A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

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## Accepted Article

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**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.201812857
*Angew. Chem.* 10.1002/ange.201812857

**Link to VoR:** http://dx.doi.org/10.1002/anie.201812857
http://dx.doi.org/10.1002/ange.201812857

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# Accessing Ambiphilic Phosphine Boronates through C–H Borylation by an Unforeseen Cationic Iridium Complex

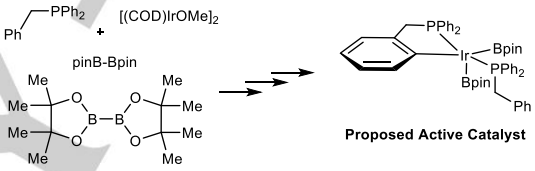
Shawn E. Wright, Stephanie Richardson-Solorzano, Tiffany N. Stewart, Christopher D. Miller, Kelsey C. Morris, Christopher J. A. Daley, and Timothy B. Clark*

**Abstract:** Ambiphilic molecules, which contain a Lewis base and Lewis acid, are of great interest based on their unique ability to activate small molecules. Phosphine boronates are one class of these substrates that have interesting catalytic activity. Direct access to these phosphine boronates is described through the iridium-catalyzed C–H borylation of phosphines. An unconventional cationic iridium catalyst was identified as optimal for a range of phosphines, providing good yields and selectivity across a diverse class of phosphine boronates (isolated as the borane-protected phosphine). A complimentary catalyst system (quinoline-based silane ligand with $[(COD)IrOMe]_2$) was optimal for biphenyl-based phosphines. Selective polyborylation was also shown providing bis- and tris-borylated phosphines. Deprotection of the phosphine boronate provided free ambiphilic phosphine boronates, which do not have detectable interactions between the phosphorus and boron atoms in solution or the solid state.

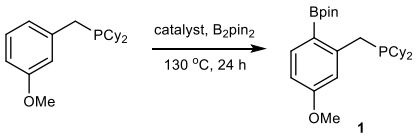
The metal-catalyzed C–H borylation reaction has garnered profound interest in recent decades based on the synthetic utility of the resulting C–B bond and the ability to selectively install a boron substituent without a pre-existing functional group.[1-3] Early work in the area of metal-catalyzed C–H borylation reactions utilized catalysts that were sterically-controlled, avoiding *ortho* C–H bonds in arenes and favoring primary C–H bonds for alkanes.[4] Starting in 2008, new systems were developed that utilized directing groups to achieve alternative selectivity patterns (*ortho*- or *meta*-directed).[5-34] The approaches used to achieve directed C–H borylation are diverse, but, the key to achieving the desired directing effect has been to modify the catalyst in a way that the directing interaction does not form a coordinatively saturated 18-electron complex, which then has no open site for activation of the C–H bond. Using these approaches, many directing groups have been used to access functionalized arylboronates.

Taking advantage of the insights gained in substrate-directed C–H borylation reactions, our group extended the available directing groups to phosphines. Our initial efforts in phosphine-directed C–H borylation were reported in 2014, providing the first example of a general phosphine-directed C–H functionalization[35-44] and providing access to phosphine boronate esters from valuable phosphine precursors.[23] The key to obtain the desired reactivity in these studies was running the reaction without added ligand. We proposed a mechanism in which the phosphine substrate served as the ligand during the catalytic reaction (Scheme 1). While these catalytic conditions were useful in the synthesis of a series of phosphine boronates, the role of the substrate as ligand severely limited the phosphines that were compatible with the reaction conditions. The proposed active catalyst utilizes the substrate as a C,P-bound ligand in which the X-type ligand interaction of the arene carbon with iridium served to replace one of the boryl ligands of the known iridium(III)trisboryl active catalyst[45] (Scheme 1), maintaining an open coordination site for C–H activation upon phosphine coordination. We herein report a general method to rapidly form a series of ambiphilic phosphine boronates by phosphine-directed C–H borylation, utilizing a unique cationic iridium complex and a known silylquinoline that provide complimentary reactivity in this selective C–H borylation reaction.

