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Iridium-Catalyzed Silylation of Five-Membered Heteroarenes: High Sterically Derived Selectivity from a Pyridyl-Imidazoline Ligand

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Supporting information for this article is given via a link at the end of the document.

Abstract: The steric effects of substituents on five-membered rings are less pronounced than those on six-membered rings because of the difference in bond angles. Thus, the regioselectivities of reactions that occur with selectivities dictated by steric effects, such as the borylation of C–H bonds, have been poor in many cases. We report that the silylation of five-membered ring heteroarenes occurs with high sterically derived regioselectivity when catalyzed by the combination of [Ir(cod)(OMe)]2 and a phenanthroline ligand or a new pyridyl-imidazoline ligand that further increases the regioselectivity. The silylation reactions with these catalysts produce high yields of heteroarylsilanes from functionalization at the most sterically accessible C–H bonds of these rings under conditions that the borylation of C–H bonds with previously reported catalysts formed mixtures of products or products that are unstable. The heteroarylsilane products undergo cross-coupling reactions and substitution reactions with ipso selectivity to generate heteroarenes that bear halogen, aryl and perfluoroalkyl substituents.

Introduction

The application of C–H bond functionalization to synthetic chemistry requires the selective activation of a single C–H bond among multiple C–H bonds that possess different steric and electronic properties. A common strategy for controlling the selectivity of catalytic reactions that functionalize the C–H bonds of arenes is to incorporate a functional group on the arene that coordinates to a transition-metal catalyst and directs the reaction to C–H bonds that are ortho, meta or para to that functional group. Undirected functionalizations of the C–H bonds of arenes occur with selectivities that are determined by the steric and electronic properties of the various types of C–H bonds. The most classical undirected functionalizations include uncatalyzed or Lewis-acid catalyzed electrophilic aromatic substitution (EAS) processes. In general, these reactions occur at the most electron-rich C–H bonds, and the steric properties of the groups impart a secondary influence on selectivity.

In contrast, the silylations and borylations of the C–H bonds of arenes catalyzed by iridium complexes of bipyrindine or phenanthroline ligands generally occur at the most sterically accessible and acidic C–H bonds. The regioselectivity of these reactions is almost exclusively determined by the steric properties of the arene; these catalysts selectively functionalize C–H bonds that are distal to functional groups in preference to C–H bonds that are more acidic, but proximal to functional groups. Thus, symmetrical 1,2-disubstituted or unsymmetrical 1,3-disubstituted or 1,2,3-trisubstituted arenes undergo borylation at the C–H meta to the nearest substituent (Figure 1).

The regioselectivity of the functionalization of heteroarenes is more complex, and the influence of steric properties on the selectivity of the functionalization of 5-membered heteroarenes is smaller, than that of 6-membered rings because the more acute bond angles in five-membered rings cause the distances between the substituents to be longer than the distances between substituents in 6-membered rings (Figure 1). Thus, catalytic functionalization of a single C–H bond in a five-membered ring heteroarene with high regioselectivity derived from steric effects is rare due to the distinct electronic properties of the positions of heteroarenes and the weaker steric influence in five-membered ring structures.

Consistent with this trend, the functionalization of these rings has been limited by the poor selectivity of iridium-catalyzed borylations, the low activity of catalysts for silylations, and the requirement of special reagents for silylations that occur with high selectivity. In particular, he current borylations of five-membered...
heteroarenes, in many cases, form isomers from the functionalization of sites ortho to small or medium-sized substituents and product from diborylation,\textsuperscript{[7]} even with the recently developed catalyst of Smith and Maleczka that contains a novel N-N ligand and with excess of thiophene.\textsuperscript{[8]} Iridium-catalyzed silylations of these rings reported by Ishiyama and Miyaura with a phenanthroline bearing a large substituent in the 2-position occurred with several 3-substituted thiophenes and one furan with high sterically derived regioselectivity, but the low activity of this catalyst caused the reactions to require a large excess of heteroarene and high temperatures, and the tetrafluoro disilane used in this process is not commercially available and requires three steps to prepare.\textsuperscript{[9]} Finally, neither the work of Ishiyama nor Smith describes the functionalization of heteroarenes containing multiple heteroatoms, even though these structures are among the most prevalent heteroarenes in medicinal chemistry and agrochemistry.\textsuperscript{[10]}

