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

Silvia Díez-González, Harneet Kaur, Fabiano Kauer Zinn, Edwin D. Stevens, and Steven P. Nolan*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

snolan@uno.edu

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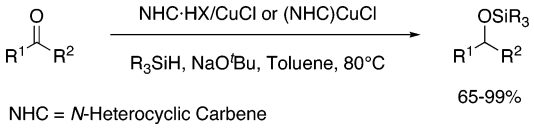

The catalytic hydrosilylation of highly hindered and functionalized ketones is described. The combination of inexpensive catalyst precursors, CuCl and NHC·HX (NHC = *N*-heterocyclic carbene), leads to a highly efficient reduction mediator for the preparation of silyl ethers from unfunctionalized and 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-

(1) (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*; Wiley-Interscience: New York, 2001. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Kluwer Academic/Plenum: New York, 2001.

(2) (a) Ojima, I. In *The Hydrosilylation Reaction*: *The Chemistry of Organosilicon Compounds*; Patai, S., Rapaport, Z., Eds.; Wiley: New York, 1989; p 1479. (b) Ojima, I.; Li, Z.; Zhu, J. In *Recent Advances in the Hydrosilylation Reaction*: *Chemistry of Organic Silicon Compounds*; Rappaport, Z., Apetorg, Y., Eds: Wiley: New York, 1998; Vol. 2, p 1687.

(3) (a) Carter, M. B.; Schiott, B.; Gutierrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667−11670. (b) Inma, H.; Mori, M.; Nakai, T. *Synlett* **1996**, 1229−1230. (c) Rahimian, K.; Harrod, J. F. *Inorg. Chim. Acta* **1998**, *270*, 330−336. (d) Yun, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5640−5644.

(4) (a) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846−848. (b) Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 111−113. (c) Sudo, A.; Yoshida, H.; Saigo, K. *Tetrahedron*: *Asymmetry* **1997**, *8*, 3205−3208. (d) Ini, S.; Oliver, A. G.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2001**, *20*, 3839−3841. (e) Tao, B.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3892−3894. (f) Reyes, C.; Prock, A.; Giering, W. P. *Organometallics* **2002**, *21*, 546−554.

(5) (a) Zhu, G.; Terry, M.; Zhang, X. *J. Organomet. Chem.* **1997**, *547*, 97−101. (b) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1998**, *17*, 3420−3422. (c) Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749−1751. (d) Hashimoto, H.; Aratani, I.; Kabuto, C.; Kira, M. *Organometallics* **2003**, *22*, 2199−2201.

(6) (a) Saito, M.; Nishibayashi, Y.; Uemura, S. *Organometallics* **2004**, *23*, 4012−4017. (b) Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486−5487. (c) Kinting, A.; Krenzfeld, H.-J.; Abicht, H.-P. *J. Organomet. Chem.* **1989**, *370*, 343−349.

(7) Shibagaki, M.; Takahshi, K.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3283−3288.

(8) (a) Caycho, J. R.; Tellado, F. G.; Aramas, P.; Juan, J.; Tellado, M. *Tetrahedron Lett.* **1997**, *38*, 277−280. (b) Yakabe, S.; Hirano, M.; Morimoto, T. *Can. J. Chem.* **1998**, *76*, 1916−1921.

(9) Chen, J.-X.; Daeuble, J. F.; Stryker, J. M. *Tetrahedron* **2000**, *56*, 2789−2798. For more details, see also: (a) Daeuble, J. F.; Stryker, J. M. *Catalysis of Organic Reactions*; Scaros, M. G., Prunier, M. L., Eds.; Marcel Dekker: New York, 1995; pp 235−247. (b) Lipshutz, B. H.; Chrisman, W.; Noson, K. *J. Organomet. Chem.* **2001**, *624*, 367−371. (c) Chen, J.-X.; Daeuble, J. F.; Brestensky, D. M.; Stryker, J. M. *Tetrahedron* **2000**, *56*, 2153−2166. (d) Mahoney, W. S.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8818−8823.

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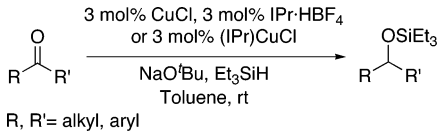
SCHEME 1. Hydrosilylation of Simple Ketones



sively studied.[11] Therefore, the development of efficient and general catalytic methods for the reduction of hindered and functionalized carbonyl compounds is highly desirable.

In the last 10 years, *N*-heterocyclic carbenes (NHC) have emerged as efficient ligands in metal-mediated reactions.[12] Compared to tertiary phosphines, the NHC ligands have a stronger interaction with the metal center, thereby minimizing ligand dissociation. In addition, their significant steric bulk results in metal−NHC complexes having unique catalytic behavior.[13]

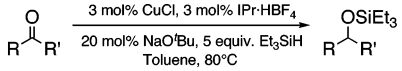
We and others[14] have recently reported the reduction of carbonyl compounds (simple or α,β-unsaturated) catalyzed by either Cu(I)Cl and a NHC salt or well-defined complexes such as (IPr)CuCl (IPr = (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol)-2-ylidene) (Scheme 1).

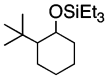
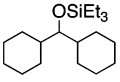
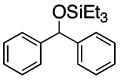
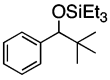
We now wish to report on a related catalytic system that is highly efficient in the hydrosilylation of hindered or functionalized alkyl, cyclic, bicyclic, aromatic, and heteroaromatic ketones.

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 diastero-directing ligand (Table 1, entries 3 and 4).

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



entry	product	time (h)	yield (%)[a] *dr*[b]
1		3	(87)
2		10	84 (74)[c]
3		7	92 (74) *25 : 25: 50*[d]
4		21	93 (79)[c] *75 : 25*[e]
5		1	100 (99)
6		4	100 (99)
7		8	100 (99)
8		20	100 (87)

[a] GC conversions (isolated yields) are the average of two runs. [b] See text for discussion. [c] Reaction at 100 °C. [d] *Meso* trans/trans:cis/trans:*meso* cis/cis. [e] Cis:trans.

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 formed 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 dicyclohexyl ketone is illustrated in Table 2. ICy·HBF_4 was found to be the most efficient ligand. The bulkiest

(10) (a) Lipshutz, B. H.; Noson, K.; Chrisman, W. *J. Am. Chem. Soc.* **2001**, *123*, 12917−12918. (b) Lipshutz, B. H.; Noson, K.; Chrisman, W.; Lower, A. *J. Am. Chem. Soc.* **2003**, *125*, 8779−8789. (c) Lipshutz, B. H.; Servesko, J. M. *Angew. Chem., Int. Ed.* **2003**, *41*, 4789−4792. (d) Lipshutz, B. H.; Caires, C. C.; Kuipers, P.; Chrisman, W. *Org. Lett.* **2003**, *5*, 3085−3088. (e) Lipshutz, B. H.; Servesko, J. M.; Petersen, T. B.; Papa, P. P.; Lover, A. A. *Org. Lett.* **2004**, *6*, 1273−1275.

(11) For selected examples of non-metal-catalyzed reduction of functionalized ketones see: (a) Yatagai, M.; Ohnuki, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, *6*, 1826−1828. (b) Ridley, D. D.; Stramow, M. *J. Chem. Soc., Chem. Commun.* **1975**, *10*, 400.

