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Iridium-Catalysed Hydrosilylation of Cyclopropanes via Regioselective Carbon–Carbon Bond Cleavage

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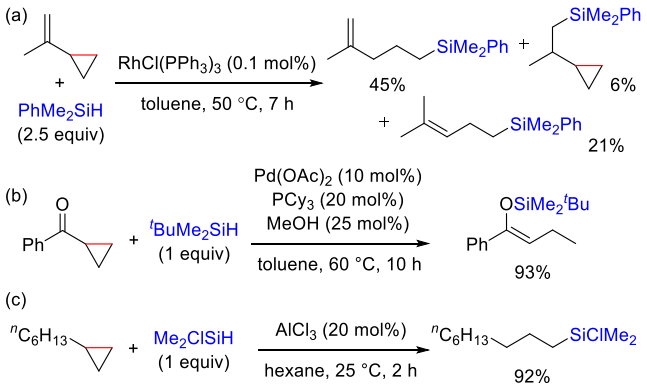
Masahito Murai,[a,*] Atsushi Nishiyama,[a] Naoki Nishinaka,[a] Haruka Morita,[a] and Kazuhiko Takai[a,*]

While cyclopropanes have been explored as synthetically valuable building blocks, transformation of cyclopropanes without conjugated substituents or directly substituted heteroatoms remains challenging. The current study describes iridium-catalysed ring-opening hydrosilylation of cyclopropanes. A nitrogen-based directing group was found to control the reactivity of iridium active species as well as the regiochemistry of carbon–carbon bond cleavage and hydrosilylation.

Catalytic hydrosilylation is an efficient and atom-economical approach to organosilanes, and represents a useful transformation due to the wide industrial utility of the resulting organosilanes.[1] In contrast to the well-studied hydrosilylation of carbon–carbon or carbon–heteroatom unsaturated bonds, such as alkenes, allenes, alkynes, carbonyl compounds, CO_2, and nitriles, much less attention has been paid to the corresponding hydrosilylation of cyclopropanes. While the formal cleavage of carbon–carbon bonds with hydrosilylation of alkylidenecyclopropanes has been investigated, insertion of a silylmetal species into carbon–carbon double bonds followed by cleavage of carbon–carbon single bonds is proposed in the reaction mechanism.[2,3] Therefore, these methods are unsuitable for hydrosilylation of other cyclopropanes with a direct cleavage of carbon–carbon bonds. Pioneering work was done by Beletskaya, who reported silylative cleavage of vinylcylopropanes and *gem*-divinylcyclopropane in the presence of Wilkinson complex, $RhCl(PPh_3)_3$ (Scheme 1(a)).[4a] Slough and Yorimitsu independently reported catalytic hydrosilylation of cyclopropyl ketones leading to silyl enol ethers (Scheme 1(b)).[4b,c] While these studies demonstrated the hydrosilylation of cyclopropanes with direct cleavage of carbon–carbon bonds, the protocols were limited in substrate scope, and were effective only for cyclopropanes with conjugated substituents, such as vinyl and acyl groups, or heteroatoms.[5] An exception was reported by Yamamoto on the aluminum(III) chloride-catalysed hydrosilylation of cyclopropanes with chlorohydrosilane *via* selective cleavage of proximal carbon–carbon bonds (Scheme 1(c)).[4d] Because the selectivity of addition was dependent on the stability of the carbocation intermediates generated from cyclopropanes, formation of regioisomer mixtures was observed in some cases, and the functional group compatibility was low.



Scheme 1. Previous catalytic hydrosilylation of cyclopropanes with direct cleavage of cyclopropyl carbon–carbon bonds

Activation and cleavage of cyclopropanes is a useful and important organic transformation because even catalytic reduction of cyclopropyl groups leading to isopropyl groups is often applied to the total synthesis of natural biologically active compounds.[6] However, *catalytic transformations of electronically unactivated cyclopropanes with the exceptions of hydrogenation and simple isomerization* remains challenging,[5] and the need exists to develop operationally simple and regioselective cleavage reactions of carbon–carbon bonds with functionalization. While developing a method for the dehydrogenative silylation of carbon–hydrogen bonds,[7] we found a catalytic cleavage of cyclopropane ring with addition of hydrosilane under neutral and mild conditions.[8] A nitrogen-based directing group was found to control the reactivity of hydrosilane as well as the regiochemistry of carbon–carbon bond cleavage and hydrosilylation.