**Scheme 1.** Proposed Active Catalyst for Phosphine-Directed C–H Borylation with No Added Ligand




A more general catalyst system for phosphine-directed C–H borylation was initially sought by examining the synthesis of pre-formed P,C-bidentate ligands that could mimic the proposed active catalyst (Scheme 1). These efforts did not provide a viable catalyst and were not consistent with our goal to identify readily available pre-catalysts and ligands for this transformation. A series of known substrate-directed C–H borylation conditions, which were expected to be compatible with phosphines, were examined with 3-methoxybenzyldicyclohexylphosphine (Table 1), a substrate that was unreactive under the original reaction conditions (entry 1).[23] By identifying optimal reaction conditions for this problematic substrate, a more general set of reaction conditions across a wide range of phosphines was expected.




| Entry[a] | Catalyst | Ligand | Conversion |
|---|---|---|---|
| 1 | $[(COD)IrOMe]_2$ | none | NR |
| 2 | $[(COD)IrOMe]_2$ | **2** | NR |
| 3 | $[(COD)IrOMe]_2$ | **3** | NR |
| 4 | $[(COD)IrOMe]_2$ | **4** | NR |
| 5 | $[Ir(P,N)]PF_6$ (**5**) | none | 33% |

**Table 1.** Condition Screen for Phosphine-Directed C–H Borylation

[a] Conditions: 0.83 equiv. $B_2pin_2$, 1.25 mol % [Ir], 2.5 mol % ligand, toluene, 130 °C, 24 h.

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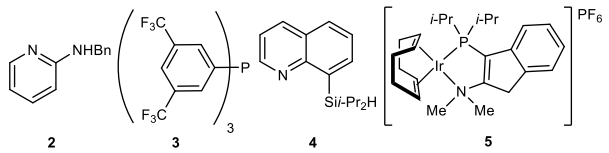
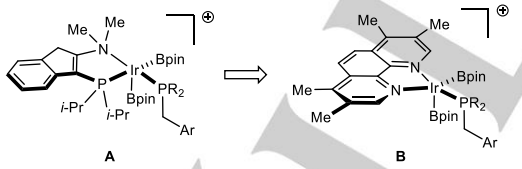
**Figure 1.** Ligands and Pre-Catalysts Used in Condition Screen




2 3 4 5

The first set of conditions examined were those developed by our group for amine-directed C–H borylation, which utilize a hemi-labile ligand (*N*-benzylaminopyridine, **2**, Figure 1),[18, 27] providing no evidence of the formation of **1** (Table 1, entry 2). Miyaura reported ester-directed C–H borylation using an electron-deficient phosphine ligand (tris[3,5-bis(trifluoromethyl)phenyl]phosphine, **3**);[10] No C–H borylation was observed under Miyaura's original conditions nor with alternative solvents and elevated temperature (entry 3). Smith and Maleczka reported silane-based bidentate ligands (**4**) that proved compatible with a range of directing groups,[25] but were also unreactive with the test phosphine (entry 4). A cationic iridium complex with a rigid bidentate ligand was examined with the idea that the cationic nature of the complex could open an additional coordination site for directed C–H borylation (vide supra). Commercially available complex **5** was found to provide modest, but promising, conversion to boronate **1** (entry 5).

The reactivity of cationic pre-catalyst **5** was surprising considering the general consensus that the active iridium complex should be electron rich.[46-47] This cationic complex, however, was the only reactive catalyst for the studied phosphine. The reactivity of the cationic complex is proposed to result from obtaining the required two open coordination sites by replacing one of the –Bpin ligands of the known iridium(III)trisboryl complex with a non-coordinating ligand. The resulting iridium(III)bisboryl complex (Figure 2, **A**) has the ability to access two open coordination sites for the Lewis basic phosphine and the adjacent C–H bond. Based on this realization, a more effective bidentate ligand was sought to increase the generality of the reaction. 3,4,7,8-Tetramethyl-1,10-phenanthroline (TMPHEN), a commonly used ligand for non-directed C–H borylation reactions,[48-50] was expected to form a more active cationic complex (**B**) while maintaining an open coordination site for directed C–H borylation.