(12) For selected examples see: (a) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194−16195. (b) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 4053−4056. (c) Lee, C. W.; Choi, T.-L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 3224−3225. (d) Herrmann, W. A.; Bohm, V. P. W.; Gstottmayr, C. W. K.; Grosche, M.; Reisinger, C. P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*, 616−628. (e) Frenzel, U.; Weskamp, T.; Kohl, J. F.; Schattenman, W. C.; Nuyken, O.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *586*, 563−265.

(13) For reviews about NHC see: (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2162−2187. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, 100, 39−91. (c) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913−921.

(14) (a) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157−1160. (b) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417−2420.

(15) For more details, see the Experimental Section.

(16) Raban, M.; Lauderback, S. K.; Kost, D. *J. Am. Chem. Soc.* **1975**, *97*, 5178−5183.

(17) Fort, Y.; Feghouli, A.; Vanderesse, R.; Caubère, P. *J. Org. Chem.* **1990**, *55*, 5911−5915 and references herein.

(18) Felföldi, K.; Kapocsi, K.; Bartók, M. *J. Organomet. Chem.* **1989**, *362*, 411−415.

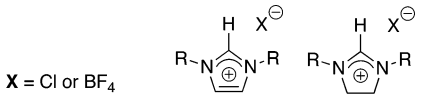
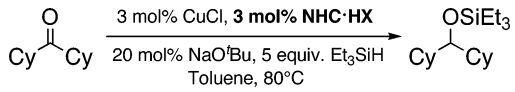


FIGURE 1. Structures of saturated and unsaturated NHC salts.

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



entry	NHC·HX	conversion after 1 h[a]	max conversion (time)[a]
1	IPr·HBF_4	20	100 (4 h)
2	IPr·HCl	2	79 (24 h)
3	SIPr·HBF_4	0	13 (24 h)
4	SIPr·HCl	0	8 (20 h)
5	IMes·HBF_4	11	100 (7 h)
6	IMes·HCl	82	100 (1.5 h)
7	SIMes·HBF_4	30	100 (4 h)
8	ICy·HBF_4	100	100 (1 h)
9	IAd·HBF_4	35	100 (3 h)
10	IAd·HCl	18	100 (5 h)
11	ItBu·HBF_4	33	100 (3.5 h)

[a] GC conversions (%) are the average of at least two runs.

carbene salts (IAd·HX and ItBu·HBF_4) yielded the hydrosilylated product in good reaction times (3−5 h, Table 2, entries 9−11), which let us presume that electronic effects rather that steric effects may be the determinant feature in this reaction. As electronic factors governing NHC ligands are not yet fully understood,[19] it is hard to rationalize the screening results. The hexameric complex $[(PPh_3)CuH]_6$, known as an excellent reagent for conducting reductions of carbonyl compounds,[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.

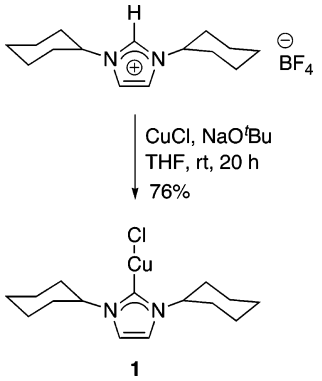
The influence of the copper source on the reaction under conditions described in Table 2 was investigated. Similar results were obtained with CuCl and CuBr, but CuI required longer reaction times (4 h). Cu(II) salts such as $CuCl_2$ and $Cu(OAc)_2$ were also screened. Interestingly, the latter afforded 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 incomplete 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, Et_3SiH 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 NaO^{t}Bu and 5 equiv of Et_3SiH, 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·HBF_4 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.[14a] Under the same conditions, the synthesis of (ICy)CuCl (**1**) was achieved in good yield (Scheme 2).[20]

SCHEME 2. Synthesis of (ICy)CuCl



1

The structure of this complex was elucidated by single-crystal diffraction from suitable crystals grown from a CH_2Cl_2/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−C1 bond length (1.925 Å) is comparable to known Cu−C bonds in carbene complexes.[21]

Optimization studies carried out with the well-defined catalyst resulted in a reduced loading of base (NaO^{t}Bu, 12 mol %) and silane (Et_3SiH, 3 equiv) as compared with the *in situ* generated catalytic system.

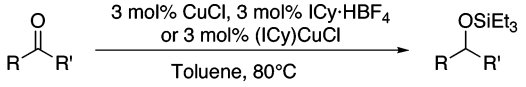
A number of dialkyl ketones with varying steric congestion around the carbonyl bond could be hydrosilylated efficiently with the *in situ* system or the well-defined catalyst as illustrated in Table 3. Even highly

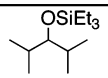
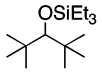
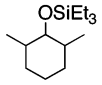
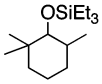
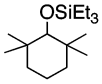
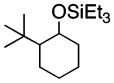
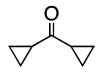
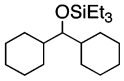
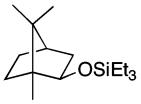
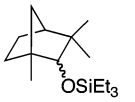
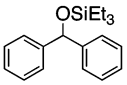
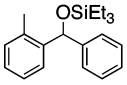
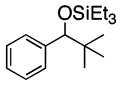
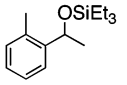
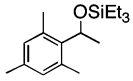
(19) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485−2495.

(20) For details of other copper complexes, see: (a) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191−1193. (b) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 3369−3371.

(21) For example, Arnold has reported a bond length of 1.960 Å in copper complexes with chelating alkoxy-*N*-heterocyclic carbenes: Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340−2341.

TABLE 3. Hydrosilylation of Hindered Ketones Mediated by CuCl/ICy·HBF$_4$ or (ICy)CuCl



		in situ[a]		well-defined[b]	
entry	product	time (h)	yield[c] (%) *dr*	time (h)	yield[c] (%) *dr*
1		1	(96)	0.5	(94)
2		12	98 (92)	9	96 (92)
3		2	100 (90) *49/49/2*	1.5	98 (97) *49/49/2*
4		3.5	98 (92) *60/40*	1.5	96 (93) *60/40*
5		24	95 (90)	9	92 (90)
6		5	100 (99.5) *50/50*	2.5	99 (92) *50/50*
7		1	95 (94)	0.15	100 (99)
8		1	100 (99)	0.5	100 (99)
9		5	99 (96) ≥ *95/5*	4	98 (91) ≥ *95/5*
10		8	99 (96) *90/10*	6.5	98 (93) *90/10*
11		0.5	100 (99)	0.25	100 (99)
12		3.5	98 (92)	3	99 (96)
13		1	100 (99)	0.5	100 (97)
14		0.5	99 (94)	0.5	100 (96)
15		24	80 (75)	18	85 (80)

[a] 20 mol % of NaO^{t}Bu, 5 equiv of Et$_3$SiH. [b] 12 mol % of NaO^{t}Bu, 3 equiv of Et$_3$SiH. [c] GC conversions (isolated yields) are the average of two runs.

