A Simple and Efficient Copper-Catalyzed Procedure for the Hydrosilylation of Hindered and Functionalized Ketones

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The catalytic hydrosilylation of highly hindered and functionalized ketones is described. The combination of inexpensive catalyst precursors, CuCl and NHC-HX (NHC = N-heterocyclic carbene), leads to a highly efficient reduction mediator for the preparation of silyl ethers from unfunctionalized and functionalized alkyl, cyclic, bicyclic, aromatic, and heteroaromatic ketones. A series of catalyst precursors have been structurally characterized and a catalyst-structure activity relationship is discussed.

Introduction

Carbonyl bond reduction in ketones and aldehydes represents an ubiquitous protocol in organic synthesis.1 Hydrosilylation is especially useful, insofar as it yields the protected alcohols and uses easy to handle starting materials.2 A number of transition metal complexes, such as Ti,3 Rh,4 Ru,5 or Ir,6 have displayed high catalytic activity in the hydrosilylation of carbonyl compounds. Although these protocols are effective for the reduction of various ketones and aldehydes, the reported catalysts are quite inactive toward sterically hindered substrates.7 Furthermore, the available stoichiometric procedures for the reduction of highly hindered carbonyl compounds require up to 40 equiv of the reducing agent.8

A less costly alternative, with copper as the metal source, has been developed by Stryker. It made use of triphenylphosphine as the ligand for the reduction of simple or α,β-unsaturated aldehydes and ketones.9 But, to date, the activity of this system has not been tested with functionalized or sterically demanding carbonyl compounds. Lipshutz explored various phosphine-ligated copper hydride systems for the transformation of simple aldehydes and ketones leading to reduced products.10 Although these systems have been shown to be effective even for asymmetric hydrosilylation of a variety of substrates, their reactivity toward highly sterically demanding or functionalized ketones has not been exten-


Hydrosilylation of Hindered and Functionalized Ketones

Results and Discussion

We began our studies using dicyclohexyl ketone as substrate utilizing the catalytic system we previously developed at room temperature (see Scheme 1). Unfortunately, the protocol failed even after long reaction times. Remarkably, on raising the temperature to 80°C, dicyclohexyl ketone was activated toward hydrosilylation and afforded 99% of the corresponding silyl ether in 4 h. These conditions were tested on different hindered ketones. These results are summarized in Table 1. Even if total conversions could be obtained in short or reasonable reaction times in some cases (Table 1, entries 5–7), the most hindered substrates required higher reaction temperatures (Table 1, entries 2 and 4). It is noteworthy that when two diastereoisomers could be formed, IPr turned out to be a moderate diastereo-directing ligand (Table 1, entries 3 and 4).

For diastereoselectivity considerations,15 the 2,6-dimethylcyclohexanone (Table 1, entry 3) is sold as a mixture of 80:20 cis:trans isomers. From the cis isomer, both meso cis/cis and meso trans/trans silyl ethers can be formed and the major product was assigned to be the meso cis/cis isomer.16 Assignment of the relative configuration of 2-(tert-butylcyclohexyloxy)silane was made by comparing experimental spectroscopic data with those reported in the literature for the corresponding alcohols.17 The cis diastereoisomer, the less stable one, was predominantly the major product, which is consistent with our catalytic system. Similar results have been observed in the rhodium-catalyzed hydrosilylation of cyclohexanones.18

To improve these results, we examined the influence of the ligand on the reaction. The structures of the screened NHC salts are shown in Figure 1. Their corresponding activity in the hydrosilylation of hindered or functionalized alkyl, cyclic, bicyclic, aromatic, and heteroaromatic ketones.

Table 1. Hydrosilylation of Hindered Ketones with CuCl/IPr·HBF4

<table>
<thead>
<tr>
<th>entry</th>
<th>product</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>cis/cis</th>
<th>trans/trans</th>
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<tbody>
<tr>
<td>1</td>
<td>OSEt3</td>
<td>3</td>
<td>87</td>
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<td>OSEt3</td>
<td>4</td>
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<td>20</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* GC conversions (isolated yields) are the average of two runs.  
** See text for discussion.  
† Reaction at 100 °C.  
‡ Meso trans/trans: cis/cis.  
§ Cis:trans.
2,6-diisopropylphenyl IPr-HX SIPr-HX 2,4,6-trimethylphenyl IMes-HX SIMes-HX cyclohexyl ICy-HX adamantyl IAd-HX tert-butyl tBu-HX

**FIGURE 1.** Structures of saturated and unsaturated NHC salts.

**TABLE 2. Effect of NHC-HX on the Hydrosilylation of Dicyclohexyl Ketone**

<table>
<thead>
<tr>
<th>Entry</th>
<th>NHC-HX</th>
<th>Conversion after 1 h</th>
<th>Max Conversion (time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IPr-HBF4</td>
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<td>100 (4 h)</td>
</tr>
<tr>
<td>2</td>
<td>IPr-HCl</td>
<td>2</td>
<td>79 (24 h)</td>
</tr>
<tr>
<td>3</td>
<td>SIPr-HBF4</td>
<td>0</td>
<td>13 (24 h)</td>
</tr>
<tr>
<td>4</td>
<td>SIPr-HCl</td>
<td>0</td>
<td>8 (20 h)</td>
</tr>
<tr>
<td>5</td>
<td>IMes-HBF4</td>
<td>11</td>
<td>100 (7 h)</td>
</tr>
<tr>
<td>6</td>
<td>IMes-HCl</td>
<td>82</td>
<td>100 (1.5 h)</td>
</tr>
<tr>
<td>7</td>
<td>SIMes-HBF4</td>
<td>30</td>
<td>100 (4 h)</td>
</tr>
<tr>
<td>8</td>
<td>ICy-HBF4</td>
<td>100</td>
<td>100 (1 h)</td>
</tr>
<tr>
<td>9</td>
<td>IAd-HBF4</td>
<td>35</td>
<td>100 (3 h)</td>
</tr>
<tr>
<td>10</td>
<td>IAd-HCl</td>
<td>18</td>
<td>100 (5 h)</td>
</tr>
<tr>
<td>11</td>
<td>tBu-HBF4</td>
<td>33</td>
<td>100 (3.5 h)</td>
</tr>
</tbody>
</table>