Treatment of 2-(cyclopropylmethoxy)pyridine (**1a**) with triethylsilane in the presence of a catalytic amount of $[IrCl(cod)]_2$ in toluene at 40 °C gave 2-[4-(triethylsilyl)butoxy]pyridine (**2a**) in 60% yield (Table 1, entry 1). The proximal carbon–carbon bond of the cyclopropane ring was cleaved selectively, and corresponding

[a] Division of Applied Chemistry, Graduate School of Natural Science and Technology, and Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan.
E-mail: masahito.murai@okayama-u.ac.jp ktakai@cc.okayama-u.ac.jp

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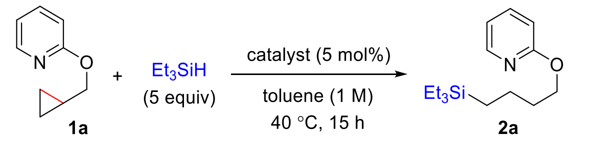
regioisomers were not obtained under the reaction conditions. In contrast, the corresponding carbon analog, cyclopropylmethyl phenyl ether (**3**), was recovered and no similar cleavage of a carbon–carbon bond was observed under identical conditions even upon heating to 135 °C.[9] These results indicate that a nitrogen-based auxiliary group is important to promote the carbon–carbon cleavage as well as hydrosilylation of cyclopropanes. Although several iridium catalysts, including [Ir(OMe)(cod)]$_2$, [IrCl(cod)]$_2$ / AgOTF, and [IrCl(cod)]$_2$ / $AgSbF_6$, exhibited marginal catalytic activity (entries 2-5), the corresponding rhodium catalysts, such as [RhCl(cod)]$_2$ and [Rh(OMe)(cod)]$_2$, as well as other transition metal complexes, were completely ineffective (entry 6).[10] In contrast to Beletskaya's report (Scheme 1(a)), Wilkinson complex, $RhCl(PPh_3)_3$, also shut down the reaction (entry 7). Examination of solvents using [IrCl(cod)]$_2$ as a catalyst revealed that the best yield was obtained in diethyl ether (entry 8).[11] Effect of reaction temperature was also an important factor, and the yield of **2a** was highest when the reaction was conducted at 50 °C, due to the competitive decomposition of **1a** at high temperatures.[12] Note that the reaction proceeded efficiently in the absence of ligands or additives under mild conditions. Addition of phosphine-, nitrogen-, or diene-based ligands decreased the reaction efficiency.[13] While the acidity of cyclopropyl carbon–hydrogen bonds is relatively high, competing activation followed by the dehydrogenative silylation was not observed in all cases.[8]

Table 1. Optimization of reaction conditions

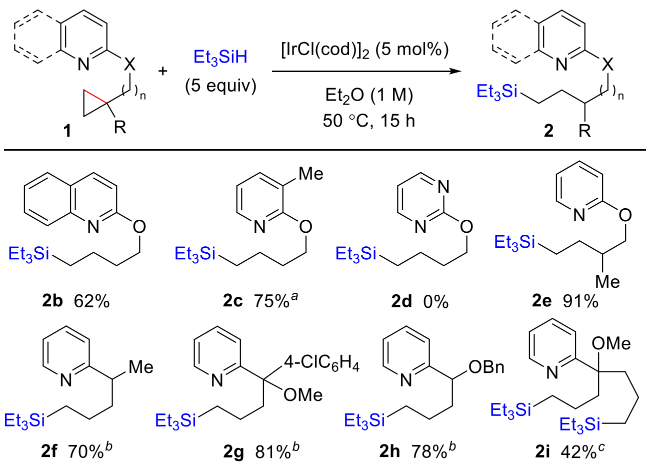


entry	catalyst	Yield of **2a**[a] / %	recovery of **1a**[a] / %
1	[IrCl(cod)]$_2$	68	0
2	[Ir(OMe)(cod)]$_2$	41	48
3	[IrCl(cod)]$_2$ / AgOTf	27	43
4	[IrCl(cod)]$_2$ / $AgSbF_6$	trace	39
5	[Cp*IrCl]$_2$	28	47
6	[RhCl(cod)]$_2$	2	35
7	$RhCl(PPh_3)_3$	trace	67
8[b]	[IrCl(cod)]$_2$	96 (90)	0

[a] Determined by ^{1}H NMR. The value in parentheses is isolated yield.
[b] In Et_2O at 50 °C.

