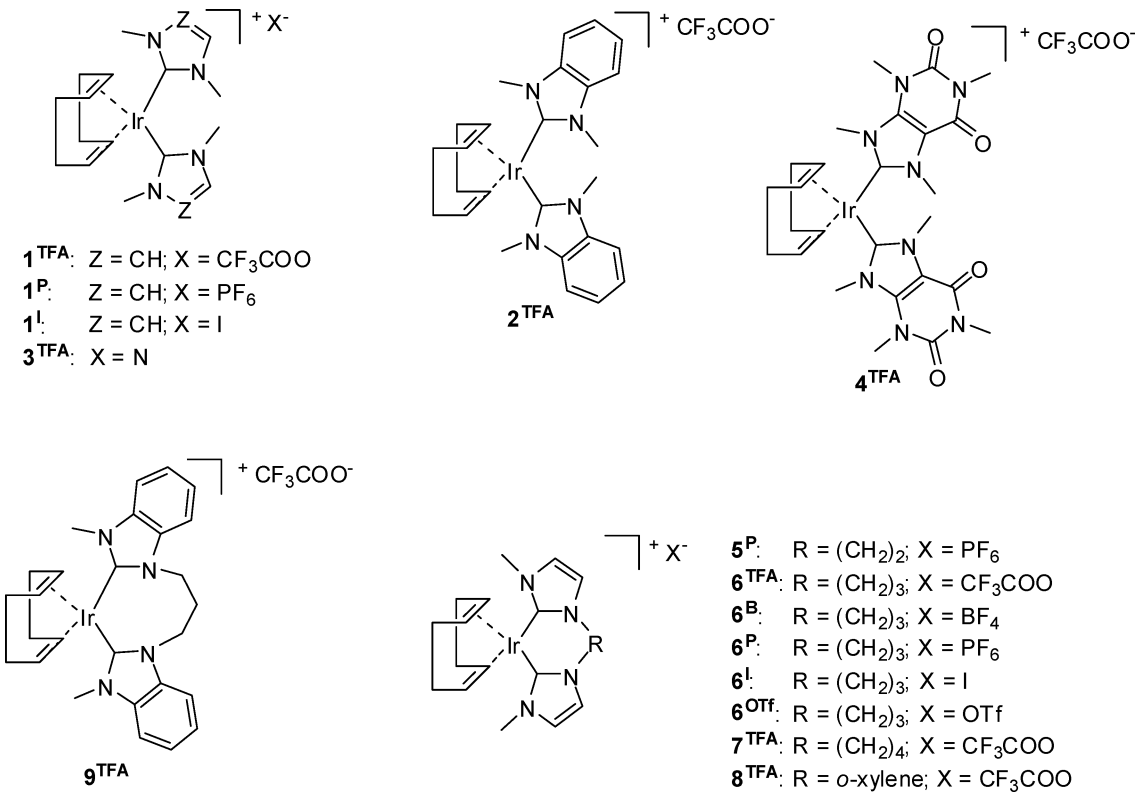
first example of a catalytic C–H borylation under microwave conditions.

Results and discussion

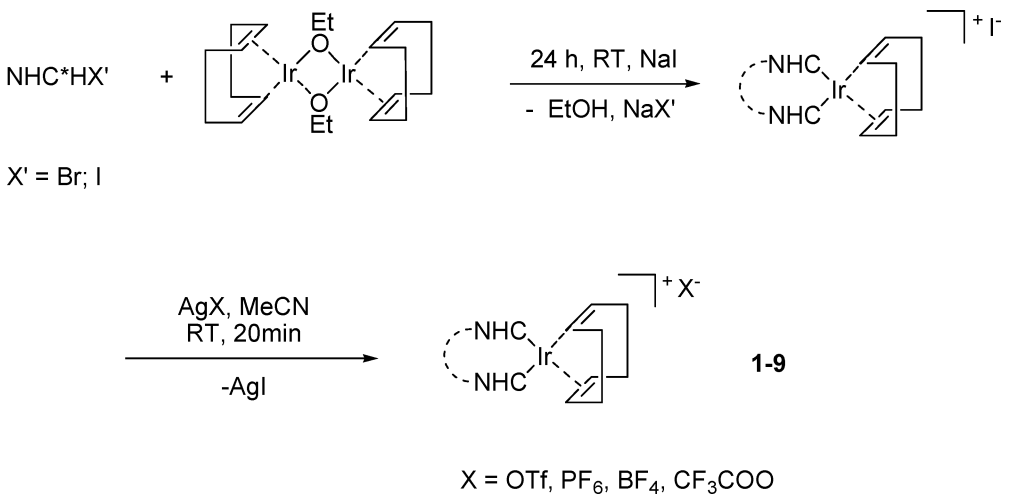
Preparation of bis-NHC complexes of iridium(I)