A B

**Figure 2.** Proposed Bis-boryl Cationic Iridium Complexes

Initial examination of TMPHEN with commercially-available cationic pre-catalysts $[Ir(COD)_2]BF_4$ resulted in no reactivity (Table 2). Switching the boron source from bis(pinacolato)diboron ($B_2pin_2$) to pinacolborane (HBpin), however, drastically increased the reactivity. With 1.7 equivalents of pinacolborane, a 72% conversion was observed after 24 h at 130 °C. Increasing the equivalents of pinacolborane to 6.7 provided full conversion, but the ratio of monoborylation product (**1**, Table 2) to bisborylation product (**1'**) was modest (87:13). Reducing the equivalents of pinacolborane to 3.3 improved the selectivity for **1** to 96% while maintaining a high conversion. Lowering the temperature to 110 °C further improved the selectivity without a subsequent loss of conversion, providing 99% conversion and a 99:1 ratio of **1**:**1'**. $B_2pin_2$ is the most commonly-used boron source in C–H borylation reactions. Formation of the active catalyst from the pre-catalyst is typically accelerated with HBpin, but the increased concentration of hydrogen gas as the reaction progresses can retard the reaction.[47] In this study, full conversions are observed with HBpin, suggesting that hydrogen gas does not hinder the reaction significantly. Further mechanistic studies are required to fully understand this effect.

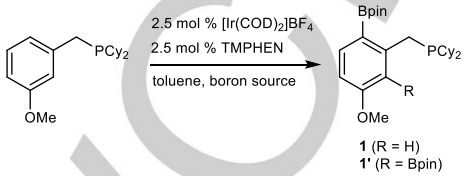
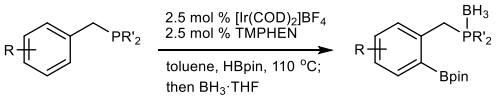



**Table 2.** Reaction Optimization with $[Ir(COD)_2]BF_4$

| Boron (equiv.) | T (°C) | t (h) | Conv. | 1:1′ |
|---|---|---|---|---|
| $B_2pin_2$ (0.83) | 130 | 24 | 0% | NA |
| HBpin (1.7) | 130 | 24 | 72% | 81:19 |
| HBpin (6.7) | 130 | 24 | 99% | 87:13 |
| HBpin (3.3) | 130 | 18 | 98% | 96:4 |
| **HBpin (3.3)** | **110** | **18** | **99%** | **99:1** |
| HBpin (3.3) | 100 | 24 | 79% | >99:1 |

The optimized reaction conditions were utilized for a series of benzylic phosphines to examine steric and electronic influences on the reaction efficiency. To simplify isolation and purification of these electron rich phosphines, the crude reaction mixture was treated with $BH_3$·THF to form the borane complex.[23, 51] High yield and selectivity for the ortho monoborylation product was observed in most cases (Table 3). Diphenyl- and dicyclohexyl-substituted benzylphosphines worked well under the reaction conditions to provide the corresponding boronate esters (**6** and **7**, entries 1,2). 3- and 4-substituted benzylic phosphines provided good yields of **8**–**11** (entries 3–5), demonstrating compatibility with chlorine or methoxy substituents. The *ortho*-substituted benzylic phosphines, however, were prone to additional reactions that resulted in low yields. The 2-chloro-substituted arene, for example, provided both C–H and C–Cl borylation (71:29).[52]

**Table 3.** Scope of Benzylic Phosphines in Directed C–H Borylation




6-11

| Entry | R | R′, R′ | Yield | Product |
|---|---|---|---|---|
| 1 | H | Ph, Ph | 87% | **6** |
| 2 | H | Cy, Cy | 81% | **7** |
| 3 | 3-Me | Cy, Cy | 76% | **8** |
| 4 | 3-Cl | Cy, Cy | 73% | **9** |
| 5 | 3-OMe | Cy, Cy | 74% | **10** |
| 6 | 4-Me | Cy, Cy | 77% | **11** |