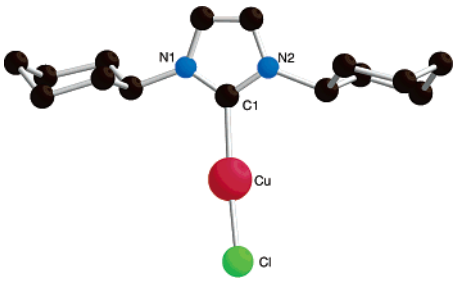
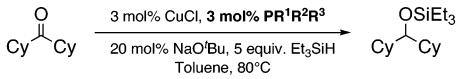


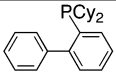
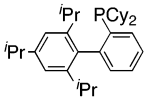
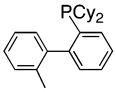
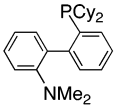
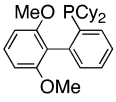
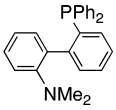
FIGURE 2. Ball-and-stick drawing for (ICy)CuCl (**1**). Selected bond lengths (Å): C1−Cu = 2.114(11), Cu−Cl = 2.136(4). Selected bond angle (deg): C1−Cu−Cl = 170.6(3). Hydrogens are omitted for clarity.

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 diastereoismers, 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 IPr·HBF$_4$ 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-

(22) Boone, J. R.; Ashby, E. C. *Top. Stereochem.* **1979**, *2*, 53−95.

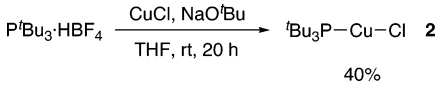
TABLE 4. Biphenylphosphine Screening for the Hydrosilylation of Dicyclohexyl Ketone



entry	phosphine	time (h)	yield (%)[a]	^{31}P NMR[b]
1		5	7	P: -9.86
		24	31 (26)	[Cu]: 6.34
2		5	1	P: -7.85
		24	4	[Cu]: 11.25
3		5	2	P: -10.59
		24	23 (18)	[Cu]: 2.11
4		5	1	P: -5.47
		24	15	[Cu]: 13.14
5		5	8	P: -5.04
		24	14	[Cu]: 12.61
6		5	0	P: -9.43
		24	0	[Cu]: --

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

SCHEME 3. Synthesis of (^{t}Bu$_3$P)CuCl



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.

As NHCs have been traditionally considered "phosphine-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 triisopropylbiphenylphosphine (Table 4, entry 2), which was only partially converted into the corresponding copper complex. However, low conversions in silylated ether were obtained and the dicyclohexyl ketone was recovered after the reaction. These facts suggest that the in situ formed complexes may have low catalytic activity under these conditions. Increasing the σ-donor effect (Table 4, entries 2 and 3) or the π-donor effect of the phosphine (Table 4, entries 4 and 5) did not lead to more efficient reactions. No reaction took place when di-*tert*-butylphosphines (biphenyl, 2-methylbiphenyl, 1,1′-binaphthyl, or 2′-(*N*,*N*-dimethylamino)biphenyl) were used, even if the quantitative formation of the corresponding complexes was observed by ^{31}P NMR.[24] This fact, along with the low reaction rates obtained in the other examples suggest that steric bulk might dictate the reactivity of the complex toward the ketone. As no complex was formed in the case of a diphenylphosphine (Table 4, entry 6), the electronic aspects may have an important influence in the formation of the complexes. It is of note that in all examples, when dicyclopropyl ketone was used as starting material, no conversion was observed even after long reaction times (24−48 h) with biphenylphosphine ligands.

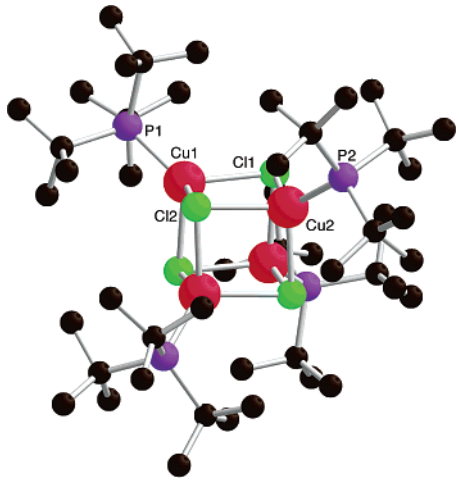


FIGURE 3. Ball-and-sick drawing for [(*t*-Bu$_3$P)CuCl]$_4$ (**2**). Selected bond lengths (Å): P1−Cu1 = 2.2005(8), P2−Cu2 = 2.2027(8), Cu1−Cl1 = 2.4265(8), Cu1−Cl2 = 2.4224(8), Cu2−Cl1 = 2.4668(8), Cu2−Cl2 = 2.4346(8). Selected bond angles (deg): P1−Cu1−Cl1 = 123.78(3), P1−Cu1−Cl2 = 123.07(3), Cl2−Cu1−Cl1 = 93.84(3), P2−Cu2−Cl2 = 124.68(3), P2−Cu2−Cl1 = 121.22(3), Cl2−Cu2−Cl1 = 93.87(3). Hydrogens are omitted for clarity.

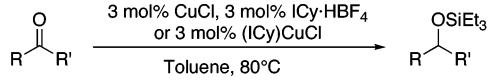
Triaryl- and trialkylphosphines were also tested under these conditions. PPh$_3$ did not yield any product after 12 h. Low conversions were observed with PEt$_3$ and P^{t}Bu$_3$·HBF$_4$ (10% and 40% after 12 h). The best results were obtained with P^{i}Pr$_3$ and PCy$_3$, 98% of conversion after 12 h.

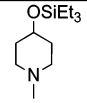
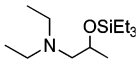
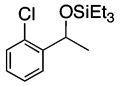
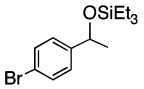
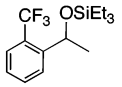
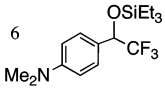
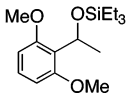
All attempts to synthesize Cu(I) well-defined complexes with P^{i}Pr$_3$ or PCy$_3$ failed. Nevertheless, we were able to prepare a (^{t}Bu$_3$P)CuCl complex under the reaction conditions described for the synthesis of (ICy)CuCl although in a considerably lower yield (Scheme 3).

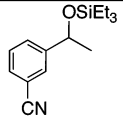
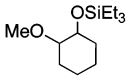
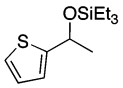
(23) Stothers, J. B.; Tan C. T.; Teo, K. C. *Can. J. Chem.* **1976**, *54*, 1211−1221.

(24) ^{31}P NMR (P = free phosphine, [Cu] = copper−phosphine complex): (a) 2-di-*tert*-butylphosphino-biphenyl, P: 39.58, [Cu]: 21.38. (b) 2-di-*tert*-butylphosphino-2′-methyldiphenyl, P: 23.89, [Cu]: 130.79. (c) racemic-2-di-*tert*-butylphosphino-1,1′-dinaphthyl, P: 24.48, [Cu]: 36.45. (d) 2-di-*tert*-butylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl, P: 28.29, [Cu]: 39.64.