Synthesis of cationic iridium bis-NHC complexes (Scheme 2, **1–9**) was performed according to the alkoxide route shown in Scheme 3.[23] The iridium precursor $[Ir(COD)OEt]_2$, was prepared *in situ* from $[Ir(COD)Cl]_2$ by reaction with NaOEt in ethanol at ambient temperature. Reaction with the azolium salt precursor (NHC*HX') in the presence of NaI resulted in the formation of the iridium biscarbene iodides, which were converted to the triflate, hexafluorophosphate, tetrafluoroborate and trifluoroacetate iridium complexes by salt metatheses reaction with the corresponding silver salts.

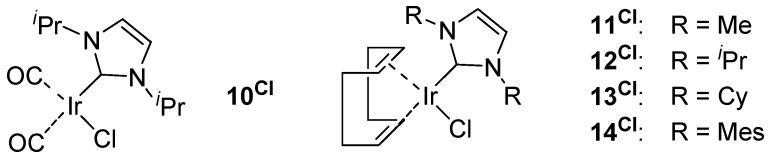
Isolation of $\mathbf{5^I}$ was not possible due to product decomposition during purification. Crabtree *et al.* have previously reported that the presence of halides can result in complexes with limited stability, while the use of PF_6^- as a counter ion often leads to more stable products, which can be isolated.[30] This proved



Scheme 2 Bis-NHC catalysts of iridium(I) for the C–H borylation reaction.



Scheme 3 Alkoxide route for the preparation of iridium NHC complexes.



Scheme 4 Monocarbene complex of iridium applied in the C–H borylation reaction.

to be the case with our system, where the *in situ* counter ion exchange of I^- for PF_6^- or $\mathbf{5}^{I}$ employing KPF_6 provides access to $\mathbf{5}^{P}$, which could be isolated. With the exception of $\mathbf{6}^{OTf}$ (56%) bis-NHC complexes with bidentate as well as monodentate ligands were prepared in good yields (67–81%). Complexes $\mathbf{5}^{P}$ and $\mathbf{6}^{P}$ were prepared in considerably higher yields than with the previously reported silver route,[28] showing the alkoxide route to be an effective strategy for the preparation of iridium biscarbene complexes.

NHC complexes **1–9** were characterized by ^{1}H NMR, ^{13}C NMR and FAB/MS, as well as ^{19}F-NMR for the fluorine containing compounds. The formation of the Ir–NHC bond is accompanied by loss of the C2 proton signal in the ^{1}H NMR spectra at ~9.3–10.0 ppm and the ^{13}C-NMR spectra displays signals at 175.9–178.2 ppm, in a region where the carbene signals for bis(imidazol-2-ylidenes) of Ir(I) would be expected, confirming the formation of Ir–C bonds.[23] The carbene signals appear low field for the coordinated azolinylidene ligand complexes $\mathbf{3}^{TFA}$, $\mathbf{4}^{TFA}$ (182 ppm, 180 ppm), and this effect is most pronounced for the benzimidazol-2-ylidene ligands in $\mathbf{2}^{TFA}$ and $\mathbf{9}^{TFA}$ (187.2 ppm, 189.1 ppm). The ^{19}F-NMR spectra displays fluorine signals for complexes $\mathbf{1}^{TFA}$–$\mathbf{9}^{TFA}$ (–72.7–75.1 ppm), $\mathbf{1}^{P}$, $\mathbf{6}^{P}$ (–69.5–70.1 ppm), $\mathbf{6}^{B}$ (–147.6 ppm) and $\mathbf{6}^{OTf}$ (–78.2 ppm) confirming the exchange reaction with fluorine containing anions has occurred.

