

# Regioselective Hydrosilylation of Olefins Catalyzed by Co-Iminobipyridine Complexes: The Role of Cyclohexyl Substituent on the Imino Nitrogen

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# Abstract

Regioselective hydrosilvlation of aliphatic olefins catalyzed by Co-iminobipyridine complexes, Co(R), were investigated, where  $\mathbf{R}$  indicates a substituent on the imino nitrogen in an iminobipyridine ligand (iminobypyridine = [2,2'-bpy]-6-C(Me)=N-R). Syntheses of two complexes, Co(Mes) (Mes = 2,4,6-trimethylphenyl) and Co(Cy) (Cy = cyclohexyl), and comparison of their catalytic activity for hydrosilylation of 1-octene with diphenylsilane revealed that the reaction system using Co(Mes) produced a mixture of anti-Markovnikov and Markovnikov hydrosilylation products, whereas that using Co(Cy) produced the anti-Markovnikov product selectively. Crystal structures of these complexes implied that a catalytically active species derived from Co(Cy) has narrower active space for hydrosilylation than that from Co(Mes). According to the Chalk-Harrod mechanism, there are two types of hydrosilylated products (anti-Markovnikov and Markovnikov products), which stem from the way of terminal olefin insertion into an M-H bond (that is 1,2- or 2,1-insertion). One of the intermediates derived from Co(Cy) in the Chalk-Harrod mechanism has hydride and silyl ligands. In the step of olefin insertion into the Co-H bond, 1,2-insertion is more likely

to occur from the steric point of view, leading to selective formation of the anti-Markovnikov product.

Keywords: Hydrosilylation of olefins | Co catalyst | Regioselectivity

#### 1. Introduction

The hydrosilylation of olefins catalyzed by transition metal complexes represents an atom economical method to obtain organosilane compounds. Among transition metal catalysts for the reaction, Pt complexes such as Speier's<sup>1</sup> and Karstedt's<sup>2</sup> catalysts have been widely used. However, the drawback is the rarity of Pt. Therefore, the development of alternative catalysts containing base metals has attracted great interest in this research field. Among these base metal alternatives, iron,<sup>3–6</sup> cobalt<sup>6–15</sup> and nickel<sup>16</sup> complexes have been especially investigated due to their earth abundancy. We reported that Feiminobipyridine complexes catalyzed the hydrosilylation of olefins<sup>5</sup> and ketones<sup>17</sup> in good yields and at appropriate reaction rates. These series of Fe complexes prefer ketone hydrosilylation to olefin hydrosilylation; the reaction of a

mixture of olefin and ketone with hydrosilane dominantly produces a corresponding ketone hydrosilylation product.<sup>8</sup> We also reported that the corresponding Co complexes containing an iminobipyridine ligand showed different and unique reactivity for hydrosilvlation toward olefin and ketone: the Co complex showed olefin selectivity and switchable chemoselectivity from olefin to ketone by addition of pyridine to the reaction system.<sup>8</sup> However, the Co-iminobipyridine system has a weakness; it provides a mixture of anti-Markovnikov and Markovnikov hydrosilylation products in the reaction of aliphatic olefins with hydrosilane. In other words, the Co-iminobipyridine complex shows good chemoselectivity for olefin/ketone hydrosilylation, but poor regioselectivity for aliphatic olefins. This is a character opposite to that of Fe-iminobipyridine complex which has good regioselectivity: anti-Markovnikov selectivity for an aliphatic olefin hydrosilylation.

Most Fe catalysts reported so far facilitate anti-Markovnikov selective hydrosilylation of olefins. For instance, Chirik and coworkers reported anti-Markovnikov selective hydrosilylation of olefins catalyzed by pyridine diimine iron dinitrogen complexes, which gave organosilicon compounds from primary, secondary and tertiary hydrosilanes.<sup>4</sup> On the other hand, although many cobalt catalysts for olefin hydrosilylation have been reported, the number of cobalt complexes exhibiting high regioselectivity is limited compared to that of iron complexes, since most cobalt catalysts give a mixture of anti-Markovnikov and Markovnikov products. Moreover, the cobalt catalysts cause some side reactions such as hydrogenation, dehydrogenative silvlation and isomerization, which afford many undesired by-products. The difficulty of suppression of these side reactions is also the major obstacle to the development of highly regioselective cobalt-catalyzed olefin hydrosilylation.