TABLE 5. Hydrosilylation of Functionalized Ketones with CuCl/ICy·HBF$_4$ or (ICy)CuCl



		in situ[a]		well-defined[b]	
entry	product	time (h)	yield (%)[c]	time (h)	yield (%)[c]
1		2	100 (92)	1	100 (93)
2		3	99 (93)	2	98 (94)
3		1.5	100 (95)	1.5	100 (97)
4		1.5	100 (95)	1	100 (99)
5		3	81 (72)	2	90 (88)
6		1.5	100 (93)	1	100 (96)
7		27	60	–	–

		in situ[a]		well-defined[b]	
entry	product	time (h)	yield [c] (%)	time (h)	yield (%)[c]
8		24	0	–	–
9		1	100 (95)	0.5	100 (94)
10		6	86 (57)	4	98 (65)
11		24	0	–	–
12		20	98	–	–
13		24	0	–	–

[a] 20 mol % of NaO^{t}Bu, 5 equiv of Et$_3$SiH. [b] 12 mol % of NaO^{t}Bu, 3 equiv of Et$_3$SiH. [c] GC conversions (isolated yields) are the average of two runs.

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*-Bu$_3$P)CuCl]$_4$ (**2**) 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−copper complex, may explain its lack of reactivity toward hydrosilylation.

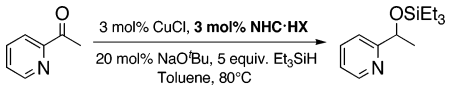
We have shown that, in the present system, NHCs are more efficient ligands in the hydrosilylation of ketones than the tested tertiary phosphines. We suspect that their specific shape may protect and stabilize the metal center facilitating the coordination of the substrate.

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-

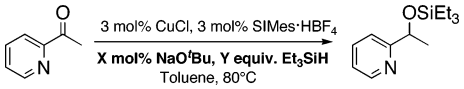
(25) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2041−2047.

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



entry	NHC·HX	conversion after 3 h[a]	max conversion[a] (time)
1	IPr·HBF$_4$	20	90 (24 h)
2	IPr·HCl	3	100 (72 h)
3	SIPr·HBF$_4$	0	60 (20 h)
4	SIPr·HCl	0	15 (29 h)
5	IMes·HBF$_4$	56	98 (4.5 h)
6	IMes·HCl	42	100 (6.5 h)
7	SIMes·HBF$_4$	100	100 (3 h)
8	ICy·HBF$_4$	40	98 (8 h)
9	IAd·HBF$_4$	27	100 (9 h)
10	IAd·HCl	35	100 (8 h)

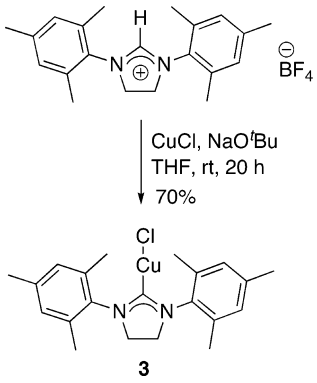
TABLE 7. Optimization of Hydrosilylation with CuCl/SIMes·HBF$_4$ Catalyst



entry	mol % of NaO^{t}Bu	equiv of Et$_3$SiH	time (h)	GC conversion (%)[a]
1	20	5	3	100
2	12	5	2	100
3	8	5	1	100
4	3	5	24	0
5	12	3	6	100
6	20	3	3.5	100

[a] GC conversions are the average of at least two runs.

SCHEME 4. Synthesis of (SIMes)CuCl



3

azolium salts in the hydrosilylation of the 2-acetylpyridine was studied. The results are presented in Table 6. In this case, SIMes·HBF$_4$ turned out to be the best ligand precursor for the hydrosilylation of 2-acetylpyridine by Et$_3$SiH. It is of note that IMes·HBF$_4$ and IMes·HCl also lead to interesting conversions but longer reaction times are required.

(26) (a) Wishka, D. G.; Graber, D. R.; Seest, E. P.; Dolak, F. H.; Watt, W.; Morris, J. *J. Org. Chem.* **1998**, *63*, 7851−7859. (b) Deeter, J.; Frazier, J.; Staten, G.; Staszak, M.; Weigel, L. *Tetrahedron Lett.* **1990**, *31*, 7101−7104. (c) Labelle, M.; Belley, M.; Gareau, Y.; Gauthier, J. Y.; Guay, D.; Gordon, R.; Grossman, S. G.; Jones, T. R.; Leblanc, Y.; McAuliffe, M.; McFarlane, C.; Masson, P.; Metters, K. M.; Ouimet, N.; Patrick, D. H.; Piechuta, H.; Rochette, C.; Sawyer, N.; Xiang, Y. B.; Pickett, C. B.; Ford-Hutchinson, A. W.; Zamboni, R. J.; Young, R. N. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 283−288.

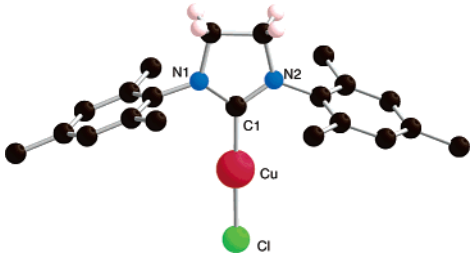
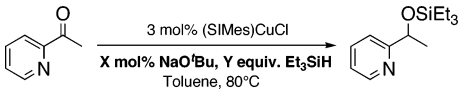


FIGURE 4. Ball-and-stick drawing for (SIMes)CuCl (**3**). Selected bond lengths (Å): C1−Cu = 1.882(4), Cu−Cl = 2.099(11). Selected bond angle (deg): C1−Cu−Cl = 178.48(13). Hydrogens are omitted for clarity but for the imidazolium ring.

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



entry	*X* mol % of NaO^{t}Bu	*Y* equiv of Et$_3$SiH	time (h)	GC conversion (%)[a]
1	12	5	1.5	100
2	8	5	1	100
3	3	5	0.5	100
4	0	5	24	0
5	3	3	0.5	100
6	3	2	0.5	100
7	3	1	18	0

[a] GC conversions are the average of at least two runs.

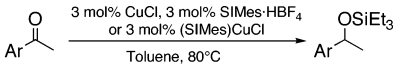
Base and hydrosilane loading optimization showed surprising results. Not only did lower base loadings not require longer reaction times but complete conversion was reached in only 1 h when 8 mol % of NaO^{t}Bu was used (Table 7). When less that 5 equiv of hydrosilane was used, the reaction still reached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

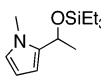
Such results led us to synthesize a well-defined copper(I) chloride complex bearing a SIMes ligand to compare its activity to the *in situ* system. The protocol employed for the preparation of (ICy)CuCl (**1**) was successful and afforded the expected (SIMes)CuCl (**3**) in good yield (Scheme 4).

The structure of **3** was elucidated by single-crystal diffraction from suitable crystals grown from a CH_2Cl_2/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·HBF$_4$, 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^{t}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 9. Hydrosilylation of Heteroaromatic Ketones



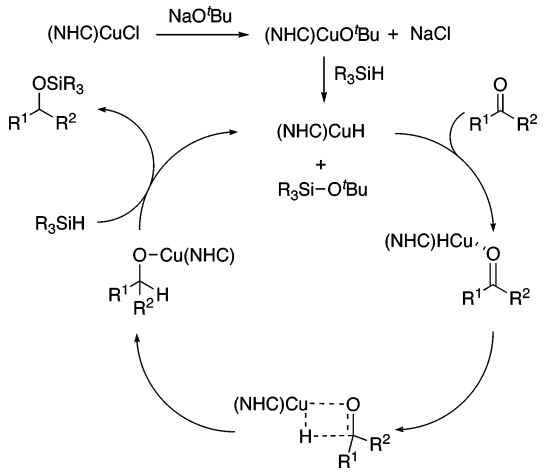
		IN SITU[a]		WELL-DEFINED[b]	
entry	product	time (h)	yield (%)[c]	time (h)	yield (%)[c]
1		1	100 (94)	0.5	100 (94)
2		1.5	100 (92)	0.5	100 (94)
3		2	100 (98)	0.5	100 (97)
4		3[d]	100 (91)	4.5[e]	100 (95)
5		6[d]	100 (97)	7[e]	100 (93)

[a] 8 mol % of NaO^{t}Bu, 5 equiv of Et_3SiH. [b] 3 mol % of NaO^{t}Bu, 2 equiv of Et_3SiH. [c] GC conversions (isolated yields) are the average of two runs. [d] 12 mol % of NaO^{t}Bu. [e] 8 mol % of NaO^{t}Bu.