Screening of iridium NHC catalysts in the C–H borylation of benzene

Microwave conditions are known to accelerate the reaction progress through rapid heating simultaneously decreasing decomposition of the catalyst due to the absence of wall effects. In addition heat loss from the system is minimal with direct heating of the reaction media.[29] Preliminary experiments at 160 °C gave higher yields in a microwave reactor than under conventional heating due to very fast and selective heating of the reaction mixture. As a result we chose to continue the catalyst screening employing microwave conditions. The C–H borylation was conducted in neat benzene or in organic solvents with B_2pin_2 or HBpin employing 0.5–3 mol% catalyst loading, thereby exploring the utility of range of precatalysts (see Scheme 2 and Scheme 4). The catalytic results are summarized in Table 1.

Catalysts $\mathbf{1}^{TFA}$–$\mathbf{4}^{TFA}$ (Table 1; entries 1, 4, 6, 7) are listed in order of decreasing σ-donor strength,[26] and the superiority of stronger donating carbene ligands in C–H borylation is clearly observed. The superior product yields of chelating bis-NHC catalysts $\mathbf{6}^{TFA}$ and $\mathbf{9}^{TFA}$ (Table 1; entries 9, 20), suggest the catalyst enhancing influence of the bidentate ligand motif. In addition, a similar sigma donor trend is observed among these two complexes.

In addition to the effects of donor strength, this work also reveals the influence of the design motif about the chelating NHC ligands on C–H borylation. Among bis-NHC catalysts bearing bidentate imidazol-2-ylidene ligands ($\mathbf{6}^{TFA}$, $\mathbf{9}^{TFA}$) the systems with a propylene bridge moiety gave the highest yield (Table 1; entries 9, 20). It may be concluded that the more sterically hindered *o*-xylene and *n*-butylene bridges (Table 1, entries 18, 19) $\mathbf{7}^{TFA}$, $\mathbf{8}^{TFA}$ hamper the coordination of the incoming arene, which has already been found to be rate determining for bipyridine iridium catalysts,[19] and as a result the reaction rate is slowed.

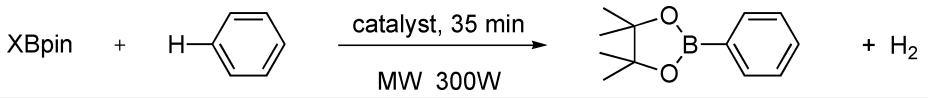
Catalysts with bidentate propylene bridged azolylidene ligands result in higher yields than their monodentate homologues (Table 1; entries 1, 4, 5). This is observed for benzimidazolylidenes ($\mathbf{2}^{TFA}$, $\mathbf{9}^{TFA}$) as well as for imidazolylidenes ($\mathbf{1}^{TFA}$, $\mathbf{6}^{TFA}$). We propose that this is caused by the greater stability of complexes bearing propylene bridged NHC ligands. Decomposition of NHC-complexes may occur through reductive elimination of NHC hydride complex intermediates. The oxidative addition of NHC-H reforming the NHC carbene is more likely for chelating complexes because of favored intra *vs.* slower inter molecular processes. Oxidative addition of the C2–H bond in imidazolium salts has already been demonstrated by Periana *et al.*[31] and C–H borylation with mono-NHC catalysts $\mathbf{10}^{Cl}\mathbf{14}^{Cl}$ resulted in lower yields than $\mathbf{6}^{TFA}$ due to decomposition, observed by the formation of a black suspension of metallic iridium (Table 1; entries 22–30).

Near quantitative conversion was observed using $\mathbf{9}^{TFA}$ after 60 min reaction time, suggesting that the difference in product yield is a result of catalyst activity and not decomposition of the catalyst (Table 1; entries 9, 20, 21). Catalyst $\mathbf{6}^{TFA}$ also facilitates the activation of benzene with catalyst loading as low as 0.5 mol% to near quantitative yields within 35 min (Table 1; entry 10).

Applying $\mathbf{6}^{TFA}$, the activity of bis-NHC catalysts in inert solvents was investigated (Table 1; entries 11–17). The best results were obtained in THF (entry 15), however activation in neat benzene proceeds considerably faster (entry 10). In a 1 : 1 mixture of benzene and HBpin in THF, C–H borylation activity is greatly reduced. In addition, the reactant also influences catalytic activity as the use of B_2pin_2 resulted in a yield of 85%, in comparison to the slower, slightly less reactive HBpin (entries 15, 16). This trend was also observed using $\mathbf{1}^{TFA}$ and $\mathbf{2}^{TFA}$ (Table 1, entries 2, 3, 5) as catalysts. The difference in catalytic activity is attributed to the difference in bond energy of B–B (332 kJ/mol) and B–H (381 kJ/mol).