There are several reports of anti-Markovnikov selective and Markovnikov selective hydrosilylations of olefins catalyzed by Co complexes. Deng<sup>10</sup> reported anti-Markovnikov selective hydrosilylation of olefins using cobalt complexes bearing an NHC ligand. Holland<sup>11</sup> performed anti-Markovnikov selective hydrosilylation of terminal olefins in a solvent free system without any external activators. Huang<sup>6</sup> reported Markovnikov selective hydrosilylation catalyzed by a Co complex bearing a PNN pincer ligand. Lu<sup>12</sup> demonstrated highly Markovnikov selective and enantioselective hydrosilylation of olefins, which tolerated other reactive functional groups such as ketone and epoxy groups.

It is not yet clear how the selectivity between anti-Markovnikov and Markovnikov compounds is expressed, although ligand substituents are considered to be related to the selectivity. We herein report that a Co complex catalyst without regioselectivity in hydrosilylation of olefins can be converted into a Co catalyst with regioselectivity simply by changing a substituent on the ligand of the complex, and we also considered the reasons for its selectivity.

#### 2. Results and Discussion

**Preparation of Co-Iminobipyridine Complexes.** Scheme 1 shows the synthetic route for Co complexes bearing an iminobipyridine ligand, **Co(R)**, where **R** indicates a substituent on the imino nitrogen in an iminobipyridine ligand. The route is similar to that of the corresponding Fe-iminobipyridine





complexes reported so far.<sup>5</sup> 6-Acetyl-2,2'-bipyridine (La) was synthesized according to the previous report.<sup>5</sup> Condensation reaction between La and 2,4,6-trimethylphenylamine or cyclohexylamine afforded corresponding iminobipyridine derivatives (Lb, Lc). Finally, the introduction of CoBr<sub>2</sub> into iminobipyrine ligands Lb and Lc resulted in the formation of Co-iminobipyridine complexes, Co{Mes} and Co{Cy}, respectively. These cobalt complexes were identified by elemental analyses and FAB-MS. Since suitable single crystals of these Co-iminobipyridine complexes were obtained from slow diffusion of ether into the acetone solution of the Co complexes, the structures were confirmed by the X-ray diffraction analyses.

Hydrosilylation Catalyzed by Co(R). In order to evaluate the catalytic activity of Co(R) complexes, Co(Mes) and Co(Cy) were subjected to catalytic hydrosilylation of 1-octene with diphenylsilane (Ph<sub>2</sub>SiH<sub>2</sub>) (Scheme 2). Complex Co(Mes) or Co(Cy) (0.1 mol% based on the initial concentration of Ph<sub>2</sub>SiH<sub>2</sub>) was placed into a Schlenk tube under N<sub>2</sub>. Then, Ph<sub>2</sub>SiH<sub>2</sub> and 1-octene (1:1 molar ratio) were added to the tube, and finally NaBHEt<sub>3</sub> (1 mol%) was added as a reductant to form a catalytically active Co(0) species. After stirring at 25 °C for 3 h, the mixture was diluted with an excess amount of hexane to quench the reaction, and the Co complex was removed through a short dry column (silica gel). After removal of hexane, the resulting solution was analyzed by GC to determine the yield of products. The results are listed in Table 1.

When Co(Mes) was used as a precatalyst, anti-Markovnikov product (1) and Markovnikov product (2) were formed in 51% and 27% yields, respectively (Entry 1). On the other hand, in the reaction when Co(Cy) was used, only anti-Markovnikov product (1) was formed in 68% yield (Entry 2).

Next, solvent effect on the hydrosilylation was investigated. Toluene, THF, CH<sub>3</sub>CN, pyridine, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> were examined. Toluene and THF were applicable to **Co(Mes)**, but the yields of **1** were lower than that in neat conditions (Entries 3 and 4). In both cases, **1** and **2** were formed, but the main product was changed depending on the solvent used. The reason has not been clear yet. The catalytic hydrosilylation when Co(Cy) was used in toluene and THF maintained anti-Markovnikov selectivity, although the product yields decreased (Entries 9 and 10). When CH<sub>3</sub>CN and pyridine were used as solvents, a remarkable decrease of the yields was observed for Co(Mes) and Co(Cy) (Entries 5, 6 for Co(Mes) and 11, 12 for Co(Cy)). These results can be interpreted that these solvents coordinate strongly to the central metal Co, to reduce or kill the catalytic activity. Halogenated solvents,  $CH_2Cl_2$  and  $CHCl_3$ were also not applicable to either reaction system (Entries 7, 8, 13, and 14). These results showed that the neat conditions were optimal for this reaction system.