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-acetylthiazole 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 asymmetric 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-acetylthiophene or 2-acetyl-1-methylpyperidine 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)CuO^{t}Bu from (NHC)CuCl and NaO^{t}Bu occurs. This step has been confirmed as formation of (NHC)copper alkoxide complexes under these conditions has been observed by ^{1}H NMR.[20b] It is then postulated that the active catalyst, a NHC copper hydride species, is formed by a σ-bond metathesis between the (NHC)CuO^{t}Bu and the hydrosilane. Addition of hydride to the carbonyl carbon would result in a copper alkoxide that would undergo another σ-bond metathesis[28] 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.

SCHEME 5. Proposed Mechanism for the Copper-Catalyzed Hydrosilylation of Ketones



Conclusions

In summary, a reagent prepared *in situ* from substoichiometric 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·HBF_4 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 O_2. 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). ^{1}H NMR and ^{13}C NMR spectra were

(27) Lipshutz, B. H.; Lower, A.; Noson, K. *Org. Lett.* **2002**, *4*, 4045−4548.

(28) Lorenz, C.; Schubert, U. *Chem. Ber.* **1995**, *128*, 1267−1269.

(29) (a) Pagenkopf, B. L.; Krüger, J.; Stojanovic, A.; Carreira, E. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3124−3126. (b) Moritami, Y.; Appella, D. H.; Jurkauskas, V.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 6797−6798. (c) Yun, J.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 1129−1131.

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 PR_3). The procedure provided in ref 14a was used for the synthesis of the complexes.

(ICy)CuCl (1). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, acetone-d_6) δ 174.2, 119.5, 62.1, 35.4, 26.3, 25.8. Elemental analysis calcd for $C_{15}H_{24}CuClN_2$ (331.17): C, 54.37; H, 7.30; N, 8.45. Found: C, 54.26; H, 7.00; N, 8.15.

[(^{t}Bu$_3$P)CuCl]$_4$ (2). ^{31}P (160 MHz, d_8-THF) δ 63.5. Elemental analysis calcd for $C_{12}H_{27}ClCuP$ (301.32): C, 47.83; H, 9.03. Found: C, 47.96; H, 9.24.

(SIMes)CuCl (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 4H), 3.96 (s, 4H), 2.32 (s, 12H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 138.7, 135.3, 135.0, 129.7, 50.9, 21.0, 18.0. Elemental analysis calcd for $C_{21}H_{26}CuClN_2$ (405.44): C, 62.21; H, 6.46; N, 6.91. Found: C, 62.60; H, 6.52; N, 6.80.

General Procedure A for the Hydrosilylation of Ketones (*in situ* system). In an oven-dried vial fitted with a septum screw cap, copper(I) chloride (3 mg, 0.03 mmol, 3 mol %), the imidazolium salt (9.6 mg if ICy·HBF_4 or 11.8 mg if SIMes·HBF_4, 0.03 mmol, 3 mol %), and sodium *tert*-butoxide (8−20 mol %) were charged inside a glovebox and stirred in dry toluene (2 mL) at 80°C outside of the glovebox for 10 min before triethylsilane (0.8 mL, 5 mmol, 5 equiv) was added through the septum with a syringe. After 20 min more of stirring, the ketone (1 mmol) was added. When the ketone was a solid, it was added as a solution in toluene. The reaction was allowed to proceed at 80°C and monitored by GC. After consumption of the starting ketone or no further conversion, the reaction mixture was allowed to cool to room temperature, opened to air, and filtered through a plug of active charcoal and Celite with ethyl acetate as solvent. The organic phase was concentrated in vacuo and the purity of the residue checked on GC and ^{1}H NMR. Flash chromatography was then performed unless crude product was estimated to be greater than 95% pure.

General Procedure B for the Hydrosilylation of Ketones (well-defined catalyst). The procedure described above was used with (NHC)CuCl (10 mg if (ICy)CuCl or 12 mg if (SIMes)CuCl, 0.03 mmol, 3 mol %), sodium *tert*-butoxide (3−12 mol %), and triethylsilane (2−3 equiv) for 1 mmol of starting ketone.

(1-Isopropyl-2-methylpropoxy)triethylsilane (Table 3, Enty 1). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,4-dimethylpentanone (0.14 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.218 g, 96% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,4-dimethylpentanone (0.14 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.217 g (94% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[31]

(1-*tert*-Butyl-2,2-dimethylpropoxy)triethylsilane (Table 3, Entry 2). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,2,4,4-tetramethylpentanone (0.175 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.237 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,2,4,4-tetramethylpentanone (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. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (s, 1H), 0.99 (t, J = 8.0 Hz) and 0.97 (s) (27H), 0.66 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 87.8, 37.8, 29.2, 7.3, 5.9; MS (EI), *m/z* 258 (M^+). Elemental analysis calcd for $C_{15}H_{34}OSi$ (268.51): C, 69.69; H, 13.26. Found: C, 69.92; H, 13.61.

(2,6-Dimethylcyclohexyloxy)triethylsilane (Table 3, Entry 3). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,6-dimethylcyclohexanone (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).[32] (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,6-dimethylcyclohexanone (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).[32] *Meso* trans/trans: ^{1}H NMR (400 MHz, $CDCl_3$) 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 Hz), 0.62 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{14}H_{30}OSi$ (242.47): C, 69.35; H, 12.47. Found: C, 69.29; H, 12.69. *Meso* cis/cis: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (t, 1H, J = 9.2 Hz), 2.78−1.61 (m, 1H), 1.61−1.51 (m, 1H), 1.49−1.28 (m, 4H), 0.98 (t, J = 8.0 Hz) and 0.96 (d, 6H, J = 8.0 Hz) (15H), 0.64 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{14}H_{30}OSi$ (242.47): C, 69.35; H, 12.47. Found: C, 69.70; H, 12.76.

Triethyl(2,2,6-trimethylcyclohexyloxy)silane (Table 3, Entry 4). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,2,6-trimethylcyclohexanone (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. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,2,6-trimethylcyclohexanone (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 (0.095 and 0.143 g respectively, 93% yield) as a colorless oil. DIA-1: ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (400 MHz, $CDCl_3$) 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 $C_{15}H_{32}OSi$ (256.22): C, 70.24; H, 12.57. Found: C, 0.70.18; H, 12.68. DIA-2: ^{1}H NMR (400 MHz, $CDCl_3$) 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), 1.31−1.08 (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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{32}OSi$ (256.22): C, 70.24; H, 12.57. Found: C, 70.00, H, 12.24.