The identification of reactions that functionalize C-H bonds in five-membered-ring heteroarenes containing one or multiple heteroatoms regioselectively is important because these structural motifs are common in pharmaceuticals, electronic materials, agrochemicals, and natural products.\textsuperscript{[11]} The regioselective silylation and borylation of heteroarenes would be particularly useful because silylarenes and aryl boronic esters undergo hydroxylation,\textsuperscript{[12]} etherification,\textsuperscript{[13]} amination,\textsuperscript{[14]} cyanation,\textsuperscript{[15]} halogenation,\textsuperscript{[16]} and arylation,\textsuperscript{[17]} and analogous derivatization of heteroarenes would provide an array of heteroarenes with substitution patterns that are derived from the catalytic system. The silylation of heteroarenes can be particularly valuable because the heteroaryl silylarenes are often more stable than the corresponding heteroarylboronates.\textsuperscript{[18]}

We report silylations of five-membered heteroarenes catalyzed by an iridium complex that contains a pyridyl-imidazoline ligand, and also silylations catalyzed by a recently disclosed complex of 2,9-Me₂-phenanthroline (Me₂phen). We demonstrate that reactions with these catalysts produce high yields of products that are formed from functionalization of the most sterically accessible C-H bonds of five-membered heteroarenes under conditions in which borylation reactions produce mixtures of products. We also illustrate the versatility of the heteroarylsilanes by developing conditions for ipso substitution reactions to produce the corresponding five-membered-ring heteroarenes bearing halogen, aryl and perfluoroalkyl substituents.

**Results and Discussion**

1. Reaction Development

To achieve the undirected functionalization of five-membered heteroarenes with regioselectivity that is dictated by steric effects, we investigated reactions catalyzed by iridium complexes of a series of ligands that contain nitrogen donors. Two of the ligands, L1 and L2, are based on pyridyl oxazine structures, and two of the ligands, L3 and L4, are based on pyridyl imidazoline structures. Ligand L4 is new, and none of the ligands have been reported for the borylation or silylation of aromatic C-H bonds. We included pyridyl imidazoline structures in our study because the nitrogen atoms should be more electron donating than those in the pyridyl oxazine structures, and substituents on the nitrogen in the imidazoline could influence the structures of these ligands.

To create a benchmark for our studies on the silylation of five-membered ring heteroarenes, we first measured the yield and selectivity of the borylation of 3-chlorothiophene that was catalyzed by the previously reported combination of [Ir(COD)(OMe)]\textsubscript{2} and 4,4'-di-tert-butylbipyridine (dtbpy).\textsuperscript{[19]} Under standard conditions, the products from functionalization at positions both proximal and distal to the chlorine substituent formed, and the major product resulted from diborylation (Scheme 1). Similarly, the silylation of 3-chlorothiophene under the conditions recently reported by our group with 2,9-dimethylphenanthroline as ligand formed a mixture of products from silylation at both the 2 and 5-positions.

In contrast, the silylation of 3-chlorothiophene that was catalyzed by the combination of [Ir(COD)(OMe)]\textsubscript{2} and L2 was selective for functionalization at the 5-position of the heteroarene. This regioselectivity was even higher when the reaction was catalyzed by [Ir(COD)(OMe)]\textsubscript{2} and the imidazoline ligand L3 and was the highest when catalyzed by [Ir(COD)(OMe)]\textsubscript{2} and imidazoline ligand L4, which contains a 2,6-Pr\textsubscript{2}-phenyl group on the imidazoline nitrogen. The silylation of 3-chlorothiophene, when catalyzed by iridium and L3, formed the product from functionalization at the 5-position in 74% yield, and the silylation of this thiophene, when catalyzed by iridium and L4, formed the product from functionalization at the 5-position in 90% yield with a 9:1 selectivity for this isomer over others and the product from di-functionalization.