Intrigued by these results we investigated kinetics for the activation of C_6D_6 by means of HBpin and B_2pin_2 comparatively, monitoring the conversion and formation of the products by ^{1}H-NMR spectroscopy with conventional heating (Fig. 1). This investigation demonstrates that B_2pin_2 undergoes C–H

Table 1 Screening of iridium catalysts in the C–H borylation of benzene



Entry	Catalyst	Catalyst mol%	X	$n_{benzene}/n_{XBpin}$	% Yield[a]
1	**1**^{TFA}	1.5	H	30/1	48
2	**1**^{TFA}	1.5	Bpin	60/1	92
3	**1**^{TFA}	0.5	Bpin	60/1	64
4	**2**^{TFA}	1.5	H	30/1	32
5	**2**^{TFA}	0.5	Bpin	60/1	40
6	**3**^{TFA}	1.5	H	30/1	36
7	**4**^{TFA}	1.5	H	30/1	12
8	**5**^{P}	1.5	H	30/1	<1
9	**6**^{TFA}	1.5	H	30/1	89
10	**6**^{TFA}	0.5	H	30/1	85
11[b]	**6**^{TFA}	0.5	H	4/1	20
12[c]	**6**^{TFA}	0.5	H	4/1	0
13[d]	**6**^{TFA}	0.5	H	4/1	<1
14[e]	**6**^{TFA}	1.5	H	4/1	4
15[f]	**6**^{TFA}	1.5	Bpin	4/1	85
16[f]	**6**^{TFA}	0.5	H	4/1	27
17[f]	**6**^{TFA}	0.5	H	1/1	5
18	**7**^{TFA}	1.5	H	30/1	17
19	**8**^{TFA}	1.5	H	30/1	40
20	**9**^{TFA}	1.5	H	30/1	60
21[g]	**9**^{TFA}	1.5	H	30/1	87
22	**10**^{Cl}	1.5	H	30/1	<1
23	**11**^{Cl}	1.5	H	30/1	9
24	**12**^{Cl}	1.5	H	30/1	72
25	**12**^{Cl}	3	H	30/1	80
26	**12**^{Cl}/PPh_3	3	H	30/1	37
27	**12**^{Cl}/Pcy_3	3	H	30/1	22
28	**12**^{Cl}/Pme_3	3	H	30/1	<1
29	**13**^{Cl}	1.5	H	30/1	68
30	**14**^{Cl}	1.5	H	30/1	75

[a] 0.5–3.0 mol%; catalyst, yields determined *via* GC-FID applying dodecane as internal standard, 35 min, 300 W, MW; [b] in 1.6 mL dioxane; [c] in 1.6 mL ether, 1 h, 125 °C, MW; [d] in 1.6 mL cyclohexane; [e] in 1.6 mL hexane; [f] in 1.6 mL THF; [g] reaction time 1 h.