Temperature Dependence on Hydrosilylation Catalyzed by Co(R). Temperature effect on this hydrosilylation system was also examined. In the neat conditions, the reactions of 1octene with  $Ph_2SiH_2$  were conducted at 25 °C, 50 °C and 80 °C, using Co(Mes) and Co(Cy) as precatalysts (Scheme 3). The results are summarized in Table 2.

Table 1. Results of hydrosilylation in several solvents

Entry	Precatalyst <sup>a</sup>	Solvent <sup>b</sup>	Yields (%) <sup>c</sup>		C -1
			1	2	Selectivity
1	Co(Mes)	neat	51	27	65:35
2	Co(Cy)	neat	68	trace	>99:<1
3	Co(Mes)	toluene	46	31	60:40
4	Co(Mes)	THF	20	36	36:64
5	Co(Mes)	CH <sub>3</sub> CN	5	2	71:29
6	Co(Mes)	pyridine	3	1	75:25
7	Co(Mes)	CH <sub>2</sub> Cl <sub>2</sub>	3	2	60:40
8	Co(Mes)	CHCl <sub>3</sub>	N.D.	N.D.	_
9	Co(Cy)	toluene	41	trace	>99:<1
10	Co(Cy)	THF	44	trace	>99:<1
11	Co(Cy)	CH <sub>3</sub> CN	N.D.	N.D.	_
12	Co(Cy)	pyridine	trace	N.D.	_
13	Co(Cy)	CH <sub>2</sub> Cl <sub>2</sub>	N.D.	N.D.	_
14	Ϲ៰⟨Ϲy⟩	CHCl <sub>3</sub>	N.D.	N.D.	

<sup>a</sup>3.7 µmol. <sup>b</sup>711 µL, <sup>c</sup>GC yield.





When Co(Mes) was used, both anti-Markovnikov product (1) and Markovnikov product (2) were produced. The total yield and the anti-Markovnikov selectivity gradually increased accompanied with elevation of temperature (Entries 1-3). However, perfect regioselectivity of Co(Mes) could not be obtained even at 80 °C. On the other hand, when Co(Cy) was used, perfect anti-Markovnikov selectivity was achieved at all temperatures (Entries 4-6). Temperature elevation from 25 °C to 50 °C improved the product yield, and quantitative conversion was achieved at 50 °C. However, the yield of 1 slightly decreased at 80 °C, which would come from less thermal stability of catalytically active species derived from Co(Cy). Therefore, in a reaction using Co(Cy) as a precatalyst, in other words, by using a complex in which the Mes substituent in Co(Mes) is changed to a Cv substituent, the anti-Markovnikov hydrosilvlation product can be quantitatively and regioselectively observed.

Crystal Structure of the Cobalt Complexes Co(R). The crystal structures of Co(Mes) and Co(Cy) are shown in Figure 1 and selected bond lengths and angles are summarized in Table 3. For both complexes, the iminobipyridine ligand coordinates to a cobalt center via three nitrogen atoms with meridional configuration. In addition, two Br ligands coordinate to the Co center to form a pseudo trigonal bipyramidal structure. The bond lengths between Co and the nitrogen in the central pyridine ring (Co-N2) are shorter than the other Co-N bonds. The situation is similar to the Fe-iminobipyridine complex<sup>5</sup> and the Co complexes with a terpyridine ligand (tpy).<sup>15</sup> The Co-N bond lengths of terminal pyridines (Co-N1) are 2.182(2) Å and 2.179(2) Å for Co(Mes) and Co(Cy) respectively, which are similar to the corresponding bond lengths of Co-terpyridine complex,  $[Co(tpy)(OAc)(H_2O)_2]OAc^{15}$  (2.1596(15)Å and 2.1700(16) Å) indicating that the donor ability of the terminal pyridine in Co(R) is similar to that in [Co(tpy)(OAc)- $(H_2O)_2$ ]OAc.

Table 2. Temperature effect on Co(R) catalyzed hydrosilylation system

Entry	Precatalyst	Temp. (°C)	Yields (%) <sup>a</sup>		Salaativity
			1	2	Selectivity
1	Co(Mes)	25	51	27	65:35
2	Co(Mes)	50	60	27	69:31
3	Co(Mes)	80	68	24	74:26
4	Co(Cy)	25	68	trace	>99:<1
5	Co(Cy)	50	>99	trace	>99:<1
6	Co(Cy)	80	85	trace	>99:<1

<sup>a</sup>GC yield.