![Scheme 1. Effect of Ligand on Selectivity](image)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Reagent</th>
<th>Yield of A</th>
<th>A : B : C</th>
</tr>
</thead>
<tbody>
<tr>
<td>dtbpy</td>
<td>B₂Pин₂</td>
<td>16%</td>
<td>28 : 8 : 64</td>
</tr>
<tr>
<td>dtbpy</td>
<td>[H[Si]]</td>
<td>45%</td>
<td>60 : 7 : 33</td>
</tr>
<tr>
<td>Me₂phen</td>
<td>[H[Si]]</td>
<td>41%</td>
<td>36 : 12 : 52</td>
</tr>
<tr>
<td>L1</td>
<td>[H[Si]]</td>
<td>44%</td>
<td>54 : 7 : 39</td>
</tr>
<tr>
<td>L2</td>
<td>[H[Si]]</td>
<td>47%</td>
<td>79 : 3 : 18</td>
</tr>
<tr>
<td>L3</td>
<td>[H[Si]]</td>
<td>74%</td>
<td>88 : 2 : 10</td>
</tr>
<tr>
<td>L4</td>
<td>[H[Si]]</td>
<td>92%</td>
<td>91 : 3 : 6</td>
</tr>
</tbody>
</table>

*See SI for detailed procedures*

We note that this regioselectivity for silylation and chemoselectivity for monosilylation is obtained with limiting heteroarene. The regioselectivity is similar to that reported for the borylation or silylation of the same substrate, but our silylation reaction occurs with the thiophene as limiting reagent. The results on borylation or silylation were obtained with an excess of thiophene, and high selectivity for mono-borylation of such a thiophene with the heteroarene as limiting reagent has not been reported with any catalyst.\textsuperscript{[8-9]}

**Scheme 1: Effect of Ligand on Selectivity**

![Scheme 1](image)
2. Reaction Scope

Having identified a ligand that greatly increases the sensitivity of the iridium-catalyzed silylation of thiophenes to the steric environment of the C–H bonds, we studied the selectivity of this catalyst for the silylation of thiophenes that contain varied functional groups. We conducted silylation reactions with the catalyst that contains L4, silylations with the catalyst that contains MePhen, and borylations with the catalyst that contains dtbpy (Scheme 2). S-Silyl-thiophenes that contain methyl, methoxy, phenyl, ester, boryl, bromide and iodide substituents in the 3-position were obtained with perfect selectivity for the monosilylation product, with perfect regioselectivity, and in yields ranging from 44% to 100% from reactions catalyzed by the combination of iridium and L4. The ethyl ester of 5 and the nitrile of 6 were tolerated: no products from reduction of these functional groups were observed. Thiophene 6, which contains a small cyano substituent, was converted to the corresponding silylarene with 85:12:3 selectivity for functionalization at the 5-position of 3-cyanothiophene to functionalization at the 2-position to disilylation. Likewise, heteroarylsilanes that contain halogen substituents were obtained from the corresponding arenes (7–9) in moderate (3-bromo and 3-chloro) to high (3-iodo) selectivity for functionalization at the 5-position of the heteroarene, but the yields were much lower than those catalyzed by iridium and L4. Likewise, borylation with dtbpy was highly selective for the 5-position of 3-phenylthiophene and ethyl 3-thiophenecarboxylate. However, the borylation of all the other thiophenes in Scheme 2 occurred with low selectivity for the 5-position. These results demonstrate that the catalyst formed from the combination of iridium and L4 is more active and more selective for the functionalization of the least sterically hindered position of thiophenes than previously reported catalysts.

The analogous silylation and borylation reactions of furans and pyrroles are shown in Scheme 3. The silylations of 3-substituted furans and pyrroles catalyzed by iridium and imidazoline ligand L4 occurred with perfect selectivity and in good yield (11–15, 60% to 100% yield). The silylation of 3-bromofuran (10) occurred with greater than 80% selectivity for the 5-position. In contrast, the silylation or borylation of 3-bromofuran under previously reported conditions led to the formation of large amounts of products from functionalization at the 2-position. In addition, the silylations of furans or pyrroles that contain esters at the 3-positions produced significant amounts of products from functionalization at the 2-position when the catalyst contained MePhen. The borylations of these nitrogen or oxygen-containing heterocycles occurred with universally poor selectivity for the least sterically hindered C–H bonds.