Encouraged by the generality of the C–H borylation with benzylic phosphines, commonly used phosphine ligands were examined under the reaction conditions. Indole-based

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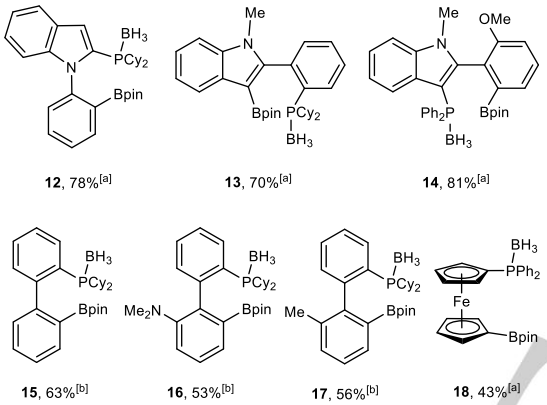
phosphines were readily borylated, providing **12**–**14** in high yield and selectivity for monoborylation products (Figure 3). Biphenyl-based phosphines, however, were less reactive under the reaction conditions using the cationic iridium system. Treatment of these phosphines with the silylquinoline ligand conditions reported by Smith[25] (**4**, Table 1, entry 4) provided high conversions to the desired borylation products when $B_2pin_2$ was used as the boron source. Therefore, borylation of the commonly used ligands CyJohnPhos, DavePhos, and MePhos,[53] provided the corresponding boronate esters (**15**–**17**) in good yields upon protection. In the case of **15**, selectivity was reduced to 83:17 mono:bis (**15**:**15'**). To verify that the C–H borylation of DavePhos (to form **16**) was directed by the phosphine, and not the amine, the structure of **16** was confirmed by X-Ray crystallography (see Figure 4). Borylation of diphenylphosphinoferrocene (**FcPPh$_2$**) was also examined; under both sets of conditions, competitive bisborylation was observed. Isolation of **18**, however, was achieved in 43% yield from a 50:25:25 mixture of **18**:**18'**:**FcPPh$_2$**.




[a] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, toluene, 3.3 equiv. HBpin, 130 °C, 16 h; then $BH_3$·THF. [b] 1.25 mol % $[Ir(COD)OMe]_2$, 7.5 mol % **4**, 2.0 equiv. $B_2pin_2$, dioxane, 130 °C, 48-72 h; then $BH_3$·THF.

**Figure 3**. Substrate Scope of Non-Benzylic Phosphines

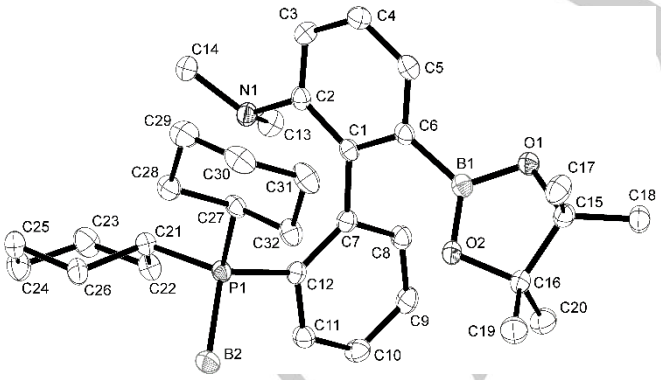
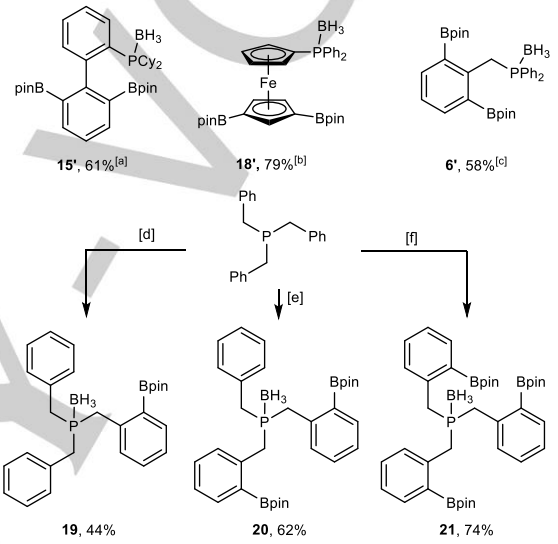