Figure 1. ORTEP drawings of Co(Mes) (left) and Co(Cy) (right) with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

The catalytically active species derived from Co(Mes) and Co(Cy) is considered to be A in Scheme 4 (vide infra). Hereafter, the active species having Mes and Cy substituents will be referred to as A(Mes) and A(Cy), respectively. In the active species A, space used for hydrosilylation of olefins (active space) is considered to be the open space where two Br ligands were located originally. Let us consider how the Mes and Cy substituents affect the active space. The bond length

	Co(Mes)	Co(Cy)
Co-N1	2.182(2)	2.179(2)
Co–N2	2.049(2)	2.0289(19)
Co–N3	2.223(2)	2.170(2)
Co-C13	3.311(3)	3.257(3)
Co-C14	4.503(3)	4.000(3)
Co-C18	4.133(3)	3.362(3)
Co-Br1	2.4135(8)	2.4203(4)
Co–Br2	2.4189(8)	2.4399(5)
C12–C13	2.838(4)	2.927(4)
C12C14	3.437(4)	3.520(4)
C12C18	3.447(4)	4.309(5)
N1–Co–Br1	93.05(6)	91.68(6)
N1–Co–Br2	95.41(7)	92.12(7)
Br1–Co–Br2	109.53(2)	118.418(18)

**Table 3.** Selected distances [Å] and angles [°]

of Co-N3 is clearly longer for Co(Mes) than for Co(Cy) (2.223(2) vs 2.170(2) Å). From this, it may be said that Mes is bulker than Cy, but this does not mean that the active space of A(Mes) is smaller than that of A(Cy). Since the Mes plane is perpendicular to the iminobipyridine plane in Co(Mes), the main steric repulsion between the Mes and the iminobipyridine ligand is considered to be caused from the repulsion between the two Me groups in the Mes and the iminobipyridine (not the two Br ligands). Actually, the length of Co-N3 in Co(Mes) is similar to those of a Co-diiminopyridine complex<sup>18</sup> reported previously which has two Cl ligands on the Co (both lengths are 2.211(3) and 2.211(3)Å).

Next, let us see the position of the two Br ligands in Co(Mes) and Co(Cy). The Br1-Co-Br2 angle is larger for Co(Cv) (118.418(18)°) than for Co(Mes) (109.53(2)°). The two bromines are situated closer to the terminal pyridine of the bipyridine fragment for Co(Cy) (N1-Co-Br1 angle = 91.68(6)°, N1-Co-Br2 angle =  $92.12(7)^{\circ}$ ) than for Co(Mes) (N1-Co-Br1 angle =  $93.05(6)^{\circ}$ , N1-Co-Br2 angle =95.41(7)°). Here, it is worth noting that the four Co-Br lengths (two for Co(Mes) and two for Co(Cy)) are almost the same (2.4135(8)-2.4399(5)Å). It suggests that these four Co-Br bonds have almost the same bond energies.

A mesityl group takes a planar geometry, while a cyclohexyl group adopts a chair conformation. The extent to which the Mes and Cy groups approach the Co was estimated from the lengths between Co and the substituents. Especially, the lengths between Co and C13, C14 and C18 can be expected to give







Figure 2. Topographic sterical map of Lb (a) and Lc (b), calculated by SambVca.

useful information. These lengths are 3.257(3), 4.000(3), and 3.362(3) Å, respectively, for **Co(Cy)** being shorter than those for **Co(Mes)** (3.311(3), 4.503(3), and 4.133(3) Å). In particular, the extent to which the length between Co and C14 becomes shorter is the greatest because the cyclohexyl group tilts from the vertical plane to the iminobipyridine ligand. These characters of **Co(Cy)** clearly indicate that the Cy substituent is located closer to Co center than the Mes of **Co(Mes)**.

All these data shown above seem to suggest that the active space of A(Cy) is smaller than that of A(Mes) (Scheme 4(a)). In addition, we estimated the protrusion of the Cy group into the active space. The topographic steric map obtained from SambVca<sup>19</sup> is useful to compare the active space of two complexes. The steric maps of Lb and Lc (Scheme 1) for A(Mes) and A(Cy) were calculated using the atomic coordinates of Co(Mes) and Co(Cy) based on the X-ray structures removing Co and Br ligands. Figure 2 shows the topographic steric maps of Lb and Lc visualized by SambVca, of which the center positions of the coordination spheres are indicated by Co. In the 3.5 Å radius coordination sphere, the ratio between occupied  $(V_{buried})$  and unoccupied  $(V_{free})$  space of  $\boldsymbol{Lb}$  was 49.5:50.5 (V<sub>buried</sub>:V<sub>free</sub>), and that of Lc was 50.8:49.2. The small difference of the occupancy of the coordination sphere comes from the large contribution of the bipyridine framework and the imino group which are common to Lb and Lc. The difference in the substituents on the imino nitrogen can be seen on the right sides of the two diagrams. The Cy group of Lc apparently overhangs the coordination center (red area on the right side in Figure 2(b)). These results strongly suggest that A(Cy) has a smaller active space than A(Mes) due to closer location of the Cy group to the central Co atom.