*GC conversions (%) are the average of at least two runs.

carbene salts (IAd-HX and tBu-HBF4) yielded the hydrosilylated product in good reaction times (3–5 h, Table 2, entries 9–11), which let us presume that electronic effects rather than steric effects may be the determinant feature in this reaction. As electronic factors governing NHC ligands are not yet fully understood,\(^\text{19}\) it is hard to rationalize the screening results. The hexameric complex ([IPPh3]CuH6), known as an excellent reagent for conducting reductions of carbonyl compounds,\(^\text{9}\) was employed in the hydrosilylation of dicyclohexyl ketone at 80 °C, but no conversion was observed. Instead, a copper mirror readily formed at this temperature. A similar reaction at room temperature failed to yield the hydrosilylated product and did not result in catalyst decomposition.

The influence of the copper source on the reaction under conditions described in Table 2 was investigated. Similar results were obtained with CuCl and CuBr, but CuI required longer reaction times (4 h). Cu(II) salts such as CuCl2 and Cu(OAc)2 were also screened. Interestingly, the latter afforded the silylated product in 80% yield after 24 h at 80 °C. The activation pathway of this Cu(II) salt is not fully understood and investigations are ongoing in our laboratories to elucidate these aspects of the chemistry.

Further sources of hydride were also examined. tert-Butyldimethylsilane yielded the expected product in 45 min but surprisingly the use of dimethylphenylsilane led to complete conversion even after 18 h. Phenyl and diphenylsilane led to complete consumption of the dicyclohexyl ketone in 30 min, but, as expected, multiple hydrosilylated products were obtained for those cases. As all products would lead to the same alcohol after acidic workup, these hydrosilanes remain interesting when an alcohol is the target product. Nevertheless, as we were interested in isolating the corresponding silyl ethers, Et3SiH was chosen as the hydride source as it is the most efficient in terms of cost and reactivity.

Base and silane loadings were optimized to 20 mol % of NaOBut and 5 equiv of Et3SiH, respectively. In some cases, the hydrosilylation reactions could be carried out with 12 mol % of base with no deleterious effect on reaction time, but this was not general. Control reactions, using the optimized conditions, where CuCl and ICy-HBF4 were used independently and exclusively resulted in the starting material recovery.

We had previously shown that well-defined (NHC)CuCl complexes, such as (IPr)CuCl, could be easily prepared from the corresponding imidazolium salt and copper(I) chloride. Moreover, they present a higher activity than the in situ catalyst.\(^\text{14a}\) Under the same conditions, the synthesis of (ICy)CuCl (1) was achieved in good yield (Scheme 2).\(^\text{20}\)

The structure of this complex was elucidated by single-crystal diffraction from suitable crystals grown from a CH2Cl2/hexane solution. The resulting ball-and-stick drawing for 1 is shown in Figure 2. Only the formation of a monocarbene complex was observed under these conditions. The Cu–C bond length (1.925 Å) is comparable to known Cu–C bonds in carbene complexes.\(^\text{21}\)

Optimization studies carried out with the well-defined catalyst resulted in a reduced loading of base (NaOBut, 12 mol %) and silane (Et3SiH, 3 equiv) as compared with the in situ generated catalytic system.

A number of dialkyl ketones with varying steric congestion around the carbonyl bond could be hydrosilylated efficiently with the in situ system or the well-defined catalyst as illustrated in Table 3. Even highly...
unreactive ketones such as 2,2,4,4-tetramethyl-3-pentanone (Table 3, entry 2) and 2,2,6,6-tetramethylcyclohexanone (Table 3, entry 5) were successfully reduced within reasonable reaction times. These catalytic systems were also employed in the hydrosilylation of bulky bicyclic and aromatic ketones (Table 3, entries 9–15). Interestingly, the purity of the ketone was not crucial in this series of experiments and technical grade benzophenone was successfully reduced under these conditions, which shows that the present catalyst is quite robust. In all examples, the well-defined catalyst allowed shorter reaction times, achieving a higher or comparable conversion. When the expected product could be obtained as two different diastereoisomers, no diastereoselectivity was observed. In the case of the dimethylcyclohexanone (Table 3, entry 3), the resulting product was obtained as a mixture 48/48/2 (meso trans/trans: meso cis/cis:cis/ trans). The different ratios of the cis/trans product obtained under these conditions or with IPrâHBF4 as ligand precursor (Table 1, Entry 3) might be obtained as a result of the base-catalyzed equilibrium between both isomers of the starting material. From the 2-tert-butylcyclohexanone (Table 3, entry 6), a 50/50 mixture of isomers was formed. In fact, it has been shown that there is only a slight difference between the two faces of the carbonyl group due to the twisted conformation of this ketone and therefore a more hindered catalyst is needed to observe a diastereoselectivity.22 Silylated products formed from trimethylcyclohexanone, fenchone, and camphor (Table 3, entries 4, 9, and 10) presented a major diastereoisomer but this diastereoselectivity can be ex-

<table>
<thead>
<tr>
<th>entry</th>
<th>product</th>
<th>time (h)</th>
<th>yield (%)</th>
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<td>94</td>
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<td>96 (92)</td>
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<td>100 (90)</td>
<td>1.5</td>
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<td>100 (99)</td>
</tr>
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<td>80 (75)</td>
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<td>85 (80)</td>
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</table>

* 20 mol % of NaO'Bu, 5 equiv of Et3SiH. b 12 mol % of NaO'Bu, 3 equiv of Et3SiH. c GC conversions (isolated yields) are the average of two runs.
plained by the structure of the starting material. In the case of the silyl ether corresponding to camphor (Table 3, entry 9), the endo isomer was only observed as traces in the $^1$H NMR spectrum, and as expected, the endo product was preferentially formed from the fenchone (Table 3, entry 10).23

As the NHC–Cu(I) complex is air stable and its handling does not require inert conditions, open air reactions were also tested. Formation of the silylated product from dicyclohexyl ketone was observed under these conditions. However, resulting yields were not reproducible as in solution the active species rapidly underwent decomposition to afford copper(II) products.