(30) (a) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534. (b) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363. (c) Arnold, P. L.; Cloke, F. G. N.; Geldbach, T.; Hitchcock, P. B. *Organometallics* **1999**, *18*, 3228−3233 (d) Arduengo, A. J.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, *116*, 4391−4393. (e) Arduengo, A. J.; Davidson, F.; Kraftczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375−3382.

(31) Barden, J.; Fleming, J. *Chem. Commun.* **2001**, *22*, 2366−2367.

(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 3.29 ppm (J = 7.6, 4.0 Hz) in the ^{1}H NMR spectrum.

Triethyl(2,2,6,6-tetramethylcyclohexyloxy)silane (Table 3, Entry 5). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,2,6,6-tetramethylcyclohexanone (0.175 mL, 1 mmol) was hydrosilylated 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,2,6,6-tetramethylcyclohexanone (0.175 mL, 1 mmol) was hydrosilylated 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. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 1H), 1.58−1.38 (m, 3H), 1.34−1.22 (m, 1H), 1.20−1.09 (m, 2H), 0.99 (t, 9H, J = 8.0 Hz), 0.885 (s) and 0.878 (s) (12H), 0.66 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.7, 40.2, 36.6, 33.0, 20.2, 18.6, 7.3, 5.8; MS (EI) *m/z* 270 (M^+). Elemental analysis calcd for $C_{16}H_{34}OSi$ (270.53): C, 71.04; H, 12.67. Found: C, 71.15; H, 12.88.

(2-*tert*-Butylcyclohexyloxy)triethylsilane (Table 3, Entry 6). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2-*tert*-butylcyclohexanone (0.175 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 (0.146 and 0.122 g respectively, 99.5% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2-*tert*-butylcyclohexanone (0.175 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 (0.136 and 0.113 g respectively, 92% yield). Cis diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (br s, 1H), 1.79−1.66 (m, 2H), 1.65−1.50 (m, 3H), 1.50−1.23 (m, 3H), 1.20−0.98 (m, 1H), 0.96 (t, 9H, J = 8.0 Hz), 0.94 (s, 9H), 0.64 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 68.8, 52.5, 35.6, 32.6, 28.5, 27.3, 21.6, 20.4, 7.1, 5.5; MS (IE) *m/z* 270 (M^+). Elemental analysis calcd for $C_{16}H_{34}OSi$ (270.53): C, 71.04; H, 12.67. Found: C, 70.71; H, 13.00. Trans diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (dt, 1H, J = 9.8, 4.3 Hz), 1.93−1.84 (m, 1H), 1.82−1.70 (m, 1H), 1.70−1.56 (m, 2H), 1.41−1.22 (m, 2H), 1.22−1.07 (m, 3H), 0.96 (t, J = 8.0 Hz) and 0.95 (s) (18H), 0.62 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.7, 53.3, 37.6, 32.9, 29.3, 26.7, 26.2, 25.1, 7.1, 5.7; MS (IE) *m/z* 270 (M^+). Elemental analysis calcd for $C_{16}H_{34}OSi$ (270.53): C, 71.04; H, 12.67. Found: C, 71.20; H, 12.36.

(Dicyclopropylmethoxy)triethylsilane (Table 3, Entry 7). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, dicyclopropyl ketone (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.212 g, 94% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, dicyclopropyl ketone (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.224 g, 99% yield). Spectroscopic data were consistent with previously reported data for this compound.[14a] Elemental analysis calcd for $C_{13}H_{26}OSi$ (226.43): C, 68.96; H, 11.57. Found: C, 68.89; H, 11.95.

(Dicyclohexylmethoxy)triethylsilane (Table 3, Entry 8). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, dicyclohexyl ketone (0.20 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as a pure product after concentration of the filtrate (0.307 g, 99% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, dicyclohexyl ketone (0.20 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.306 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (t, 1H, J = 6.0 Hz), 1.85−1.70 (m, 6H), 1.70−1.59 (m, 2H), 1.59−1.48 (m, 2H), 1.47−1.33 (m, 2H), 1.28−0.93 (m) and 0.97 (t, J = 8.1 Hz) (19H), 0.61 (q, 6H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.9, 41.1, 30.7, 28.1, 26.7, 7.2, 5.6; MS (IE) *m/z* 310 (M^+). Elemental analysis calcd for $C_{19}H_{38}OSi$ (310.59): C, 73.47; H, 12.33. Found: C, 73.75; H, 12.50.

Triethyl(1,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy)-silane (Table 3, Entry 9). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, D(+)-camphor (0.152 g, 1 mmol) was hydrosilylated 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, D(+)-camphor (0.152 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.244 g (91% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (dd, 1H, J = 7.6, 3.2 Hz), 1.78−1.58 (m, 4H), 1.52−1.41 (m, 1H), 1.00 (s, 3H), 0.98−0.88 (m) containing 0.94 (t, J = 7.9 Hz) (11H), 0.83 (s, 3H), 0.79 (s, 3H), 0.54 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.6, 49.1, 46.5, 45.3, 42.4, 34.0, 27.4, 20.6, 20.1, 11.9, 6.9, 4.9; MS (EI) *m/z* 268 (M^+). Elemental analysis calcd for $C_{16}H_{32}OSi$ (268.51): C, 71.57; H, 12.01. Found: C, 71.34; H, 12.04.

Triethyl(1,3,3-trimethylbicyclo[2.2.1]hept-2-yloxy)-silane (Table 3, Entry 10). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, (+)-1,3,3-trimethyl-2-norbornanone (0.16 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.194 g (96% yield) of the title compound as a 90/10 mixture of isomers as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, (+)-1,3,3-trimethyl-2-norbornanone (0.16 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography (pentane) and obtained as a 90/10 mixture of isomers as a colorless oil in 93% yield (0.188 g).[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (s, 1H, E), 2.96 (s, 1H, e), 1.84−1.69 (m, 1H, E+e), 1.68−1.59 (m, 2H, e), 1.59−1.49 (m, 2H, E), 1.46−1.36 (m, 2H, E+e), 1.08−0.92 (m) containing 1.01 (s, E+e), 0.97 (t, J = 8.0 Hz, E+e), 0.94 (s, E+e) (17H), 0.87 (s, 3H, E), 0.78 (s, 3H, e), 0.59 (q, J = 8.0 Hz, E) and 0.58 (q, J = 8.0 Hz, e) (6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.8 (e), 85.4 (E), 49.7 (E), 49.6 (e), 48.4 (E), 41.22 (e), 40.97 (E), 39.7 (E), 33.6 (e), 30.5 (E), 26.29 (E), 26.16 (e), 25.76 (e), 25.39 (E), 24.3 (e), 21.1 (E), 20.0 (E), 17.9 (e), 7.04 (E), 5.27 (E), 5.17 (e); MS (EI) *m/z* 268 (M^+). Elemental analysis calcd for $C_{16}H_{32}OSi$ (268.51): C, 71.57; H, 12.01. Found: C, 71.71; H, 12.51.