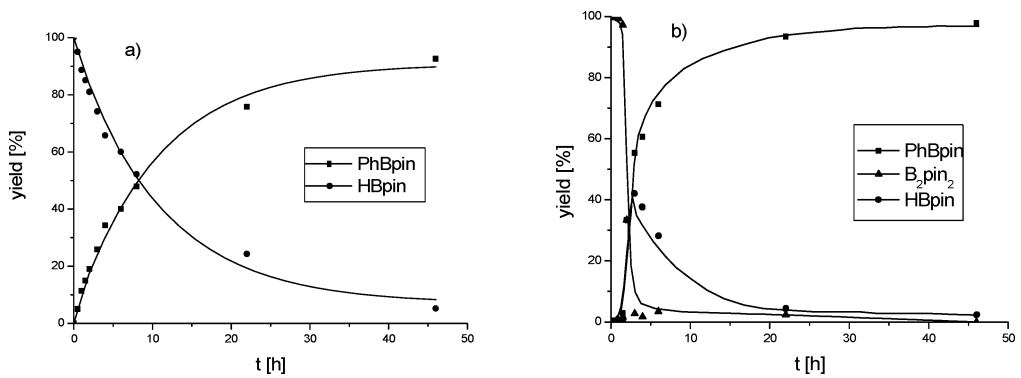


Fig. 1 Reaction progress. (a) Reaction of 1 eq. HBpin, (b) reaction of 0.5 eq. B_2pin_2, conditions: 30 eq. benzene-d6, 0.5 mol% **6**^{TFA}, 125 °C, NMR-tube; reaction progress is monitored by 1H-NMR spectroscopy; δ = 1.10 (CH_3, PhBpin), 1.01 (CH_3, B_2pin_2), 0.98 (CH_3, HBpin).

borylation more readily, however, an initiation period of approximately 1 h was observed. The initiation period of the C–H borylation is attributed to the formation of hydrogen while generating NHC boryl complexes of iridium.[16] In the case of B_2pin_2 the formation of H_2 is slowed as activation of a stronger C–H bond (461 kJ/mol) is more difficult than activation of the B–H bond (381 KJ/mol). As a side reaction hydrogenation of the COD ligand was observed and formation of the reduction products cyclooctene (COE) and cyclooctane were detected *via* GC-MS analysis of the reaction mixture. In accordance with previous suggestions of Hartwig *et al*., the initial step of the catalytic cycle seems to be the partial dissociation of the olefin ligand.[16] The monodentate COE is more readily dissociated than the bidentate COD as a result of the chelate effect. Hence, a slower formation of H_2 when using B_2pin_2 results in slower dissociation of the olefin ligand which results in slower

Table 2 Influence of the counter ions on C–H borylation with cationic iridium(I) complexes

Entry	Catalyst	Catalyst mol%	% Yield[a]	pK_a value[b]
1	$\mathbf{1}^{TFA}$	1.5	48	0
2	$\mathbf{1}^{I}$	1.5	<1	−11
3	$\mathbf{1}^{P}$	1.5	<1	−20
4	$\mathbf{5}^{P}$	1.5	<1	−20
5	$\mathbf{6}^{TFA}$	1.5	89	0
6	$\mathbf{6}^{TFA}$	0.5	85	0
7	$\mathbf{6}^{B}$	0.5	68	−4.9
8	$\mathbf{6}^{P}$	1.5	<1	−20
9	$\mathbf{6}^{I}$	1.5	<1	−11
11	$\mathbf{6}^{OTf}$	1.5	<1	−14

[a] 1 eq. HBpin, 30 eq. benzene, 0.5–1.5 mol% catalyst, 35 min, 300 W, MW, yields determined *via* GC-FID with dodecane as an internal standard; [b] pK_a value of the corresponding acid.[32]

hydrogenation of the COD ligand. Thus dissociation of the olefin ligand is retarded explaining the appearance of an induction period.

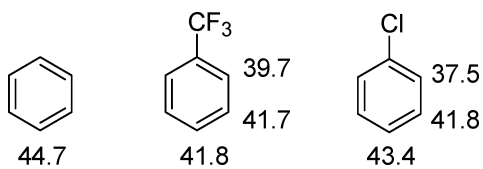
As mentioned previously, the catalytic potential of mono-NHC complexes was also investigated. C–H borylation was unsuccessful applying carbonyl complex $\mathbf{10}^{Cl}$ (Table 1; entry 22). Though within the family of all other studied monocarbene complexes ($\mathbf{11}^{Cl}$, $\mathbf{12}^{Cl}$, $\mathbf{13}^{Cl}$ and $\mathbf{14}^{Cl}$), comparable yields were observed with the exception of less sterically hindered $\mathbf{11}^{Cl}$ (Table 1; entries 22 *vs.* 23, 24, 29, 30). The addition of 1 eq. phosphine results in a decreased product yield, and the addition of $P(Me)_3$ quenches catalytic activity (Table 1; entries 25–28).

For the first time, the use of mono-NHC complexes of iridium as catalysts in the C–H borylation reaction is examined. During subsequent studies of iridium catalysts **1**, **5**, **6** (Table 2), we found out that the basicity of employed counter ions[32] is crucial for the catalytic activity. Reactions conducted with catalysts bearing PF_6^-, OTF^- and I^- resulted in yields of less than 1% (Table 2, entries 2–4, 8–11), however catalysts containing BF_4^- and CF_3COO^- gave good to excellent yields (Table 2, entries 1, 5–7). As such we are able to demonstrate that catalytic activity in the C–H borylation increases with growing basicities of the applied counter ions.