All attempts to synthesize Cu(I) well-defined complexes with PPr$_3$ or PCy$_3$ failed. Nevertheless, we were able to prepare a (Bu$_3$P)CuCl complex under the reaction conditions described for the synthesis of (ICy)CuCl although in a considerably lower yield (Scheme 3).

TABLE 4. Biphenylphosphine Screening for the Hydrosilylation of Dicyclohexyl Ketone

<table>
<thead>
<tr>
<th>entry</th>
<th>phosphine</th>
<th>time (h)</th>
<th>yield (%)$^a$</th>
<th>$^{31}$P NMR$^b$</th>
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<td>P: -9.86</td>
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<td>Pr</td>
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<td>4</td>
<td>[Cu]: 6.34</td>
</tr>
<tr>
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<td>PrOCy$_2$</td>
<td>5</td>
<td>1</td>
<td>P: -7.85</td>
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<tr>
<td></td>
<td>Pr</td>
<td>24</td>
<td>4</td>
<td>[Cu]: 11.25</td>
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<td>PrOCy$_2$</td>
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<td>2</td>
<td>P: -10.59</td>
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<td></td>
<td>Pr</td>
<td>24</td>
<td>23 (18)</td>
<td>[Cu]: 2.11</td>
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<td>15</td>
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<tr>
<td></td>
<td>Pr</td>
<td>24</td>
<td>0</td>
<td>[Cu]: --</td>
</tr>
</tbody>
</table>

$^a$ GC conversions (isolated yields) are the average of two runs. $^b$ P = free phosphine; [Cu] = corresponding complex.

FIGURE 3. Ball-and-sick drawing for [(t-Bu$_3$P)CuCl]$_2$ (2). Selected bond lengths (Å): P1–Cu1 = 2.2005(8), P2–Cu2 = 2.2027(8), Cu1–Cl1 = 2.4265(8), Cu1–Cl2 = 2.4224(8), Cu2–Cl1 = 2.4686(8), Cu2–Cl2 = 2.4346(8). Selected bond angles (deg): P1–Cu1–Cl1 = 123.78(3), P1–Cu1–Cl2 = 123.07(3), Cl2–Cu1–Cl1 = 93.84(3), P2–Cu2–Cl2 = 124.68(3), P2–Cu2–Cl1 = 121.22(3), Cl2–Cu2–Cl1 = 93.87(3). Hydrides are omitted for clarity.

As NHCs have been traditionally considered “phos- phine-mimics” and complementary to elegant work by Lipshutz using bidentate phosphines,10 some tertiary phosphines were screened to allow a comparison. The results for the hydrosilylation of dicyclohexyl ketone catalyzed by CuCl/biphenylphosphine systems are presented in Table 4. $^{31}$P NMR experiments were performed for each screened phosphine to ensure the formation of the corresponding phosphine–copper complex. Total transformation of the starting phosphines was observed in all cases but for the trisopropylbiphenylphosphine (Table 4, entry 2), which was only partially converted into the corresponding copper complex. However, low conver-
Suitable single crystals of this phosphine–copper complex were grown from a saturated THF solution, to elucidate its structure by single-crystal diffraction. The corresponding ball-and-stick drawing for \((t\text{-Bu}_3\text{P})\text{CuCl}_4\) is shown in Figure 3. For the phosphine–copper complex, formation of a “cubane-like” structure was observed. It adopts a slightly distorted cubic arrangement with four copper atoms, each having a tetrahedral environment with three bridging chlorides and a phosphine ligand. This type of structure has already been observed for other phosphine–Cu(I) complexes.\(^{(25)}\) The average distances in the core are Cu–Cl \(2.438\) Å and Cu–P \(2.202\) Å. The high steric congestion and degree of coordination around the metal centers in this phosphine–copper complex, when compared with the monomeric NHC–Cu(I) complex, may explain its lack of reactivity toward hydrosilylation.

We have shown that, in the present system, NHCs are more efficient ligands in the hydrosilylation of ketones than the tested tertiary phosphines. We suspect that their specific shape may protect and stabilize the metal center facilitating the coordination of the substrate.

To enlarge the scope of our catalytic system, a number of functionalized ketones were tested with the in situ catalyst as well as with the well-defined complex. Amines and ethers (Table 5, entries 1, 2, and 9) reacted successfully under these conditions. In the presence of halogen and trifluoromethyl substituents on the aromatic ring, good yields were obtained in short reaction times (Table 5, entries 3–5). However, electron-donating groups in the aromatic ring or a pyranyl ring led to slower reaction rates (Table 5, entries 7 and 10) and no reaction was observed in the case of an acetylbenzonitrile and tetrahydrothiopyranone (Table 5, entries 8 and 11). A long reaction time was required to reduce the 2-acetylpyridine, and 2-acetylthiophene did not yield any hydrosilylated product under these conditions (Table 5, entries 12 and 13). In the case of 2-methoxycyclohexanone (Table 5, entry 9), no steric or chelation effect was observed and the corresponding silyl ether was obtained as a 50/50 mixture of diastereoisomers.