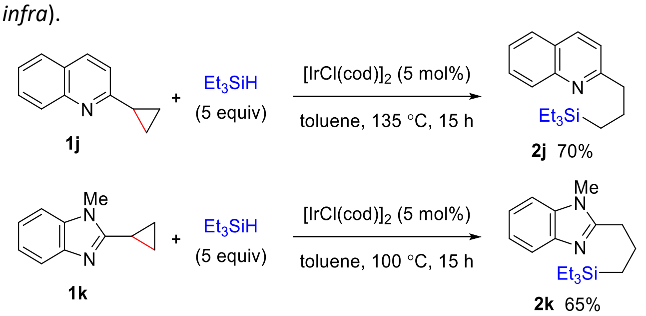
After optimized reaction conditions were established, substrate scope was examined (Table 2). Reaction of cyclopropanes having 2-quinolyl and 2-picolyl groups provided the corresponding hydrosilylation products **2b** and **2c**, respectively, in yields lower than those obtained from reaction of **1a**, which indicated that the basicity of nitrogen-containing directing group significantly affected the efficiency of the reaction. Hydrosilylation, as well as carbon–carbon bond cleavage of substrates containing other directing groups, including a 2-pyrimidyl group, or cyclobutane derivatives, did not occur (see Figure S1 in ESI). Using a pyridyl group as a directing group, **2e** was obtained in 91% yield from a substrate with a methyl group on the cyclopropane ring. Although a higher temperature was required, 2-(1-cyclopropylethyl)pyridine was a good substrate for the current ring-opening hydrosilylation to provide **2f** in 70% yield. For the hydrosilylation of 2-alkylpyridines, better results were obtained in toluene than in diethyl ether. Chloride functionality, which can be reduced by hydrosilanes, was also applicable to yield **2g** in 81% yield. Without elimination of a benzyl group protecting a hydroxyl group, the expected adduct **2h** was obtained in 78% yield. Treatment of triethylsilane with a substrate having two cyclopropane rings underwent smooth ring-opening hydrosilylation twice to furnish **2i** in moderate yield. Proximal carbon–carbon bonds were cleaved selectively in all reactions, and the regioselectivity of hydrosilylation was well-controlled without producing other ring-opening hydrosilylation adducts.[14]

Table 2. Iridium-catalysed hydrosilylation of cyclopropanes with regioselective cleavage of proximal carbon–carbon bonds



[a] 60 °C. [b] In toluene (1 M) at 100 °C. [c] In toluene (0.1 M) at 100 °C.

The current catalyst system was also effective for silylative ring-opening of arylcyclopropanes (Scheme 2). Reaction of 2-cyclopropylquinoline **1j** with triethylsilane took place efficiently to afford 2-[3-(triethylsilyl)propyl]quinoline **2j** in 70% yield.[9,15] Cyclopropane **1k** containing a benzimidazolyl group as a directing group underwent hydrosilylation to afford **2k** in 65% yield. Although cyclopropane rings of arylcyclopropanes are generally reactive compared to that of alkylcyclopropanes, a higher temperature was required for the complete consumption of **1j** and **1k**, probably due to the ring strain of the iridacycle intermediates generated (*vide infra*).