With the most active catalyst $\mathbf{6}^{TFA}$ we investigated selectivity of mono substituted aromatic compounds. In addition, the relative rates k_{rel}, k_o, k_m and k_p were determined in a competitive reaction of benzene and a corresponding aromatic in THF (Table 3).

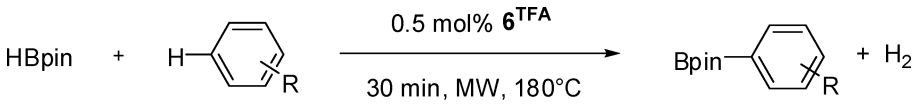
Experiments performed in neat aromatic compounds result in observed values for k_{rel} conclusively showing that electron withdrawing groups favour the formation of C–H borylation product (Table 3; entries 1–6). This observation is backed by the relative reaction rate k_{rel}, emphasizing the electron withdrawing groups accelerate the reaction progress. The activation of iodobenzene and bromobenzene in neat educts failed. However, borylation performed in THF employing 4 eq. HBpin gave halophenyl boronic acid pinacole ester in small quantities, while activation of the C–X bond (X = Br, I) and formation of phenyl boronic acid pinacole ester was also observed (Table 3; entries 8, 9). The reactivity of these substrates is attributed to the comparatively low stability of the C–Br (81 kcal/mol) and C–I (65 kcal/mol) bond (C–Cl, 96 kcal/mol; C–F 126 kcal/mol).[33]

The regioselectivity is influenced by the steric hindrance of reactant substituents. Thus, functionalization is preferred in *meta*- and *para*-position, while the small fluoro substituent also enables activation of the *ortho*-position. In addition there is a weak electronic effect that regulates the *meta vs. para* distribution. The C–H acidities are employed to quantify the electronic properties of aromatic compounds. In trifluorobenzene, *meta* and *para* product are formed in a nearly statistic ratio (*meta* : *para* is 2 : 1) due to the nearly equal acidity of the *meta*- and *para*-position. In contrast activation of chlorobenzene preferentially gave the *para*-product due to a difference of 1.6 pK_a units (Scheme 5).



Scheme 5 C–H acidities of aromatic compounds[34]

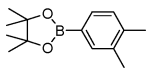
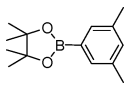
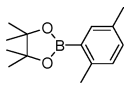
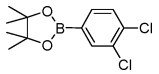
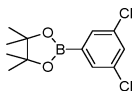
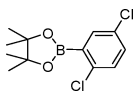
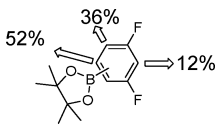
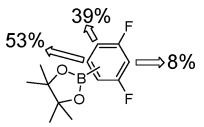
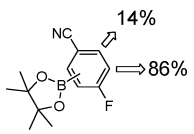
Table 3 C–H borylation of mono substituted benzene derivatives



Entry	R	Yield (*o*/*m*/*p*) [%][a]	k_{rel} (k_o/k_m/k_p)[b]
1	Me_2N	<1 (0/64/35)	0.25 (0/0.15/0.10)
2	Me	35 (4/64/32)	0.47 (0.02/0.30/0.15)
3	OMe	47 (5/67/28)	0.52 (0.05/0.33/0.14)
4	Cl	85 (0/76/24)	3.38 (0/2.54/0.84)
5	CF_3	86 (0/69/31)	3.61 (0/2.42/1.19)
6	F	90 (17/55/28)	2.89 (0.46/1.59/0.84)
8[c]	I	11 (4)	—
9[c]	Br	25 (1)	—

[a] 0.64 mmol HBpin, 19.2 mmol benzene, 0.5 mol% $\mathbf{6}^{TFA}$, 30 min, 180 °C, MW, yields and selectivities determined *via* GC-FID (using dodecane as an internal standard) GC-MS and ^{13}B-NMR; [b] $k_{rel} = Y_{aromatic}/Y_{benzene}$, 0.64 mmol HBpin, 2.56 mmol benzene, 2.56 mmol benzene derivative, 0.5 mol% $\mathbf{6}^{TFA}$, 1.6 mL THF, 35 min, 300 W, yields and selectivities determined by GC-FID (using dodecane as internal standard) GC-MS and ^{13}B-NMR; [c] 0.64 mmol HBpin, 2.56 mmol aromatic, 1.6 mL THF, 35 min, 300 W, MW; yields of byproduct PhBpin in parentheses; regioselectivity not determined.