Since reduced products from heteroaromatic ketones can be useful intermediates for the synthesis of biologically active compounds,\(^{(26)}\) we closely examined the reactivity of pyridine and thiophene acetophenones (Table 5, entries 12 and 13). It is well-known that copper forms strong bonds with nitrogen or sulfur and so the presence of these heteroatoms in the starting material might sequester the metal center inhibiting the catalytic cycle. To avoid this process, the reactivity of different imid-

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TABLE 5. Hydrosilylation of Functionalized Ketones with CuCl/ICy-HBF₄ or (ICy)CuCl

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
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<td>N-OEt</td>
<td>2</td>
<td>100 (92)</td>
<td>1</td>
<td>100 (93)</td>
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<td>N-OEt</td>
<td>3</td>
<td>99 (93)</td>
<td>2</td>
<td>98 (94)</td>
</tr>
<tr>
<td>3</td>
<td>Cl-N-OEt</td>
<td>1.5</td>
<td>100 (95)</td>
<td>1.5</td>
<td>100 (97)</td>
</tr>
<tr>
<td>4</td>
<td>Br-N-OEt</td>
<td>1.5</td>
<td>100 (95)</td>
<td>1</td>
<td>100 (99)</td>
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<td>90 (88)</td>
</tr>
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<td>CF₃-N-OEt</td>
<td>1.5</td>
<td>100 (93)</td>
<td>1</td>
<td>100 (96)</td>
</tr>
<tr>
<td>7</td>
<td>Me₂N-N-OEt</td>
<td>27</td>
<td>60 (95)</td>
<td>–</td>
<td>–</td>
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</table>

<sup>a</sup> 20 mol % of NaOBut, 5 equiv of Et₃SiH. <sup>b</sup> 12 mol % of NaOBut, 3 equiv of Et₃SiH. <sup>c</sup> GC conversions (isolated yields) are the average of two runs.

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azolium salts in the hydrosilylation of 2-acetylpyridine was studied. The results are presented in Table 6. In this case, SIMes-HBF4 turned out to be the best ligand precursor for the hydrosilylation of 2-acetylpyridine by Et3SiH. It is of note that IMes-HBF4 and IMes-HCl also lead to interesting conversions but longer reaction times are required.

Base and hydrosilane loading optimization showed surprising results. Not only did lower base loadings not require longer reaction times but complete conversion was reached in only 1 h when 8 mol % of NaO’Bu was used (Table 7). When less than 5 equiv of hydrosilane was used, the reaction still reached completion but in longer reaction times.

Such results led us to synthesize a well-deﬁned copper(I) chloride complex bearing a SIMes ligand to compare its activity to the in situ system. The protocol employed for the preparation of (ICy)CuCl (1) was successful and afforded the expected (SIMes)CuCl (3) in good yield (Scheme 4).

The structure of 3 was elucidated by single-crystal diffraction from suitable crystals grown from a CH2Cl2/hexane solution. The resulting ball-and-stick drawing for 3 is shown in Figure 4. In the case of (SIMes)CuCl, the structure is analogous to that observed for (ICy)CuCl (1), but the bond length between the copper center and the carbenic carbon is shorter than that for the latter (1.882 and 1.925 Å, respectively). This suggests that the saturated NHC ligand binds more strongly to the metal center.

Base and silane loadings were optimized for the hydrosilylation reaction mediated by (SIMes)CuCl (3). As for the in situ system with SIMes-HBF4, decreasing base loading led to faster completion of the reaction and we were able to reach total conversion in 30 min with only 3 mol % of NaO’Bu (Table 8). As expected, no reaction was observed in the absence of base. The same reaction times leading to identical conversions were observed with 5, 3, or 2 equiv of silane.

**TABLE 6. Effect of NHC-HX on the Hydrosilylation of 2-acetylpyridine**

<table>
<thead>
<tr>
<th>entry</th>
<th>NHC-HX</th>
<th>conversion after 3 h&lt;sup&gt;a&lt;/sup&gt;</th>
<th>max conversion&lt;sup&gt;a&lt;/sup&gt; (time)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>IPr-HBF4</td>
<td>20</td>
<td>90 (24 h)</td>
</tr>
<tr>
<td>2</td>
<td>IPr-HCl</td>
<td>0</td>
<td>100 (72 h)</td>
</tr>
<tr>
<td>3</td>
<td>SIPr-HBF4</td>
<td>60</td>
<td>60 (20 h)</td>
</tr>
<tr>
<td>4</td>
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<tr>
<td>5</td>
<td>IMes-HBF4</td>
<td>56</td>
<td>98 (4.5 h)</td>
</tr>
<tr>
<td>6</td>
<td>IMes-HCl</td>
<td>42</td>
<td>100 (6.5 h)</td>
</tr>
<tr>
<td>7</td>
<td>SIMes-HBF4</td>
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<td>100 (3 h)</td>
</tr>
<tr>
<td>8</td>
<td>ICy-HBF4</td>
<td>40</td>
<td>98 (3 h)</td>
</tr>
<tr>
<td>9</td>
<td>ICy-HCl</td>
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<tr>
<td>10</td>
<td>ICy-HCl</td>
<td>35</td>
<td>100 (8 h)</td>
</tr>
</tbody>
</table>

<sup>a</sup> GC conversions are the average of at least two runs.

**FIGURE 4.** Ball-and-stick drawing for (SIMes)CuCl (3).

**TABLE 7. Optimization of Hydrosilylation with CuCl/ SIMes-HBF4 Catalyst**

<table>
<thead>
<tr>
<th>entry</th>
<th>mol % of NaO’Bu</th>
<th>equiv of Et3SiH</th>
<th>time (h)</th>
<th>GC conversion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>3</td>
<td>3.5</td>
<td>100</td>
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</tbody>
</table>

<sup>a</sup> GC conversions are the average of at least two runs.

**TABLE 8. Optimization of Hydrosilylation with (SIMes)CuCl Catalyst**

<table>
<thead>
<tr>
<th>entry</th>
<th>X mol % of NaO’Bu</th>
<th>Y equiv of Et3SiH</th>
<th>time (h)</th>
<th>GC conversion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
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<td>100</td>
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<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>18</td>
<td>0</td>
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</tbody>
</table>

<sup>a</sup> GC conversions are the average of at least two runs.

Base and hydrosilane loading optimization showed surprising results. Not only did lower base loadings not require longer reaction times but complete conversion was reached in only 1 h when 8 mol % of NaO’Bu was used (Table 7). When less than 5 equiv of hydrosilane was used, the reaction still reached completion but in longer reaction times.