(Diphenylmethoxy)triethylsilane (Table 3, Entry 11). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, benzophenone (0.189 g, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.295 g, 99% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, benzophenone (0.189 g, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.296 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, 4H, J = 7.2 Hz), 7.28 (t, 4H, J = 7.2 Hz), 7.20 (t, 2H, J = 7.2 Hz), 5.75 (s, 1H), 0.88 (t, 9H, J = 7.9 Hz), 0.56 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 128.1, 126.9, 126.3, 76.3, 6.7, 4.8; MS (EI), *m/z* 298 (M^+). Elemental analysis calcd for $C_{19}H_{26}OSi$ (298.18): C, 76.45; H, 8.78. Found: C, 76.81; H, 8.80.

(Phenyl-*o*-tolylmethoxy)triethylsilane (Table 3, Entry 12). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2-methylbenzophenone (0.18 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was

(33) After several flash chromatographies, a fraction which contained only the major isomer was isolated. This allowed us to assign partially the NMR signals of each diastereoisomer (E: *endo*, major; e: *exo*, minor). For the minor diastereoisomer not all the ^{13}C resonances could be unequivocally assigned because of overlap with those from the *endo* diastereoisomer.

purified by flash chromatography on silica gel (pentane:Et_2O, 99:1) to afford 0.287 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2-methylbenzophenone (0.18 mL, 1.0 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as a pure product after concentration of the filtrate (0.300 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.7, 134.7, 130.4, 128.0, 127.1, 127.0, 126.8, 126.7, 125.8, 74.1, 19.5, 6.7, 4.9; MS (EI) *m/z* 312 (M^+). Elemental analysis calcd for $C_{20}H_{28}OSi$ (312.52): C, 76.86; H, 9.03. Found: C, 76.87; H, 9.03.

(2,2-Dimethyl-1-phenylpropoxy)triethylsilane (Table 3, Entry 13). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2,2-dimethylpropiophenone (0.17 mL, 1.0 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.264 g, 99% yield). (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2,2-dimethylpropiophenone (0.17 mL, 1.0 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.262 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.28 (m, 5H), 4.29 (s, 1H), 0.86 (s, 9H), 0.84 (t, 9H, J = 8.2 Hz), 0.45 (q, 6H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.0, 127.0, 126.7, 82.8, 36.3, 26.1, 6.8, 4.8; MS (EI) *m/z* 278 (M^+). Elemental analysis calcd for $C_{17}H_{30}OSi$ (278.50): C, 73.31; H, 10.86. Found: C, 73.18; H, 11.12.

Triethyl(1-*o*-tolylethoxy)silane (Table 3, Entry 14). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2′-methylacetophenone (0.175 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.235 g (94% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2′-methylacetophenone (0.175 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.240 g (96% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 1H, J = 7.2 Hz), 7.22−7.07 (m, 3H), 5.05 (q, 1H, J = 6.4 Hz), 2.31 (s, 3H), 1.38 (d, 3H, J = 6.4 Hz), 0.91 (t, 9H, J = 7.9 Hz), 0.56 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{26}OSi$ (250.45): C, 71.23; H, 10.46. Found: C, 71.00; H, 10.72.

Triethyl[1-(2,4,6-trimethylphenyl)ethoxyl]silane (Table 3, Entry 15). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2′,4′,6′-trimethylacetophenone (0.17 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.209 g (75% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2′,4′,6′-trimethylacetophenone (0.17 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.222 g (80% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 5.25 (q, 1H, J = 6.6 Hz), 2.40 (s, 6H), 2.24 (s, 3H), 1.45 (d, 3H, J = 6.6 Hz), 0.89 (t, 9H, J = 7.9 Hz), 0.54 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 135.8, 135.2, 130.1, 67.8, 23.2, 20.7, 20.5, 6.9, 5.0; MS (EI) *m/z* 278 (M^+). Elemental analysis calcd for $C_{17}H_{30}OSi$ (278.50): C, 73.31; H, 10.86. Found: C, 73.06; H, 10.83.

4-(*N*-Methylpiperidinoxy)triethylsilane (Table 5, Entry 1). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, *N*-methylpiperidin-4-one (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. As the crude product decomposed on silica gel, it was purified by filtration on alumina (pentane) to afford 0.211 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, *N*-methylpiperidin-4-one (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by filtration on alumina (pentane) to afford 0.213 g (93% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75−3.59 (m, 1H), 3.59−2.74 (m, 2H), 2.25 (s, 3H), 2.20−2.05 (m, 2H), 1.85−1.71 (m, 2H), 1.70−1.51 (m, 2H), 0.96 (t, 9H, J = 8.0 Hz), 0.58 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.7, 53.3, 46.2, 35.0, 6.7, 4.8; MS (EI), *m/z* 229 (M^+). Elemental analysis calcd for $C_{12}H_{27}NOSi$ (229.43): C, 62.82; H, 11.86; N, 6.10. Found: C, 62.96; H, 11.65; N, 5.92.

2-(3-Diethylamino)propyloxytriethylsilane (Table 5, Entry 2). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 1-diethylaminopropan-2-one (0.155 mL, 1 mmol) was hydrosilylated 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, 1-diethylaminopropan-2-one (0.155 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.230 g (94% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (sextuplet, 1H, J = 6.3 Hz), 2.68−2.36 (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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.5, 61.7, 48.1, 22.5, 12.0, 6.8, 4.9; MS (EI), *m/z* 245 (M^+). Elemental analysis calcd for $C_{13}H_{31}NOSi$ (245.48): C, 63.61; H, 12.73; N, 5.71. Found: C, 63.83; H, 12.83; N, 5.82.

[1-(2-Chlorophenyl)ethoxy]triethylsilane (Table 5, Entry 3). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2′-chloroacetophenone (0.13 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, 2′-chloroacetophenone (0.13 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 98:2) to afford 0.262 g (97% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 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 = 8.0 Hz), 0.58 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 130.6, 128.9, 127.8, 127.0, 126.9, 67.1, 25.5, 6.7, 4.7. MS (EI), *m/z* 272 (M^+), 270 (M^+). Elemental analysis calcd for $C_{14}H_{23}ClOSi$ (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·HBF_4 and 20 mol % of NaO^{t}Bu, 4′-bromoacetophenone (0.20 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, 4′-bromoacetophenone (0.20 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 98:2) to afford 0.314 g (99% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{14}H_{23}BrOSi$ (315.32): C, 53.33; H, 7.35. Found: C, 53.49; H, 7.45.

[1-(2-(Trifluoromethyl)phenyl)ethoxy]triethylsilane (Table 5, Entry 5). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2′-(trifluoromethyl)acetophe-

none (0.15 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 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 NaO^{t}Bu, and 3 equiv of Et_3SiH, 2′-(trifluoromethyl)acetophenone (0.15 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.268 g (88% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 1H, J = 7.8 Hz), 7.60−7.46 (m, 2H), 7.30 (t, 1H, J = 7.8 Hz), 5.25 (q, 1H, J = 6.1 Hz), 1.41 (d, 3H, J = 6.1 Hz), 0.87 (t, 9H, J = 8.0 Hz), 0.54 (q, 6H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 123.1, 127.6, 126.7, 125.9, 124.9 (q, J_{C-F} = 6 Hz), 123.2, 66.1, 27.8, 6.6, 4.6. Elemental analysis calcd for $C_{15}H_{23}F_3OSi$ (304.42): C, 59.18; H, 7.62. Found: C, 58.96; H, 7.34.