Results from the silylations catalyzed by the complex of MePhen and the borylations catalyzed by the complex of dtbpy in Scheme 2 show the value of the silylation of the catalyst that contains L4 for obtaining high regioselectivity. The silylation of thiophenes that contain smaller substituents occurred with low selectivity for functionalization at the 5-position (1, 6, 7) when catalyzed by the combination of iridium and MePhen. The borylations of these heteroarenes with iridium and dtbpy also produced mixtures of products. Silylations of thiophenes that contain larger phenyl, boryl, ester, bromide, and iodide substituents (3–5, 8, 9) and that were catalyzed by iridium and MePhen occurred with complete selectivity for functionalization at the 5-position of the heteroarene, but the yields were much lower than those catalyzed by iridium and L4. Likewise, borylation with dtbpy was highly selective for the 5-position of 3-phenylthiophene and ethyl 3-thiophenecarboxylate. However, the borylation of all the other thiophenes in Scheme 2 occurred with low selectivity for the 5-position. These results demonstrate that the catalyst formed from the combination of iridium and L4 is more active and more selective for the functionalization of the least sterically hindered position of thiophenes than previously reported catalysts.

See SI for detailed procedures. Yields correspond to 1H NMR yield of desired product (desired product : undesired, mono- : undesired, di-)
Five-membered ring heterocycles that contain multiple heteroatoms also underwent silylation in good yield and with high selectivity (Scheme 4). In these cases, the reactions occurred in the highest yields when catalyzed by (Ir(COD)(OMe)2 and Me2phen. The functionalized product formed with high regioselectivity from steric effects with electronic effects influencing selectivity when potentially reactive C–H bonds were present in similar steric environments.

Three examples of the silylation of pyrazoles are provided in Scheme 4. The reactions of 1,3-dimethylpyrazole 16, in which the two aromatic C–H bonds are in similar steric environments was completely selective for the 5-position, and this selectivity was consistent with the high preference for functionalization α to heteroatoms observed for the functionalization of thiophenes, furans and pyroles. However, the silylation of pyrazoles that contain larger tert-butyl carbonate or tosyl substituents on nitrogen occurred distal to the nitrogen that bears that substituent. These results indicate that the silylation of azoles occurs with a selectivity that is determined primarily by the steric environment of the C–H bonds, with electronic effects imparting a secondary influence.

Scheme 4. C–H Silylation of Azoles

The silylations of the thiazoles occurred at the position that is most sterically accessible. One might expect that the reaction would occur at the position more distal to the basic nitrogen because borylations of pyridines were shown previously not to form products from reaction at the position alpha to a basic nitrogen atom. However, the silylation reaction formed a stable product from reaction at the 2-position of 4-substituted thiazoles due to the steric congestion at the 5-position, even if the substituent at the 4-position was as small as a methyl group.

The silylations of heteroarenes containing multiple nitrogen atoms also formed stable products in good yield. The silylation of imidazole 21 containing substituents at the 1 and 2 positions gave a single product from reaction at the 4 position. The imidazole unit of caffeine gave a stable product from reaction at the only available aromatic C–H bond. Silylation of the 1,2,3- and 1,2,4-triazoles also occurred at the sterically more accessible of the two heteroaryl C–H bonds to form stable products albeit with 5 mol % catalyst.

The selectivity of the borylations of 16, 18 and 21-23 was the same as the selectivity of the silylation of these azoles, but the borylated products were unstable. The borylations of 16-18, 21, and 22 gave the functionalized product in only 35-74% yields, and reactions of 19, 20, and 24 gave no borylated product, as determined by evaluating the crude reaction mixtures. Moreover, the amounts of borylated products from the reactions of 16 and 18 were lower after the reaction mixtures were filtered through silica, and no borylated products were present from reactions of 21, 22 and 23 after the reaction mixtures were filtered through silica. Thus, consistent with prior literature, the products from the silylation of azoles are, in many cases, unstable to air and, in most cases, unstable to silica. In contrast, the products from the silylation of azoles 16-23 are stable to air, moisture from solvents stored on the benchtop, and silica. The greater stability of silyl-azoles than of boryl-azoles renders the silylation of the C–H bonds of azoles particularly useful.