Table 4 C–H borylation of disubstituted benzene derivatives

Entry	Aromatic	Catalyst mol%	% Yield[a]	
1	1,2-Xylene	1.5	51	
2	1,3-Xylene	1.5	28	
3	1,4-Xylene	1.5	21	
4	1,2-Dichlorobenzene	1.5	81	
5	1,3-Dichlorbenzene	1.5	59	
6	1,4-Dichlorobenzene	1.5	21	
7[b]	1,3-Difluorobenzene	0.5	84	
8[c]	1,3-Difluorobenzene	0.5	7	
9[d]	4-Fluorobenzonitrile	0.5	81	

[a] 0.64 mmol HBpin, 19.2 mmol aromatic, 0.5–1.5 mol% **6**^{TFA}, 30 min, 180 °C, MW, yields and selectivities determined *via* GC-FID (using dodecane as internal standard), GC-MS and ^{13}B-NMR; [b] 0.64 mmol HBpin, 2.56 mmol aromatic, 1.6 mL THF, 2% C-F activation; [c] **6**^{I}; [d] 0.32 mmol HBpin, 1.28 mmol 4-fluorobenzonitrile, 0.4 mL hexane, 4% double borylation; regioselectivity determined *via* F-NMR.

Those results were confirmed by comparison of the relative rates k_m and k_p (Table 3, entries 4, 5).

The C–H borylation of disubstituted aromatic compounds was conducted in neat reactants or inert solvents under microwave conditions confirming results found for mono substituted compounds (Table 4). In comparison with xylene derivatives (Table 4; entries 1–3) electron withdrawing groups (F, Cl) were found to undergo C–H borylation more readily and increased yields were observed (Table 4; entries 4–9), with the exception of the 1,4-derivatives. Reaction of the 1,4-isomers proceeded relatively slowly due to the steric hindrance of the substituents in the *ortho*-position (Table 4; entries 3,6). Borylation of 1,3- and 1,2-isomers occurred only in the *meta* or *para*-position though not in the *ortho*-position (Table 4; entries 1, 2, 4, 5). The 1,3-difluorobenzene was activated in the normally hampered *ortho*-position due to the low steric impact and strong electronegativity of fluoro substituents (Table 4, entry 7). Comparing the reactivity 1,3- and 1,2-isomers of xylene and dichlorobenzene derivatives activation of 1,2-isomers resulted in higher yields due to the twofold availability of active positions. In addition the otherwise unreactive catalyst **6**^{I} promoted the formation of difluorophenyl boronic acid pinacoleester in small quantities (Table 4; entry 8). Activation of 4-fluorobenzonitrile gave high yields due to substitution with strongly electron withdrawing groups. Regioselectivity is determined by the steric impact of the substituents, with *ortho* subsitution (with respect to the fluorine group) occurring preferentially.

Analogous to the studies of Hartwig *et al.*[19] the π-coordination of the aromatic compound on an iridium(III) centre is proposed to be the limiting step in the catalytic cycle. This is confirmed by high yields observed in the presence of strong σ-donor ligands and electron withdrawing substituents located on the aromatic ring, as both effects favour the formation of arene complexes.[35]

Recently Periana and coworkers described C–H activation of benzene at Ir(III) or Pt(II) to proceed *via* an η^1-aryl intermediate, wherein the deprotonation step is mediated by a basic ligand.[36] We therefore postulate the mechanism proceeds *via* an η^1-aryl intermediate in which deprotonation of the benzene derivative is mediated by an anionic CF_3COO^- ligand. The primary kinetic isotope effect of 3.0 ± 0.1 determined in a mixture of benzene and deuterated benzene is attributed to the increased energy level of the η^1-aryl intermediate formed with deuterated aromatics resulting in a slower reaction rate. This isotope effect could also be indicative of an oxidative addition mechanism. However, recently Milstein *et al.* have demonstrated that the regioselectivity for C–H activation of benzene derivatives mediated by iridium(I) pincer complexes, which occurs by an oxidative addition pathway, is directed by electronic effects to give *ortho*-substituted products.[37] In contrast, the NHC complexes of iridium were shown to activate selectively in sterically unhindered *meta*- or *para*- positions, thereby confirming acidity is the determining factor for selectivity in the system described herein.