Scheme 2. Ring-opening hydrosilylation of arylcyclopropanes

Preliminary insights into the mechanism was obtained by reaction of **1a** with a deuterium-incorporated triethylsilane (*d*-content 97%) under standard conditions (Scheme 3). Introduction of deuterium into **2a** was observed at the α- and β-positions of the

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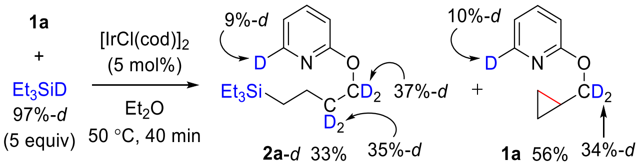
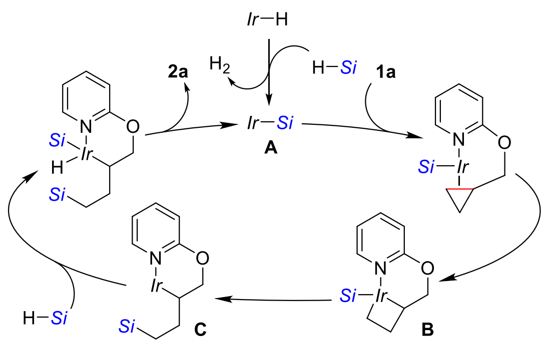
oxygen atom as well as the 6-position of the pyridine ring. Partial incorporation of deuterium into recovered **1a** was also observed at the α-position of the oxygen and nitrogen atoms (see Figure S1 in SI for details). These results indicate that the competitive and reversible cleavage of carbon–hydrogen bonds occurred during and after ring-opening of cyclopropanes, and silylation occurred selectively after carbon–carbon bond cleavage of cyclopropane rings.[16] The recovery of cyclopropane **1a** in the absence of triethylsilane indicated that the presence of silane was required for carbon–carbon bond cleavage, and that direct activation of the cyclopropane ring prior to hydrosilane with $[IrCl(cod)]_2$ could be ruled out.[17]



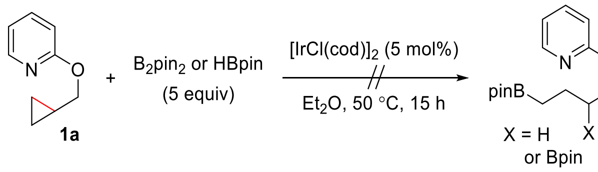
Scheme 3. Deuterium labelling experiment

Based on these results, a plausible mechanism is illustrated in Scheme 4, which exemplifies the hydrosilylation of **1a**. The silicon–hydrogen bond is initially activated by a iridiumhydride species[18] coordinated to a nitrogen-based directing group, followed by reductive elimination of dihydrogen. The resulting silyliridium species **A**, in which an iridium centre is in close proximity to the proximal carbon–carbon bond of the cyclopropane ring, induced oxidative addition to produce the iridacyclobutane intermediate **B**. Coordination of silyliridium species **A** with a pyridyl directing group is inevitable because: (1) hydrosilylation did not occur when phosphine and nitrogen-based ligands were added,[12] and (2) (phenoxymethyl)cyclopropane **3** without a directing group remained intact under the present reaction conditions.[9] Subsequent reductive elimination of the carbon–silicon bond furnished the alkyliridium species **C**.[19] Regioselectivity of silylation in this step was determined by the greater stability of the resulting six-membered iridacycle intermediate **C**, compared with the possible eight-membered iridacycle intermediate possessing a silyl group at the β-position of the oxygen atom.[20] Intermediate **C** was then added oxidatively to a second hydrosilane, followed by reductive elimination to provide **2a** along with regeneration of catalytically active silyliridium species **A**. The final reductive elimination to form **2a** accounted for the deuterium introduction at the β-position of the oxygen atom observed in Scheme 3.



Scheme 4. Proposed reaction mechanism (*Si* = SiR_3)

Reaction of **1a** with HBpin or B_2pin_2 in place of triethylsilane was conducted to investigate the ability of the corresponding boryliridium species to mediate activation of carbon–carbon bonds in a similar manner (Scheme 5). However, none of the ring-opening borylated products was observed, which confirms that the silyl ligand on the iridium centre was important for cleavage of the cyclopropyl rings.



Scheme 5. Attempted borylation of cyclopropane

In conclusion, iridium-catalysed regioselective hydrosilylation of electronically unactivated cyclopropanes was accomplished, promoted by a nitrogen-based directing group. The combination of an iridium complex with a hydrosilane was key for the cleavage and functionalization of cyclopropyl carbon–carbon bonds. Due to slight differences in covalent radius and electronegativity between carbon and silicon, introduction of a silyl functionality could produce drug molecules with novel and unique physiological and biological properties.[21] The present silylation with cyclopropane ring-opening provides new opportunities for the design of silicon-containing functional molecules.