Such results led us to synthesize a well-deﬁned copper(I) chloride complex bearing a SIMes ligand to compare its activity to the in situ system. The protocol employed for the preparation of (ICy)CuCl (1) was successful and afforded the expected (SIMes)CuCl (3) in good yield (Scheme 4).

The structure of 3 was elucidated by single-crystal diffraction from suitable crystals grown from a CH2Cl2/hexane solution. The resulting ball-and-stick drawing for 3 is shown in Figure 4. In the case of (SIMes)CuCl, the structure is analogous to that observed for (ICy)CuCl (1), but the bond length between the copper center and the carbenic carbon is shorter than that for the latter (1.882 and 1.925 Å, respectively). This suggests that the saturated NHC ligand binds more strongly to the metal center.

Base and silane loadings were optimized for the hydrosilylation reaction mediated by (SIMes)CuCl (3). As for the in situ system with SIMes-HBF4, decreasing base loading led to faster completion of the reaction and we were able to reach total conversion in 30 min with only 3 mol % of NaO’Bu (Table 8). As expected, no reaction was observed in the absence of base. The same reaction times leading to identical conversions were observed with 5, 3, or 2 equiv of silane.

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Hydrosilylation of Hindered and Functionalized Ketones

<table>
<thead>
<tr>
<th>TABLE 9. Hydrosilylation of Heteroaromatic Ketones</th>
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<tbody>
<tr>
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<td>4</td>
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<td>5</td>
</tr>
</tbody>
</table>

*8 mol % of NaOBU, 5 equiv of Et3SiH. b 3 mol % of NaOBU, 2 equiv of Et3SiH. c GC conversions (isolated yields) are the average of two runs. d 12 mol % of NaOBU. e 8 mol % of NaOBU.

The optimized conditions for the hydrosilylation of 2-acetylpyridine were tested with other heteroaromatic ketones. The results are shown in Table 9. Good results were obtained for all the examined substrates, except in the case of 2-acetyltiazole and 2-acetyl-1-methylpirrole (Table 9, entries 4 and 5) where larger amounts of base were required to carry out the reaction in reasonable reaction times. The asymmetrical hydrosilylation of heteroaromatic ketones has already been reported by Lipshutz et al.27 Interestingly, their chiral phosphine—Cu(I) system failed to yield any product from 2-acetyltiazole or 2-acetyl-1-methylpirrole even though it allowed the formation of several alcohols in excellent yields and moderate to good ee.

These results for the hydrosilylation of heteroaromatic ketones are also interesting in terms of mechanistic insights. The proposed mechanism for the copper-catalyzed hydrosilylation of ketones is shown in Scheme 5. First, formation of (NHC)CuCl and NaOBU occurs. This step has been confirmed as formation of (NHC)copper alkoxide complexes under these conditions has been observed by 1H NMR.20 It is then postulated that the active catalyst, a NHC copper hydride species, is formed by a σ-bond metathesis between the (NHC)CuOBO and the hydrosilane. Addition of hydride to the carbonyl carbon would result in a copper alkoxide that would undergo another σ-bond metathesis28 with the hydrosilane to form the expected silyl ether and regenerate the active catalyst. This proposed mechanism is in agreement with the experimental evidence for the phosphine—copper catalyst systems,29 but it does not explain why an excess of base is generally required to complete the reaction. The (SIMes)CuCl-catalyzed hydrosilylation of heteroaromatic ketones is the first example of this reaction where no excess of base is used. As it is well-known that hydrosilanes are prone to nucleophilic attack, we propose that the excess of base that is generally required would interact with the hydrosilane and facilitate the second σ-bond metathesis. Further efforts to fully understand the mechanism of this catalytic system are underway.

Conclusions

In summary, a reagent prepared in situ from sub-stoichiometric quantities of CuCl and a NHC salt as ligand precursor has been found to possess excellent reactivity in the hydrosilylation of hindered and functionalized ketones. This method combines the versatility of ICy-HBF₄ toward a wide variety of substrates with the possibility of varying the ligand precursor to improve conversions/activity as a function of specific carbonyl compounds. This has been demonstrated in the hydrosilylation of heteroaromatic ketones with SIMes as the NHC of choice. The corresponding well-defined complexes, (NHC)CuCl, can be readily prepared by a general scheme that is applicable to numerous imidazolium salts. Both the in situ generated and the well-defined systems give cleanly, high yields of products in short to intermediate reaction times. The combination of a copper(I) salt and an inexpensive ligand precursor would appear to be a practical and economical methodology in the area of reduction of carbonyl compounds. Applications to other carbonyl and carbonyl-type substrates and further studies on the diastereoselectivity of this catalyst system are currently being pursued in our laboratories.

Experimental Section

General Considerations. All ketones were used as received. Copper(I) chloride and sodium tert-butoxide were stored under argon in a glovebox containing less than 1 ppm O₂. The imidazolium salts were synthesized according to literature procedures.30 Solvents were distilled from appropriate drying agents. Flash column chromatography was performed on silica gel 60 (320–400 mesh). 1H NMR and 13C NMR spectra were
recorded on a 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. All reported yields are isolated yields and are the average of at least two runs.

**Synthesis of (L)CuCl Complexes (L = NHC or PR₃).** The procedure provided in ref 14a was used for the synthesis of the complexes.

(I Cy)CuCl (1). ¹H NMR (400 MHz, CDCl₃) δ 6.93 (s, 2H), 4.37–4.23 (m, 2H), 2.14–2.02 (m, 4H), 1.94–1.83 (m, 4H), 1.80–1.57 (m, 6H), 1.55–1.37 (m, 4H), 1.31–1.14 (m, 2H). ¹C NMR (100 MHz, acetone-δ₆) δ 174.2, 119.5, 62.1, 35.4, 26.3, 25.8. Elemental analysis calcd for C₁₂H₂₇ClCuP (301.32): C, 47.83; H, 9.03.

Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. Tetrahedron Lett. 1997, 38, 3081–3084. (A) Using the general procedure with ICy-CuCl, 12 mol % of NaOBF₄, and 3 equiv of Et3SiH, 2,2,6,4, 4-tetramethylpentane (0.175 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.238 g (92% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.13 (s, 1H), 0.99 (t, J = 8.0 Hz) and 0.97 (a) (27H), 0.66 (q, 6H, J = 8.0 Hz); ¹C NMR (100 MHz, CDCl₃) δ 87.8, 37.9, 28.2, 7.3, 5.9; MS (EI), m/z 258 (M⁺). Elemental analysis calcd for C₁₀H₁₅OSi (288.51): C, 69.69; H, 13.26. Found: C, 69.2; H, 13.61.

(2,6-Dimethylcyclohexyl)triethylsilane (Table 3, Entry 3). (A) Using the general procedure with ICy-HBF₄, and 20 mol % of NaO'Bu, 2,6-dimethylcyclohexane (0.14 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford two diastereoisomers of the title compound (0.111 and 0.107 g respectively, 90% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO'Bu, and 3 equiv of Et3SiH, 2,6-dimethylcyclohexane (0.14 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford two diastereoisomers of the title compound (0.118 and 0.114 g respectively, 97% yield). Meso trans/trans: ¹H NMR (400 MHz, CDCl₃) δ 3.61 (br s, 1H), 1.69–1.56 (m, 2H), 1.48–1.16 (m, 6H), 0.99 (t, 9H, J = 8.0 Hz), 0.88 (d, 6H, J = 6.0 Hz), 0.62 (q, 6H, J = 8.0 Hz); ¹C NMR (100 MHz, CDCl₃) δ 76.7, 38.4, 27.8, 26.2, 19.5, 7.2, 5.7; MS (EI), m/z 242 (M⁺). Elemental analysis calcd for C₁₁H₁₅OSi (242.47): C, 69.35; H, 12.47. Found: C, 69.29; H, 12.69. Meso cis/cis: ¹H NMR (400 MHz, CDCl₃) δ 2.78 (t, 1H, J = 9.2 Hz), 2.78–1.61 (m, 1H, J = 1.61–1.51 (m, 1H), 1.49–1.28 (m, 4H), 0.98 (s, 6H, J = 8.0 Hz) and 0.96 (d, 6H, J = 8.0 Hz) (15H), 0.64 (q, 6H, J = 8.0 Hz); ¹C NMR (100 MHz, CDCl₃) δ 83.8, 40.3, 34.6, 25.6, 19.7, 7.2, 5.7; MS (EI), m/z 242 (M⁺). Elemental analysis calcd for C₁₁H₁₅OSi (242.47): C, 69.35; H, 12.47. Found: C, 69.70; H, 12.76.

**Triethyl(2,2,6-trimethylcyclohexyl)silane** (Table 3, Entry 4). (A) Using the general procedure with ICy-HBF₄ and 20 mol % of NaO'Bu, 2,2,6,trimethylcyclohexane (0.14 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford two diastereoisomers of the title compound (0.094 and 0.142 g respectively, 92 % yield) as a colorless oil. DIA-1: ¹H NMR (400 MHz, CDCl₃) δ 3.24 (br s, 1H), 1.81–1.67 (m, 1H), 1.55–1.36 (m, 3H), 1.36–1.23 (m, 2H), 1.23–1.16 (m, 1H), 0.98 (t, 9H, J = 8.0 Hz), 0.87 (s) and 0.85 (d, J = 7.2 Hz) (9H), 0.62 (q, 6H, J = 8.0 Hz); ¹C NMR (400 MHz, CDCl₃) δ 80.8, 35.8, 33.1, 32.6, 29.0, 28.0, 25.0, 21.6, 19.4, 7.2, 5.7; MS (EI), m/z 256 (M⁺). Elemental analysis calcd for C₁₂H₁₇OSi (256.22): C, 70.24; H, 12.57. Found: C, 70.18; H, 12.68. DIA-2: ¹H NMR (400 MHz, CDCl₃) δ 2.90 (d, 1H, J = 9.6 Hz), 1.68–1.58 (m, 1H), 1.56–1.42 (m, 2H), 1.42–1.31 (m, 3H), 1.91–1.08 (m, 1H), 0.98 (t, 9H, J = 8.0 Hz), 0.91 (s) and 0.89 (d, J = 6.0 Hz) and 0.85 (s) (9H), 0.65 (q, 6H, J = 8.0 Hz); ¹C NMR (100 MHz, CDCl₃) δ 85.1, 40.0, 36.5, 35.2, 34.7, 30.5, 21.6, 20.1, 18.8, 7.2, 5.7; MS (EI), m/z 256 (M⁺). Elemental analysis calcd for C₁₂H₁₇OSi (256.22): C, 70.24; H, 12.57. Found: C, 70.00, H, 12.24.


(32) In the second fraction of the flash chromatography, two diastereoisomers were present but only the major one, the meso cis/cis, could be fully characterized. The presence of the cis/trans isomer as minor product was evidenced by the presence of a doublet of doublets at 2.92 ppm (J = 7.6, 4.0 Hz) in the ¹H NMR spectrum.
Hydrosilylation of Hindered and Functionalized Ketones

Triethyl(2,2,6,6-tetramethyltetrahydro-2H-pyran-endo,endo,exo,exo-diol)triethylsilane (Table 3, Entry 5). (A) Using the general procedure with Icy-HBF₄ and 20 mol % of NaOBu, 2,2,6,6-tetramethyltetrahydro-2H-pyran-endo,endo,exo,exo-diol (0.175 mL, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.244 g (90% yield) of the title compound as a colorless oil. (B) Using the general procedure with (Icy)CuCl, 12 mol % of NaOBut, and 3 equiv of Et₃SiH, 2,2,6,6-tetramethyltetrahydro-2H-pyran-endo,endo,exo,exo-diol (0.175 mL, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.224 g (99% yield) of the title compound as a colorless oil. (C) Using the general procedure with Icy-HBF₄ and 20 mol % of NaOBut, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography (pentane) to afford 0.257 g (96% yield) of the title compound as a colorless oil. (B) Using the general procedure with (Icy)CuCl, 12 mol % of NaOBut, and 3 equiv of Et₃SiH, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.194 g (99% yield) of the title compound as a colorless oil.

