Helicenes represent a unique class of polycyclic aromatic hydrocarbons where the benzene rings are all ortho-fused, fully conjugated, and with a non-planar topology. They have attracted increasing attention owing to their unrivalled structural features\(^1\-^3\) and many potential applications in chiral materials,\(^4\-^8\) self-assembly,\(^9\-^{11}\) asymmetric synthesis,\(^12\-^{14}\) and opto-electronic materials.\(^15\-^{19}\) Of importance, unique properties of helicenes can be addressed by introducing substituents at the periphery of the helical core. From a synthetic point of view, helicenes can be addressed by introducing substituents at the substrates. Substituted helicenes are usually made from pre-functionalized materials, it has been underdeveloped in the history of aromatic compounds under the standard conditions \(1,2\) and restricts, to some extent, practical applications of helicenes.

Based on our previous results on borylation of [4]helicene\(^21\) we envisioned that [5]helicene (Fig. 1) could be selectively functionalized by an iridium catalyzed C–H bond activation/borylation process. Since regioselectivity of direct borylation of aromatic compounds under the standard conditions ([Ir(OMe)(cod)]\(_2\)/dbtpy) is sterically driven, it is generally accepted that C–H bonds ortho to the substituent and ortho to ring junction (peri-position) do not usually react.\(^22,23\) Hence, [5]helicene should be borylated at sterically more accessible positions 2 and 3. Out of these two, position 2 is more sterically hindered (overlapping by the other end of the molecule), therefore the appropriate choice of catalytic system and the third dimension (helicity) of the molecule should contrive an additional level of regioselectivity to distinguish between these two positions.

According to our previous study of [4]helicene\(^21\) and the preceding studies of iodium-catalyzed borylation of arenes\(^24\-^{27}\) and fused polyarenes,\(^28\-^{40}\) we subjected [5]helicene 1 to standard borylation conditions. Thus, equimolar quantities of 1 and \(\text{B}_3\text{pin}_2\) (pin = pinacolato), a catalytic amount of \([\text{Ir}(\text{OMe})(\text{cod})]_2\) (5 mol%) and 4,4'-di-tert-butyl-2,2'-bipyridine (dbtpy) (10 mol%) were allowed to react in cyclohexane. A reaction carried out at 23 °C for 16 h afforded only the starting material and traces of monoborylated products (according to EI/MS analysis). An increase of the reaction temperature to 50 °C and subsequently to 80 °C resulted in better conversion of 1 and a mixture of two monoborylated compounds in slightly better yield (~10%) was obtained. These results clearly showed that C–H activation/borylation of [5]helicene is possible but requires harsher reaction conditions than sterically distinct [4]helicene. In view of the aforementioned, borylation of [5]helicene at 100 °C for 24 h was attempted (Scheme 1). After removal of the volatiles and the subsequent column chromatography of the residue on silica gel (hexane/DCM from 100 : 0 to 0 : 100) three colorless fractions

![Fig. 1 Molecular structure of [5]helicene.](image-url)
were obtained: unreacted $1$ (79%), a mixture of 2- and 3-borylated $[5]$helicenes (16%) and a small fraction containing a trace amount of bisborylated $[5]$helicene (~1%). The subsequent separation of the second fraction by non-aqueous reverse phase chromatography (NARP) afforded two regioisomers: 2-borylated $[5]$helicene $2a$ (4%) and 3-borylated $[5]$helicene $2b$ (12%). The structure of the major product $2b$ was unequivocally confirmed by a single-crystal X-ray diffraction analysis (Fig. 2). The third fraction contained only one compound, structure of which was later on assigned to symmetrical 3,12-bisborylated $[5]$helicene $2c$. The formation of unsymmetrical 2,12-bisborylated $[5]$helicene was neither observed by EI/MS (entry 7) nor confirmed by single-crystal X-ray diffraction. A lower selectivity, a combined yield of 14% (entry 9), ligands $L3$ successfully used for para-borylation of benzene derivatives$^{47-48}$ or regioselective borylation of $[4]$helicene.$^{49}$ These bis(phosphine) type ligands in combination with $[Ir(OH)cod]_2$ afforded the products $2a$ and $2b$ with ratios in the range of 1 : 4.7–6. DM-MeO-BIPHEP $L_1$ and $L_2$, or regioselective borylation of $[4]$helicene, provided $2a$ and $2b$ in combined yields of 21% and 18% and regioselectivity of 1 : 2.3 and 1 : 6, respectively (see the ESI† for the complete list of conditions tested).

These unsatisfactory results turned our attention back to rigid phenanthrene type ligands. We prepared several iridium complexes and carried out the reactions in cyclohexane at 120 °C (Table 2). In general, these pre-prepared bench stable complexes afforded highest yields of $2a$ and $2b$ and also highest regioselectivity. The use of $[Ir((dibpy)(cod)Cl)]$ C1 afforded $2a$ and $2b$ in 60% yield and 1 : 5.4 ratio (entry 1). Complexes based on neocuproin $C_2$, 4,7-dimethoxy-1,10-phenanthroline $C_3$, bathophenanthroline $C_4$ and 3,8-bis[3,5-bis(trifluoro-methyl)phenyl]-1,10-phenanthroline $C_5$ gave $2a$ and $2b$ in a moderate yields (~50%) and lower regioselectivity in the range of 1 : 2.3–

![Fig. 2 ORTEP drawing of 2b with 30% thermal ellipsoids.](Image)
Table 2. Effect of the catalysts on the regioselectivity of the Ir-catalyzed C–H borylation of [5]helicene

| Entry | Catalyst | Yield \(2a + 2b^a\) | Ratio \(2a : 2b^b\) |
|-------|----------|----------------|----------------|
| 1     | C1       | 60             | 5:1            |
| 2     | C2       | 66             | 1:3            |
| 3     | C3       | 51             | 1:4.3          |
| 4     | C4       | 49             | 1:3.3          |
| 5     | C5       | 42             | 1:2.3          |
| 6     | C6       | 52             | 1:6            |
| 7     | C7       | 89             | 1:8            |

\(^a\) Determined by \(^1\)H NMR, based on 1 equiv. of \(^1\).  \(^b\) Determined by \(^1\)H NMR.

4.3 (entries 2–5). A complex with a simple 1,10-phenanthroline C6 gave better regioselectivity of 1 : 6 in a moderate yield 52% (entry 6). The best result, in terms of the yield and selectivity (89%, 1 : 8), was obtained with the Ir-tmphen complex C7 (entry 7). The use of other solvents did not result in any improvement and the use of a [Ir(cod)Cl]2/tmphen mixture resulted in a lower yield (70%) and a drop in selectivity to 1 : 6.4 (see the ESI† for the complete list of conditions tested).

In summary, we have shown that the Ir-tmphen complex C7 can be successfully used for selective monoborylation of [5]helicene to 3-Bpin-[5]helicene 2b. The reaction proceeded with a high regioselectivity (2a : 2b = 1 : 8) and a high yield (89%). In addition, both formed borylated [5]helicenes were stable and were successfully used in Suzuki–Miyaura cross-coupling reactions to furnish the corresponding 2-aryl and 3-aryl[5]helicenes. Application of this chemistry and extension for higher helicenes are underway in our laboratory.

Conflicts of interest

There are no conflicts of interest to declare.

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