3. Functionalization of Heteroaarylcarboxylates

To demonstrate the utility of C–H silylation to the preparation of functionalized heteroarenes, we assessed the ability to convert the silyl heteroarenes to heteroarenes that are functionalized with halogens or with aryl or trifluoromethyl groups (Scheme 5, right). In addition, we compared the products one would obtain from the combination of silylation and functionalization to those from more classical processes (Scheme 5, left). The silylation of ethyl 3-furan carboxylate, followed by functionalization with N-chlorosuccinimide in the presence of AgF formed ethyl 2-chloro-4-furan carboxylate 25 in 63% yield over two steps. In contrast, directed metatation of the related 3-furan carboxylate, followed by quenching with hexachloroethane, is known to produce 2-chloro-3-furan carboxylate, (21) The silylation of 3-chlorothiophene, followed by functionalization with N-bromosuccinimide and AgF, formed bromide 2-bromo-4-chlorothiophene 26 in 72% yield over two steps. In contrast, the direct bromination of 3-chlorothiophene with NBS has been reported to form 2-bromo-3-chlorothiophene. (22) Likewise, the sequential silylation and iodination of 3-methoxythiophene formed 2,4-functionalized product 27, whereas direct iodination of the unfunctionalized arene is known to form the 2,3 functionalized product. Heteroaarylcarboxylates also undergo coupling reactions to form aryalted products. The silylation of 3-methoxythiophene, when catalyzed by rhodium or palladium complexes, leads to arylation with high selectivity for...
the 2-position. Similarly, the 5-arylated product 29 formed in 67% yield over two steps by the sequential silylation and cross-coupling of ethyl 3-furan-2-carboxylate. In contrast, ethyl 3-furan-2-carboxylate is known to undergo direct arylation at the 2-position in the presence of a palladium catalyst.

Finally, the silylation of 3-methylthiophene, followed by coupling (phen)CuCF₃ under an atmosphere of oxygen, formed the product from trifluoromethylation of the 5-position of the thiophene. In contrast, the direct addition of trifluoromethyl radicals is known to occur at the 2-position of 3-methylthiophene. Due to the volatility of 2-trifluoromethyl-4-methylthiophene, this product, was characterized by the ¹⁹F NMR of the crude reaction mixture. However, to form an isolable analog, the silylation of 3-octylthiophene was formed by this process in 61% yield by NMR spectroscopy and 37% isolated yield. These results demonstrate that the silylation of heteroarenes with high sterically derived regioselectivity, followed by functionalizations of the resulting heteroarylsilanes, generate products that are distinct from those accessible from the direct functionalization of the same heteroarenes.

Scheme 5. Regio-Divergent Functionalization of Heteroarenes

Scheme 6. Transformations of Silyl-Pyrazole

Suzuki couplings are widely used, in part, because the aryl boronic acid and ester reagents are stable to air and moisture and can be stored. However, as discussed, the boronic acids or esters of azoles are often unstable. Therefore, coupling of the more stable silyl derivatives of five-membered heteroarenes would be valuable. We found that the silyl-thiophenes and silyl-furans that result from the silylation of C-H bonds couple with aryl iodides in the presence of AgF and catalytic amounts of Pd(P₃Bu₃)₂. However, under similar conditions, only 10% of the product from the reaction of the silyl thiophene 2-silyl-4-thiazolecarboxylate methyl ester formed from coupling the representative partner m-Cl-iodobenzene (Scheme 7). After conducting reactions with a series of fluoride additives and phosphine ligands, we found that a high yield of biaryl product (85%) was obtained from reactions with CsF as activator and the combination of Pddba₂-CHCl₃ and BINAP as catalyst. The 2-silyl-4-thiazolecarboxylate methyl ester also coupled with heteroaryl bromides catalyzed by the same system to form biaryls 37 and 38 in 76% and 50% yield. Although bithiazole 39 formed in a modest 22% yield from the same coupling of the silyl thiophene with 2-bromothiazole, this reaction has not been accomplished previously by Suzuki coupling of the

See SI for detailed procedures.

The silyl-azoles presented in Scheme 4 are more electron-deficient than the silyl-thiophenes and silyl-furans in Scheme 5. To determine whether silyl-azoles are nucleophilic enough to undergo transformations that are similar to those of other silylarenes and heteroarenes, we conducted a series of derivatizations of silyl pyrazole 31 (Scheme 6). The reaction of 31 with NCS in the presence of AgF formed chloropyrazole 32 in 52% yield. Similarly, the reaction of 31 with NBS formed bromopyrazole 33 in 81% yield. Silyl-pyrazole 31 also coupled with 3,5-(MeO)₂-phenyl triflate to form bismut 34 in 70% yield when catalyzed by Pddba₂-CHCl₃ and BINAP. The identification of that catalyst system is discussed in greater detail below. In addition, 31 coupled with (phen)CuCF₃ under an atmosphere of oxygen to form 1-Ts-3-Me-4-CF₃-pyrazole (35) in 50% yield. These results demonstrate that the silylation of azoles, followed by the functionalization of the product, also can lead to products containing a diverse array of functional groups.