Conclusion

Catalytic examinations using the energy efficient microwave as a heating source to screen a large family of in part highly active iridium catalysts bearing NHC moieties have been performed. Although these systems require higher temperatures of activation than previously reported systems, our systems have the advantage of fast reaction times and the employment of an efficient heating system.[1–7] It is also possible to carry out catalysis in the atom efficient neat systems. The iridium(I) bis-NHC catalyst **6**^{TFA} is shown to be particularly active. By varying different ligands and counter ions, the basicity of the counter ion proved to be the most important feature of the complex design motif. For the first time, the use of iridium mono-NHC catalysts in the C–H borylation is reported, however, the lower stability of these complexes, when compared to bis-NHC

complexes, leads to decreased product yields. The influence of the counter ion, the ligand, the observed regioselectivity and chemoselectivity as well as the kinetic studies indicate a mechanism proceeding *via* an η^1-aryl intermediate with the formation of η^2-arene intermediate as the rate determining side reaction. Further work is on going in our laboratories to produce immobilized systems based on the iridium complexes studied to take full advantage of the microwave heating method and facilitate catalyst product separation in solventless systems, expanding efforts to include atom economical approaches to the selective functionalization of organic compounds. Additional efforts will be dedicated to the full elucidation of the reaction mechanism.

Experimental

Bis-NHC complexes were prepared according to the literature employing the alkoxide route.[23] Mono-NHCs have been prepared according to previously reported literature methods.[23,22d,38] All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H, ^{11}B, ^{19}F and ^{13}C-NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. ^{11}B-NMR was referenced to $BF_3{\cdot}OEt_2$ and ^{19}F to C_6F_6. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using FAB technique.

General procedure for the catalytic C–H borylation of benzene applying NHC complexes of iridium(I)

In a glove box pressure sealed microwave tubes were filled with 1.25×10^{-3}–7.5×10^{-3} mmol (0.5–3 mol%) iridium(I) catalyst, 7.5 mmol benzene (1 mmol: experiments in inert solvents), 25 µL dodecane and 0.25 mmol HBpin (0.125 mmol B_2pin_2). The reaction mixture was treated for 35 min in a microwave reactor with 300 W and the maximum temperature was set to 180 °C. After cooling an aliquot of 0.2 mL was diluted in 0.8 mL THF and yield was determined using GC-FID.

General procedure for the catalytic C–H borylation of substituted benzenes applying NHC complexes of iridium(I)

In a glove box, pressure sealed microwave tubes were filled with 3.2×10^{-3} to 9.6×10^{-3} mmol (0.5–1.5 mol%) iridium(I) catalyst, 19.2 mmol benzene derivative, 25 µL dodecane and 0.64 mmol pinacolborane. The samples were then removed and irradiated in the microwave reactor while heating the reaction mixture to 180 °C for 30 min. After cooling an aliquot of 0.2 mL was diluted in 0.8 mL THF and the product solution was examined with GC-FID, GC-MS and ^{13}B-NMR.

General procedure for the investigation of relative reaction rates and the kinetic isotope effect

In a glove box, pressure sealed microwave tubes were charged with 3.2×10^{-3} mmol iridium(I) catalyst, 2.56 mmol benzene, 2.56 mmol benzene derivative, 25 µL dodecane, 0.64 mmol HBpin and 1.6 mL THF. The reaction mixture was then irradiated for 35 min in a microwave reactor with 300 W set to a maximum temperature of 180 °C. After cooling an aliquot of 0.2 mL was diluted in 0.8 mL THF. This solution was then analyzed by GC-FID, GC-MS and ^{13}B-NMR.

Reaction progress studies

A J-Young NMR tube was charged with 1.6×10^{-3} mmol iridium(I) catalyst, 9.6 mmol C_6D_6 and 0.32 mmol HBpin (0.16 B_2pin_2). The reaction mixture was heated to 125 °C and reaction progress is monitored by ^{1}H-NMR spectroscopy.

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