Notes and references

1 For recent reviews, see: (a) *Hydrosilylation: A Comprehensive Review on Recent Advances*; B. Marciniec, Ed.; Springer: Berlin, 2009; (b) Y. Nakajima and S. Shimada, *RSC Adv.*, 2015, **5**, 20603; (c) J. Sun and L. Deng, *ACS Catal.*, 2016, **6**, 290.

2 (a) A. G. Bessmertnykh, K. A. Blinov, Y. K. Grishin, N. A. Donskaya, E. V. Tveritinova, N. M. Yur'eva and I. P. Beletskaya, *J. Org. Chem.*, 1997, **62**, 6069; (b) M. Itazaki, Y. Nishihara and K. Osakada, *J. Org. Chem.*, 2002, **67**, 6889; (c) Y. Nishihara, M. Itazaki and K. Osakada, *Tetrahedron Lett.*, 2002, **43**, 2059; (d) S. Simaan, A. F. G. Goldberg, S. Rosset and I. Marek, *Chem. Eur. J.*, 2010, **16**, 774.

3 For reviews on the catalytic transformation of alkylidenecyclopropanes. See: (a) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2003, **103**, 1213; (b) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2014, **114**, 7317; (c) H. Pellissier, *Tetrahedron*, 2014, **70**, 4991; (d) L. Yu, M. Liu, F. Chen and Q. Xu, *Org. Biomol. Chem.*, 2015, **13**, 8379.

4 (a) A. G. Bessmertnykh, K. A. Blinov, Y. K. Girishin, N. A. Donskaya and I. P. Beletskaya, *Tetrahedron Lett.*, 1995, **36**, 7901; (b) C. Sun, A. Tu and G. A. Slough, *J. Organomet. Chem.*, 1999, **582**, 235; (c) Y. Sumida, H. Yorimitsu and K. Oshima, *J. Org. Chem.*, 2009, **74**, 7986; (d) S. Nagahara, T. Yamakawa and H. Yamamoto, *Tetrahedron Lett.*, 2001, **42**, 5057.

5 For reviews of catalytic transformation of cyclopropanes via C–C bond cleavage, see: (a) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117; (b) K. Ruhland, *Eur. J. Org. Chem.*, 2012, 2683; (c) L. Souillart and N. Cramer, *Chem. Rev.*, 2015, **115**, 9410; (d) C. T. To and K. S. Chan, *Tetrahedron Lett.*, 2016, **57**, 4664; (e) G. Fumagalli, S. Stanton and J. F. Bower, *Chem. Rev.*, 2017, **117**, 9404. For the synthetic application of activated cyclopropanes, such as cyclopropanols and cyclopropylamines, see: (f) A. Nikolaev and A. Orellana, *Synthesis*, 2016, **48**, 1741; (g) V. A. Rassadin and Y. Six, *Tetrahedron*, 2016, **72**, 4701. For

(3+1+2)cycloaddition reaction with unactivated cyclopropanes, see: (h) Y. Koga, K. Narasaka, *Chem. Lett.* 1999, 705; (i) G.-W. Wang, N. G. McCreanor, M. H. Shaw, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc.*, 2016, **138**, 13501.

6 For selected examples, see: (a) M. Harmata and P. Rashatasakhon, *Org. Lett.*, 2000, **2**, 2913; (b) D. C. Harrowven, M. C. Lucas and P. D. Howes, *Tetrahedron*, 2001, **57**, 9157; (c) G. Mehta, A. S. K. Murthy and J. D. Umarye, *Tetrahedron Lett.*, 2002, **43**, 8301; (d) S. Karimi and P. Tavares, *J. Nat. Prod.*, 2003, **66**, 520; (e) D. F. Taber and K. J. Frankowski, *J. Org. Chem.*, 2005, **70**, 6417; (f) D. F. Taber and W. Tian, *J. Org. Chem.*, 2008, **73**, 7560; (h) S. Hendrata, F. Bennett, Y. Huang, M. Sannigrahi, P. A. Pinto, T.-M. Chan, C. A. Evans, R. Osterman, A. Buevich and A. T. McPhail, *Tetrahedron Lett.*, 2006, **47**, 6469; (i) Z.-Y. Zhang, Z.-Y. Liu, R.-T. Guo, Y.-Q. Zhao, X. Li, X.-C. Wang *Angew. Chem. Int. Ed.*, 2017, **56**, 4028.