**Table 3, Entry 9.** Using the general procedure with Icy-HBF₄ and 20 mol % of NaOBut, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography (pentane) to afford 0.257 g (96% yield) of the title compound as a colorless oil. (B) Using the general procedure with (Icy)CuCl, 12 mol % of NaOBut, and 3 equiv of Et₃SiH, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.194 g (99% yield) of the title compound as a colorless oil.

**Table 3, Entry 9.** Using the general procedure with Icy-HBF₄ and 20 mol % of NaOBut, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography (pentane) to afford 0.257 g (96% yield) of the title compound as a colorless oil. (B) Using the general procedure with (Icy)CuCl, 12 mol % of NaOBut, and 3 equiv of Et₃SiH, t, poured+camphor (0.152 g, 1 mmol) was hydrodlsilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.194 g (99% yield) of the title compound as a colorless oil.
purified by flash chromatography on silica gel (pentane:EtO, 99:1) to afford 0.257 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy-CuCl, 12 mol % of NaOBut, and 3 equiv of Et3SiH, N-methylpyrroli-4-one (0.125 mL, 1 mmol) was hydro- silylated by triethylsilane. A colorless oil was obtained as a pure product after filtration (0.300 g, 96% yield). 1H NMR (400 MHz, CDCl3) δ 7.60 (d, 1H, J = 7.2 Hz), 7.10–7.45 (m, 7H), 7.06 (d, 1H, J = 7.2 Hz), 5.89 (s, 1H), 2.20 (s, 3H), 0.87 (t, 9H, J = 8.0 Hz), 0.56 (q, 6H, J = 8.0 Hz); 13C NMR (100 MHz, CDCl3) δ 144.1, 142.7, 134.7, 130.4, 128.0, 127.1, 127.0, 126.8, 126.7, 145.0, 132.8, 129.8, 126.0, 125.3, 67.3, 25.7, 18.7, 6.6, 4.6; MS (EI) m/z 311 (M+) . Elemental analysis calcd for C20H28OSi (312.52): C, 76.86; H, 10.46; N, 5.82. Found: C, 78.76; H, 10.93; N, 5.92.

2-(3-Diethylamino)propoxytriethylsilane (Table 5, Entry 2). (A) Using the general procedure with ICy-HBF4 and 20 mol % of NaOBut, 1-diethylaminopropan-2-one (0.155 mL, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.228 g (93% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy-CuCl, 12 mol % of NaOBut, and 3 equiv of Et3SiH, 1-diethylaminopropan-2-one (0.155 mL, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.203 g (94% yield) of the title compound as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 3.82 (sextuplet, 1H, J = 6.3 Hz), 2.68–2.56 (m, 5H), 2.35–2.20 (m, 1H), 1.17 (d, 3H, J = 6.3 Hz), 1.02–0.92 (m, 15H), 0.60 (q, 6H, J = 7.9 Hz); 13C NMR (100 MHz, CDCl3) δ 67.5, 61.7, 48.1, 22.5, 21.2, 12.0, 6.8, 4.9; MS (EI) m/z 245 (M+). Elemental analysis calcd for C13H21NOSi (245.48): C, 63.61; H, 12.73; N, 5.71. Found: C, 62.88; H, 11.65; N, 5.92.

1-(2-Chlorophenyl)ethoxy]triethylsilane (Table 5, Entry 3). (A) Using the general procedure with ICy-HBF4 and 20 mol % of NaOBut, 2-chloroacetophenone (0.13 mL, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 98:2) to afford 0.256 g (95% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy-CuCl, 12 mol % of NaOBut, and 3 equiv of Et3SiH, 2-chloroacetopheno- none (0.13 mL, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 98:2) to afford 0.262 g (97% yield) of the title compound as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.64 (d, 1H, J = 8.0 Hz), 7.26 (d, 1H, J = 8.0 Hz), 7.14 (t, 2H, J = 8.0 Hz), 5.24 (q, 1H, J = 6.4 Hz), 1.40 (d, 3H, J = 6.4 Hz), 0.91 (t, 9H, J = 7.9 Hz), 0.56 (q, 6H, J = 7.9 Hz); 13C NMR (100 MHz, CDCl3) δ 145.0, 132.8, 129.8, 126.4, 126.0, 125.3, 67.3, 25.7, 18.7, 6.6, 4.6; MS (EI) m/z 250 (M+). Elemental analysis calcd for C13H23BrOSi (315.32): C, 62.08; H, 8.56. Found: C, 62.43; H, 8.58.

1-(4-Bromophenyl)ethoxy]triethylsilane (Table 5, Entry 4). (A) Using the general procedure with ICy-HBF4 and 20 mol % of NaOBut, 4-bromooctacacetophenone (0.20 g, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 98:2) to afford 0.299 g (95% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy-CuCl, 12 mol % of NaOBut, and 3 equiv of Et3SiH, 4-bromooctaceto- none (0.20 g, 1 mmol) was hydro- silylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 98:2) to afford 0.314 g (99% yield) of the title compound as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.42 (d, 2H, J = 8.4 Hz), 7.21 (d, 2H, J = 8.4 Hz), 4.82 (q, 1H, J = 6.4 Hz), 1.39 (d, 3H, J = 6.4 Hz), 0.91 (t, 9H, J = 8.0 Hz), 0.57 (q, 6H, J = 8.0 Hz); 13C NMR (100 MHz, CDCl3) δ 146.0, 137.8, 131.2, 127.0, 69.9, 27.2, 6.7, 4.8; MS (EI) m/z 316 (M+), 314 (M`). Elemental analysis calcd for C13H23BrO2Si (316.39): C, 53.33; H, 7.48; Br, 9.41. Found: C, 52.98; H, 7.40.
none (0.15 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.221 g (72% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy/CuCl, 12 mol % of NaOBF₄, and 3 equiv of Et₂SiH, 2′-(trifluoromethyl)acetophenone (0.15 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.268 g (88% yield) of the title compound as a colorless oil. 1H NMR (400 MHz, CDCl₃) δ 7.66 (d, 1H, J = 7.8 Hz), 7.60–7.46 (m, 2H), 7.31 (t, 1H, J = 7.8 Hz), 2.95 (s, 6H), 1.49 (m, 4H), 1.43 (m, 3H), 1.34 (m, 3H). 13C NMR (100 MHz, CDCl₃) δ 150.9, 128.4, 125.9, 123.0 (q, J = 6.1 Hz), 111.7, 73.3 (q, J = 32 Hz), 40.3, 6.4, 4.5. Elemental analysis calcd for C₁₇H₂₄O₂Si (333.46): C, 75.63; H, 7.86; N, 4.20. Found: C, 58.96; H, 7.34.