**Figure 4**. X-ray Crystal Structure of **16** Confirming Structure. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

The increased reactivity of certain substrates (especially CyJohnPhos and diphenylphosphinoferrocene) toward bisborylation led to the examination of conditions that could selectively provide polyborylated products. Treatment of CyJohnPhos with excess $B_2pin_2$ (2 equiv.) at 130 °C provided bisborylated product **15'** (>90% selective for **15'** over **15**) in 61% yield (Scheme 2). Subjecting diphenylphosphinoferrocene to the standard cationic iridium conditions (3.3 equiv. HBpin at 130 °C) provided bisborylation (**18'**) as the sole product. Likewise, benzyldiphenylphosphine could be pushed to bisborylation product **6'** (67% selective for **6'**). Encouraged by these results, tribenzylphosphine was examined under a variety of borylation conditions, ultimately providing moderate to good yields of mono- (**19**), bis- (**20**), and tris-borylated (**21**) products upon purification by column chromatography. The synthesis of polyborylated products is expected to provide intriguing polyfunctionalized phosphines and useful comparisons with monoborylated products as organocatalysts[54-61] and ambiphilic catalysts and ligands[62-63] upon removal of the borane protecting group.

**Scheme 2**. Phosphine-Directed Polyborylation Reactions




[a] 1.25 mol % $[Ir(COD)OMe]_2$, 7.5 mol % **4**, 2 equiv. $B_2pin_2$, toluene, 130 °C, 48 h (>90:10 **15'**:**15**); then $BH_3$·THF. [b] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, toluene, 3.3 equiv. HBpin, 130 °C, 24 h (>99:1 **18'**:**18**); then $BH_3$·THF. [c] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, toluene, 10 equiv. HBpin, 110 °C, 24 h (67:33 **6'**:**6**); then $BH_3$·THF. [d] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, dioxane, 1.7 equiv. HBpin, 100 °C, 24 h (93% conv.; 63:37:0 **19**:**20**:**21**); then $BH_3$·THF. [e] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, toluene, 3.3 equiv. HBpin, 100 °C, 24 h (99% conv.; 14:77:8 **19**:**20**:**21**); then $BH_3$·THF. [f] 2.5 mol % $[(COD)_2Ir]BF_4$, 2.5 mol % TMPHEN, toluene, 10 equiv. HBpin, 130 °C, 72 h (100% conv.; >99% **21**); then $BH_3$·THF.

Removal of the borane protecting group was examined to demonstrate the facile access to a variety of ambiphilic phosphine boronates with steric, electronic, and geometrical variations. Monoborylated phosphines **22**–**24** and polyborylated phosphines **25** and **26** were readily accessed upon heating in diethylamine with yields ranging from 60–95% (Scheme 5).

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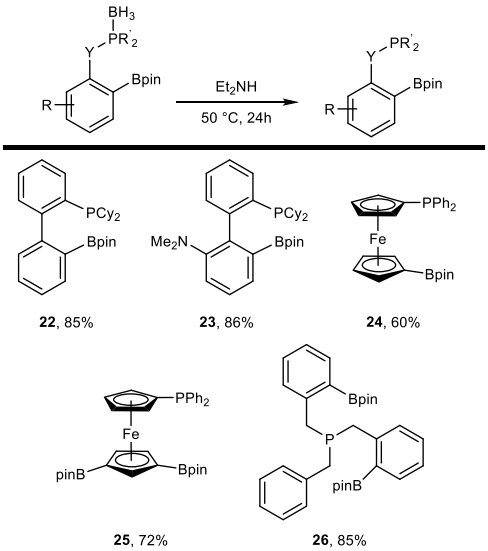
**Scheme 5.** Deprotection of Phosphine Boronates




Upon deprotection of the phosphine, an interaction between the Lewis basic phosphorus atom and the Lewis acidic boron atom (of –Bpin) becomes possible.[16] To examine if such an interaction is taking place, the $^{11}$B NMR spectra were compared to the corresponding protected phosphines. If an interaction was taking place, an upfield chemical shift would be expected. As shown in Table 4, no significant chemical shift changes were observed, consistent with no interaction in the solution state. The lack of interaction was probed in the solid state by X-ray crystallography of **23** (Figure 5). As expected from the spectral data, no interaction was observed for **23** in the solid state.