See SI for detailed procedures.

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See SI for detailed procedures.
analogous boronate, presumably due to the instability of this boronate. As noted in the previous paragraph, these conditions were also suitable for the coupling of the silyl-pyrazole 31 to form 3-aryl pyrazole 34. Thus, the combination of CsF activator and BINAP-ligated palladium is an effective system to catalyze the coupling of silylazoles with aryl halides under mild conditions.

Scheme 7. Hiyama Coupling of Sily-Azoles

The ratio of deuterated products was distinct from the ratio of silylated products. The reaction catalyzed by the complex of Me₃P⁺phen formed deuterated products 7c and 7d in a ratio of 1.5:1 but formed the silylated products 7a and 7b in a higher ratio of 2.9:1 (Scheme 8). The reaction catalyzed by a complex of L4 formed the deuterated products 7c and 7d in a ratio of only 1:1 but formed the silylated products 7a and 7b in a high ratio of 14:1. Thus, the cleavage of C–H bonds by the catalyst that contains Me₃P⁺phen, but the formation of silylated products by the catalyst that contains L4 occurs with much greater regioselectivity than that of the catalyst that contains Me₃P⁺phen. These results demonstrate that the regioselectivity of these two catalysts for the silylation of C–H bonds does not reflect the propensity of the catalysts to cleave C–H bonds. Rather, the selectivity of the silylation reaction is controlled by the relative rates of formation of the carbon-silicon bond from 2- or 5-heteroaryliridium intermediates that are formed reversibly. These experimental results resemble the computations reported by Sakaki for the selectivity of the borylations of β over α C–H bonds in THF, as well as the experiments and computations our group reported previously on the origins of selectivity of Rh-catalyzed borylations and silylations of primary over secondary alkyl C–H bonds.²²

Scheme 8. Reactions of Deuterated Silane with Excess Arene

4. Origin of Regioselectivity

To determine the elementary steps controlling the high selectivity for the silylation of unhindered C–H bonds of heteroarenes catalyzed by complexes of L₄, we conducted studies on the reactions of deuterated silane with 3-chlorothiophene (7). The reactions of an excess of 7 with deuterated silane catalyzed by iridium and Me₃P⁺phen or L₄ exchanged deuterium between the silane Si–D bond and the 2-positions and 5-positions of the heteroarene to form deuterated products 7c and 7d, respectively. This reaction occurred in concert with the formation of silylated products 7a and 7b. After 15 min at 65 °C, the amounts of deuterated products 7c and 7d were greater than the amounts of silylated products 7a and 7b by factors of about 2:1 and 6:1 for the catalysts containing ligands Me₃P⁺phen and L₄, respectively. This incorporation of deuterium into the heteroarene reactant indicates that cleavage of the C–H bond is reversible.

Conclusion

In summary, we have developed a method for the silylation of heteroaromatic compounds with high sterically derived regioselectivity. In many cases, these high selectivities are achieved with a new pyridyl-imidazoline ligand L₄. The selectivity of this silylation to form functionalized products from reaction at the least sterically hindered position of five-membered heteroarenes is much higher than that of previously reported borylations of these heteroarenes, and the products formed are much more stable than the analogous boronates. Moreover, functionalizations of the heteroarylboranes form products with substitution patterns that are orthogonal to those that have been reported by traditional methods and other catalytic processes. Mechanistic studies showed that the rates of formation of the carbon-silicon bond from isomeric heteroaryliridium complexes influences the selectivities of the silylation reactions more than the rates of the cleavage of carbon-hydrogen bonds to form these complexes and that the selectivities from the reactions catalyzed by the combination of iridium and the pyridyl-imidazoline ligand L₄ result almost exclusively from the rates of formation of the carbon-silicon bond. Additional studies on the mechanism and
origin of high selectivity of the silylation reaction with catalysts that contain imidazoline ligands are ongoing in our laboratory.

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The silylation of five-membered heteroarenes occurs with high sterically derived regioselectivity when catalyzed by the combination of [Ir(cod)(OMe)]_2 and a novel pyridyl-imidazoline ligand. The silylation reactions with this catalyst produce high yields of heteroarylsilanes under conditions in which the borylation of C–H bonds with previously reported catalysts formed mixtures of products or products that are unstable.

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