7 (a) T. Ureshino, T. Yoshida, Y. Kuninobu, and K. Takai, *J. Am. Chem. Soc.*, 2010, **132**, 14324; (b) Y. Kuninobu, K. Yamauchi, N. Tamura, T. Seiki and K. Takai, *Angew. Chem. Int. Ed.*, 2013, **52**, 1520; (c) Y. Kuninobu, T. Nakahara, H. Takeshima and K. Takai, *Org. Lett.* 2013, **15**, 426; (d) M. Murai, H. Takeshima, H. Morita, Y. Kuninobu and K. Takai, *J. Org. Chem.*, 2015, **80**, 5407; (e) M. Murai, K. Takami and K. Takai, *Chem.-Eur. J.*, 2015, **21**, 4566; (f) M. Murai, K. Takami, H. Takeshima and K. Takai, *Org. Lett.*, 2015, **17**, 1798; (g) M. Murai, K. Matsumoto, Y. Takeuchi and K. Takai, *Org. Lett.*, 2015, **17**, 3102; (h) M. Murai, Y. Takeuchi, K. Yamauchi, Y. Kuninobu and K. Takai, *Chem.-A Eur. J.*, 2016, **22**, 6048; (i) M. Murai, R. Okada, A. Nishiyama and K. Takai, *Org. Lett.*, 2016, **18**, 4380; (j) M. Murai, Y. Takeuchi and K. Takai, *Chem. Lett.*, 2017, **46**, 1044; (k) M. Murai, R. Okada, S. Asako and K. Takai, *Chem. Eur. J.*, 2017, doi:10.1002/chem.201701579. See also for our recent work on the dehydrogenative borylation and germylation: (l) Y. Kuninobu, T. Iwanaga, T. Omura, and K. Takai, *Angew. Chem. Int. Ed.*, 2013, **52**, 4431; (m) M. Murai, K. Matsumoto, R. Okada and K. Takai, *Org. Lett.*, 2014, **16**, 6492; (n) M. Murai, T. Omura, Y. Kuninobu and K. Takai, *Chem. Commun.*, 2015, **51**, 4583.

8 Catalytic intramolecular dehydrogenative silylations of C–H bonds of cyclopropanes have been reported. See: (a) N. Ghavtadze, F. S. Melkonyan, A. V. Gulevich, C. Huang, and V. Gevorgyan, *Nat. Chem.*, 2014, **6**, 122; (b) T. Lee and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2016, **55**, 8723.

9 Ring-opening reaction were not observed by the treatment of triethylsilane with **3** in the presence of 2-methoxypyridine, or 2-cyclopropylnahthalene in the presence of 2-methylquinoline. These results confirm that pyridyl and quinolyl groups act not only as ligands but also as directing groups to cleave the cyclopropyl carbon–carbon bonds.

10 The following metal complexes (5 mol%-M) did not convert **1a** into **2a** in toluene at 40 or 135 °C for 15 h: $Re_2(CO)_{10}$, $[ReBr(CO)_3(thf)]_2$, $Ru_3(CO)_{12}$, $[RuCl_2(p\text{-cymene})]_2$, $CoCl(PPh_3)_3$, $CoCl_2$, $Co(OAc)_2$, $[RhCl(cod)]_2$, $[Cp^*RhCl_2]_2$, $[RhCl(CO)_2]_2$, $RhCl(PPh_3)_3$, $[RhCl(cod)]_2$ / AgOTf, $IrCl_3$, $NiCl_2$, $Ni(OAc)_2$, $NiCl_2$(dppp), $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $Pd(OAc)_2$, and AgOTf.