**Table 4.** Comparison of $^{11}$B NMR Chemical Shift of Protected and Unprotected Phosphine Boronates

| Phosphine-Borane | $^{11}$B δ (ppm) | Phosphine | $^{11}$B δ (ppm) |
|---|---|---|---|
| **15** | 30.5 | **22** | 30.9 |
| **16** | 31.1 | **23** | 31.6 |
| **18** | 32.8 | **24** | 33.2 |
| **18'** | 32.6 | **25** | 33.5 |
| **20** | 31.7 | **26** | 31.7 |

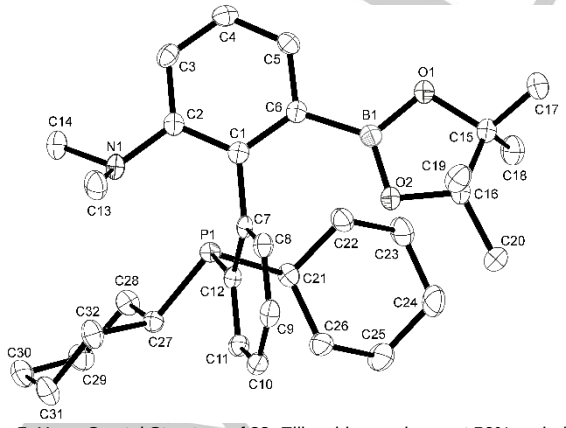



**Figure 5**. X-ray Crystal Structure of **23**. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

In summary, efficient methods for phosphine-directed C–H borylation have been reported. These catalysts were active in a wide range of benzylic and aryl phosphines including indole- and ferrocene-based substrates. Polyborylation of a series of phosphines was also possible. Deprotection of the phosphine boronates with diethylamine provided a series of ambiphilic phosphine boronates, none of which showed interactions between the free phosphorus and the boron atoms.

## Acknowledgements

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund (54825-UR3), the Henry Dreyfus Foundation, and that National Science Foundation (CHE-1764307) for support of the research. National Science Foundation is acknowledged for NMR (0417731) and X-ray (CHE-1126585). S.E.W. thanks the Doheny Foundation and the Farrell Family for summer research fellowships.

**Keywords:** homogeneous catalysis • C–H functionalization • ambiphilic • borylation • phosphorus

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10.1002/anie.201812857

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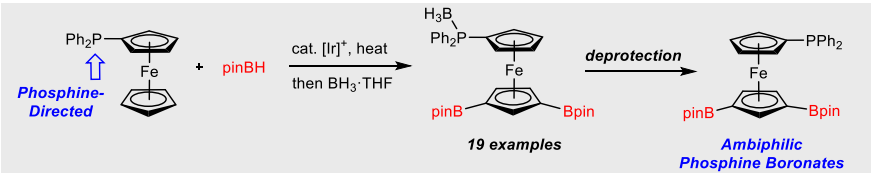
# COMMUNICATION




*Shawn E. Wright, Stephanie Richardson-Solorzano, Tiffany N. Stewart, Christopher D. Miller, Kelsey C. Morris, Prof. Christopher J. A. Daley, and Prof. Timothy B. Clark**

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**Accessing Ambiphilic Phosphine Boronates by C–H Borylation by an Unforseen Cationic Iridium Complex**

**Phosphine-Directed C–H Borylation:** A series of commonly used phosphines undergo iridium-catalyzed C–H borylation, providing a series of ambiphilic phosphine boronates. Unexpected cationic iridium catalyst overcomes limited reactivity allowing a large range of phosphines to be selectively functionalized, including selective polyborylation of several phosphines.