[1-(4-(Dimethylamino)phenyl)-2,2,2-trifluoroethoxy]-triethylsilane (Table 5, Entry 6). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 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:Et_2O, 95:5) to afford 0.310 g (93% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 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). ^{1}H NMR (400 MHz, $CDCl_3$) 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), 0.62−0.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 128.4, 125.9, 123.0 (q, J_{C-F} = 14 Hz), 111.7, 73.3 (q, J_{C-F} = 32 Hz), 40.3, 6.4, 4.5. Elemental analysis calcd for $C_{16}H_{26}F_3NOSi$ (333.46): C, 57.63; H, 7.86; N, 4.20. Found: C, 58.00; H, 8.01; N, 3.99.

(2-Methoxycyclohexyloxy)triethylsilane (Table 5, Entry 9). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, 2-methoxycyclohexanone (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.232 g (95% yield) of the title compound as a 50/50 mixture of two diastereoisomers as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, 2-methoxycyclohexanone (0.125 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.229 g (94% yield) of the title compound as a 50/50 mixture of two diastereoisomers as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86−3.80 (m, 1H), 3.53−3.45 (m, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 3.21−3.15 (m, 1H), 2.98−2.81 (m, 1H), 2.02−1.91 (m, 1H), 1.87−1.70 (m, 3H), 1.69−1.49 (m, 4H), 1.43−1.36 (m, 3H), 1.34−1.16 (m, 5H), 0.97 (t, 18H, J = 7.8 Hz), 0.61 (q, J = 7.8 Hz) and 0.60 (q, J = 7.8 Hz) (12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.7, 80.9, 73.7, 70.4, 57.4, 56.6, 33.6, 31.4, 28.8, 27.0, 23.3, 22.0, 21.8, 6.83, 6.79, 4.9. Elemental analysis calcd for $C_{13}H_{28}O_2Si$ (244.45): C, 63.87; H, 11.55. Found: C, 63.53; H, 11.51.

Triethyl(tetrahydro-2*H*-pyran-4-yloxy)silane (Table 5, Entry 10). (A) Using the general procedure with ICy·HBF_4 and 20 mol % of NaO^{t}Bu, tetrahydropyran-4-one (0.093 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane−Et_2O, 90:10) to afford 0.123 g (57% yield) of the title compound as a colorless oil. (B) Using the general procedure with (ICy)CuCl, 12 mol % of NaO^{t}Bu, and 3 equiv of Et_3SiH, tetrahydropyran-4-one (0.093 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 90:10) to afford 0.141 g (65% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01−3.88 (m, 2H), 3.88−3.75 (m, 1H), 3.51−3.33 (m, 2H), 1.83−1.70 (m, 2H), 1.67−1.48 (m, 2H), 0.96 (t, 9H, J = 7.9 Hz), 0.60 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.0, 65.5, 36.0, 6.8, 4.8. Elemental analysis calcd for $C_{11}H_{24}O_2Si$ (216.39): C, 61.05; H, 11.18. Found: C, 60.96; H, 11.31.

[1-(Pyridin-2-yl)ethoxy]triethylsilane (Table 9, Entry 1). (A) Using the general procedure with SIMes·HBF_4 and 8 mol % of NaO^{t}Bu, 2-acetylpyridine (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.222 g (94% yield) of the title compound as a light yellow oil. (B) Using the general procedure with (SIMes)CuCl, 3 mol % of NaO^{t}Bu, and 2 equiv of Et_3SiH, 2-acetylpyridine (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane−Et_2O, 95:5) to afford 0.222 g (94% yield) of the title compound as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.3, 136.5, 121.6, 119.2, 71.8, 25.5, 6.7, 4.7. Elemental analysis calcd for $C_{13}H_{23}NOSi$ (237.15): C, 65.77; H, 9.76; N, 5.90. Found: C, 65.56; H, 10.01; 5.79.

[1-(Furanyl-2-yl)ethoxy]triethylsilane (Table 9, Entry 2). (A) Using the general procedure with SIMes·HBF_4 and 8 mol % of NaO^{t}Bu, 2-acetylfurane (0.110 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.209 g (92% yield) of the title compound as a colorless oil. (B) Using the general procedure with (SIMes)-CuCl, 3 mol % of NaO^{t}Bu, and 2 equiv of Et_3SiH, 2-acetylfurane (0.110 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.212 g (94% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 141.2, 109.9, 104.7, 64.1, 22.9, 6.6, 4.6. Elemental analysis calcd for $C_{12}H_{22}O_2Si$ (226.14): C, 63.66; H, 9.80. Found: C, 63.62; H, 10.08.

[1-(Thien-2-yl)ethoxy]triethylsilane (Table 9, Entry 3). (A) Using the general procedure with SIMes·HBF_4 and 8 mol % of NaO^{t}Bu, 2-acetylthiophene (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane−Et_2O, 95:5) to afford 0.237 g (98% yield) of the title compound as a colorless oil. (B) Using the general procedure with (SIMes)-CuCl, 3 mol % of NaO^{t}Bu, and 2 equiv of Et_3SiH, 2-acetylthiphene (0.11 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.235 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, 1H, J = 3.6 Hz), 6.95−6.87 (m, 1H), 6.88 (d, 1H, J = 3.6 Hz), 5.14 (q, 1H, J = 6.4 Hz), 1.55 (d, 3H, J = 6.4 Hz), 0.96 (t, 9H, J = 7.9 Hz), 0.63 (q, 6H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 126.3, 123.6, 122.0, 66.9, 27.1, 6.8, 4.7. Elemental analysis calcd for $C_{12}H_{22}OSSi$ (242.45): C, 59.75; H, 9.15. Found: C, 59.62; H, 9.45.

[1-(Thiazol-2-yl)ethoxy]triethylsilane (Table 9, Entry 4). (A) Using the general procedure with SIMes·HBF_4 and 12 mol % of NaO^{t}Bu, 2-acetylthiazole (0.10 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.222 g (91% yield) of the title compound as a colorless oil. (B) Using the general procedure with (SIMes)-CuCl, 8 mol % of NaO^{t}Bu, and 2 equiv of Et_3SiH, 2-acetylthiazole (0.10 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et_2O, 95:5) to afford 0.230 g (95% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 2.8 Hz), 7.22 (d, 1H, J = 2.8 Hz), 5.17 (q, 1H, J = 6.4 Hz), 1.58 (d, 3H, J = 6.4 Hz), 0.97 (t, 9H, J = 7.8 Hz), 0.66 (q, 6H, J = 7.8 Hz); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 178.1, 142.3, 118.3, 69.2, 25.4, 6.7, 4.7. Elemental analysis calcd for $C_{12}H_{21}NOSSi$ (243.44): C, 54.27; H, 8.69; N, 5.75. Found: C, 54.48; H, 8.80; N, 5.60.

[1-(*N*-Methylpiperin-2-yl)ethoxy]triethylsilane (Table 9, Entry 5). (A) Using the general procedure with SIMes·HBF_4 and 12 mol % of NaO^{t}Bu, 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:Et_2O, 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 NaO^{t}Bu, and 2 equiv of Et_3SiH, 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:Et_2O, 95:5) to afford 0.222 g (93% yield) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 122.6, 106.2, 106.0, 64.4, 34.4, 23.9, 6.8, 5.0. Elemental analysis calcd for $C_{13}H_{25}NOSi$ (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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