[1-(4-Dimethylamino)phenyl]-2,2,2-trifluoroethyltriethylsilane (Table 5, Entry 6). (A) Using the general procedure with ICy-HBF₄ and 20 mol % of NaOBF₄, 4′-(dimethylamino)-2,2,2-trifluoroacetophenone (0.217 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.222 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy/CuCl, 12 mol % of NaOBF₄, and 3 equiv of Et₂SiH, 4′-(dimethylamino)-2,2,2-trifluoroacetophenone (0.217 g, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.320 g, 96% yield). 1H NMR (400 MHz, CDCl₃) δ 7.28 (d, 2H, J = 8.4 Hz), 7.68 (d, 2H, J = 8.8 Hz), 4.82 (q, 1H, J = 6.4 Hz), 2.95 (s, 6H), 0.90 (t, 9H, J = 8.0 Hz); 13C NMR (100 MHz, CDCl₃) δ 150.9, 128.4, 125.9, 123.0 (q, J = 6.1 Hz), 111.7, 73.3 (q, J = 32 Hz), 40.3, 6.4, 4.5. Elemental analysis calcd for C₁₇H₂₄O₂Si (333.46): C, 75.63; H, 7.86; N, 4.20. Found: C, 58.00; H, 8.01; N, 3.99.

[1-(4-Fluorophenyl)ethoxy]triethylsilane (Table 5, Entry 9). (A) Using the general procedure with ICy-HBF₄, and 20 mol % of NaOBF₄, 2-methoxycyclohexanone (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.220 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with ICy/CuCl, 12 mol % of NaOBF₄, and 3 equiv of Et₂SiH, 2-methoxycyclohexanone (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.222 g (92% yield) of the title compound as a colorless oil. 1H NMR (400 MHz, CDCl₃) δ 7.34 (d, 1H, J = 2.6 Hz), 6.34–6.24 (m, 1H), 6.18 (d, 1H, J = 2.6 Hz), 4.88 (q, 1H, J = 6.4 Hz), 1.50 (d, 3H, J = 6.4 Hz), 0.94 (t, 9H, J = 8.0 Hz), 0.61 (q, 6H, J = 8.0 Hz); 13C NMR (100 MHz, CDCl₃) δ 168.5, 148.3, 136.5, 121.6, 119.2, 71.8, 25.5, 6.7, 4.7. Elemental analysis calcd for C₁₂H₂₂O₂Si (262.14): C, 63.66; H, 9.80. Found: C, 63.62; H, 10.08.

[1-(4-Fluorophenyl)ethoxy]triethylsilane (Table 9, Entry 1). (A) Using the general procedure with SIMes-HBF₄, and 8 mol % of NaOBF₄, 2-acetylthiophene (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:EtO, 95:5) to afford 0.222 g (94% yield) of the title compound as a light yellow oil. 1H NMR (400 MHz, CDCl₃) δ 8.44 (d, 1H, J = 4.0 Hz), 7.72–7.63 (m, 1H), 7.51 (d, 1H, J = 8.0 Hz), 7.17–7.06 (m, 1H), 4.92 (q, 1H, J = 6.4 Hz), 1.44 (d, 3H, J = 6.4 Hz), 0.89 (t, 9H, J = 8.0 Hz), 0.51 (q, 6H, J = 8.0 Hz); 13C NMR (100 MHz, CDCl₃) δ 165.8, 148.3, 136.5, 121.6, 119.2, 71.8, 25.5, 6.7, 4.7. Elemental analysis calcd for C₁₁H₂₄O₂Si (216.39): C, 61.05; H, 11.18. Found: C, 60.96; H, 11.31.
(A) Using the general procedure with SIMes·HBF₄ and 12 mol % of NaOBu, 2-acetyl-N-methylpiperidine (0.12 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.232 g (97% yield) of the title compound as a colorless oil. (B) Using the general procedure with (SIMes)CuCl, 8 mol % of NaOBu, and 2 equiv of Et₃SiH, 2-acetyl-N-methylpiperidine (0.12 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.222 g (93% yield) of the title compound as a colorless oil.

**1H NMR (400 MHz, CDCl₃)**: δ 6.52 (d, 1H, J = 4.4 Hz), 6.06–5.91 (m, 2H), 4.95 (q, 1H, J = 6.4 Hz), 3.68 (s, 3H), 1.54 (d, 3H, J = 6.4 Hz), 0.91 (t, 9H, J = 8.0 Hz), 0.55 (q, 6H, J = 8.0 Hz);

**13C NMR (100 MHz, CDCl₃)**: δ 135.8, 122.6, 106.2, 106.0, 64.4, 34.4, 23.9, 6.8, 5.0. Elemental analysis calcd for C₁₁H₁₆NOSi (239.43): C, 65.21; H, 10.52; N, 5.85. Found: C, 65.42; H, 10.69; N, 5.92.

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**Supporting Information Available:** Crystallographic information files (CIF) of complexes 1–3. This material is available free of charge via the Internet at http://pubs.acs.org. These files also have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 264856–264858.

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