11 Investigation of solvents with 5 mol% of $[IrCl(cod)]_2$ at 40 °C for 15 h: Yield of **2a** was 61% in C_6H_5Cl, 68% in toluene, 62% in octane, 59% in $ClCH_2CH_2Cl$, 80% in 1,4-dioxane, 78% in THF, 84% in Et_2O, 8% in DMF. Ethereal solvents prevented the side-reaction *via* the cleavage of C–O bond leading to 2-pyridone, and gave better results in the hydrosilylation of 2-(cyclopropylalkoxy)pyridines.

12 Effect of temperature with 5 mol% of $[IrCl(cod)]_2$ in toluene for 15 h: Yield of **2a** was 47% at 25 °C, 69% at 40 °C, 42% at 80 °C, 35% at 100 °C, and 26% at 135 °C. Investigation of reaction time with 5 mol% of $[IrCl(cod)]_2$ in toluene at 40 °C: Yield of **2a** was 18% for 1 h, 38% for 2 h, 50% for 3 h, 59% for 6 h, 69% for 15 h, 70% for 24 h.

13 When 1,10-phenanthroline (5 mol%) was added under the condition shown in Table 1, entry 8, **2a** was obtained in 8% yield. Formation of **2a** was not observed with the following additives: PPh_3, PCy_3, 1,2-bis(diphenylphosphino)ethane, (*R*)-DTBM-SEGPHOS, 3,4,7,8-tetramethyl-1,10-phenanthroline, 4,4'-di-*tert*-butyl-2,2'-bipyridyl, and 1,5-cyclooctadiene.

14 Reaction of **1a** or **1f** with other hydrosilanes, such as $(EtO)_3SiH$, $ClSiMe_2H$, $BnMe_2SiH$, $^nDocMe_2SiH$, $PhMe_2SiH$, and Et_2SiH_2, gave the expected hydrosilylation products in low yields (less than 10% yield).

15 2-^{n}Propylquinoline was obtained in 10% yield as a byproduct.

16 Pyridyl group directed the incorporation of deuterium atom at the specific locations based on the site-selective cleavage of carbon–hydrogen bonds.

17 Chirik *et al.* reported a catalytic hydrosilylation of a terminal olefin, which was generated *in situ* from subsequent ring-opening and double-bond migration reaction of a cyclopropylcarbinol derivative with a Wilkinson complex. See: S. C. Bart and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 886. Because olefins were not detected in the current study with or without hydrosilanes, direct addition of silyliridium species **A** with cyclopropane derivatives appears to be more plausible for the reaction mechanism.

18 The $HIr(PR_3)_n$ species, generated *via* oxidative addition of $ClIr(PR_3)_n$ to R'_3SiH followed by reductive elimination of R'_3SiCl, is proposed as an active catalytic species in the hydrosilylation of alkynes. See: M. A. Esteruelas, M. Oliván and A. Vélez, *Inorg. Chem.*, 2013, **52**, 12108.

19 Attempted intercept of alkyliridium species **C** and the corresponding benzyliridium species generated from **1j** and **1k** with alkynes, alkenes, and aldehydes failed due to the rapid hydrosilylation of these additives.

20 The *trans* effect may be another controlling factor involved in the regioselective C–Si bond formation, although we do not have any structure and configuration information of the intermediate **B** and difficult to discuss exactly.

21 (a) N. A. Meanwell, *J. Med. Chem.*, 2011, **54**, 2529; (b) S. Fujii, Y. Miyajima, H. Masuno and H. Kagechika, *J. Med. Chem.*, 2013, **56**, 160; (c) A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388; (d) G. K. Min, D. Hernández and T. Skrydstrup, *Acc. Chem. Res.*, 2013, **46**, 457.

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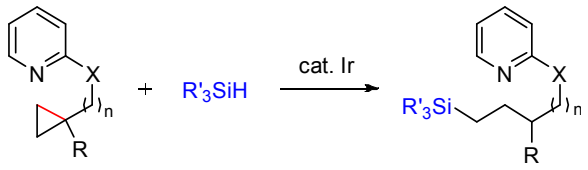

Catalytic and regioselective hydrosilylation of electronically unactivated cyclopropanes *via* the selective cleavage of proximal carbon–carbon bonds was developed.