**Plausible Reaction Mechanism.** A plausible reaction mechanism is shown in Scheme 4. The precatalyst Co(R) first reacts with NaBHEt<sub>3</sub> to give the corresponding dihydrido complex, followed by H<sub>2</sub> elimination to give a Co species (A) being the active catalyst (Scheme 4(a)). Then, A reacts with hydrosilane to give a silyl hydrido complex (B) (Scheme 4(b)). Next, an olefin is inserted into the Co-H bond of B in 1,2- or 2,1-fashion, resulting in the formation of a linear alkyl complex (C) or a branched one (C'). Finally, C or C' undergoes reductive elimination to give the anti-Markovnikov product or the

Markovnikov one, together with the recovery of **A**. A similar reaction sequence has been proposed by Fout *et al.*<sup>91</sup> although the ligand on Co is slightly different; the oxidative addition of an Si-H bond in hydrosilane to Co forms a silyl hydride Co complex, followed by olefin insertion into the Co-H bond to proceed catalytic hydrosilylation of olefin. In 2017, Deng *et al.* reported that Si-H oxidative addition to a Co complex with NHC ligands takes place to form a silyl hydrido Co complex being a hydrosilylation catalyst.<sup>10b</sup>

In Scheme 4, the Co complexes that give rise to the anti-Markovnikov and the Markovnikov products are C and C', respectively. The branched alkyl group of C' apparently requires larger active space than the linier alkyl group of C.

The crystal structures of Co(Mes) and Co(Cy) suggest that the cyclohexyl substituent narrows the active space around Co more than the Mes substituent (*vide supra*). It can be speculated that the steric effects of Mes and Cy observed for Co(Mes) and Co(Cy) are also observed for C and C'. In other words, when Co(Mes) is used, two intermediates C and C' are probably formed because the Mes substituent does not narrow the active space as much as the Cy substituent (Figure 3a), leading to a mixture of 1,2- and 2,1-insertion products (anti-Markovnikov and Markovnikov products). On the other hand, when Co(Cy)is used, the narrowed active space due to the Cy substituent allows formation of only C intermediate (Figure 3b). Thus, Co(Cy) selectively produces the anti-Markovnikov product.

The catalytic cycle shown in Scheme 4 is a tentative one, which proceeds through a silyl hydride Co complex (**B**) formed by oxidative addition of an Si-H bond in HSiR<sub>3</sub> to **A**. It should be added that the experimental results obtained in this study cannot rule out other mechanisms starting from a Co-H or Co-Si complex; it was suggested that Co-H forms from the reaction of CoCl<sub>2</sub> complex with NaBHEt<sub>3</sub> generating 0.5 eq H<sub>2</sub>,<sup>9i,9j</sup> and Co-Si forms via  $\sigma$ -bond metathesis of hydrosilane and Co-alkyl species appeared in the catalytic cycle of Co-H.<sup>9i,13</sup>

Substrate Scope of Olefins. Since it was found that the anti-Markovnikov product was obtained selectively when Co(Cy) was used as a precatalyst in the reaction of 1-octene, we examined hydrosilylation reactions of several other olefins by using Co(Cy) in the optimized conditions (Table 2, Entry 5). The results are shown in Scheme 5. Vinylcyclo-





hexane reacted with  $Ph_2SiH_2$  effectively to give the corresponding product (3) in 91% yield. An aromatic olefin (styrene) also reacted to give 4. Next, the catalytic system was extended to the reactions of olefins containing a functional group. As for an olefin bearing an epoxy group, 1,2-epoxy-5-hexene was converted into the corresponding alkylsilane compound (5) in

84% yield without any by-product. A tertiary amino group was applicable, but the reaction was slow. The reaction of *N*,*N*-dimethylallylamine with  $Ph_2SiH_2$  for 3 h produced the corresponding product (6) in 33% yield but when the reaction time was extended to 72 h, the yield of 6 was significantly improved (87%). Co(Cy) was not available for the hydrosilylation of olefins bearing a chloro group, although the Fe-iminobipyridine complex was catalytically active for them.<sup>5</sup> Similarly, Co(Cy) was not effective for an olefin with an ester group. Although Fe-iminobipyridine complexes catalyze the hydrosilylation of cyclohexene as a model compound of an internal olefin,<sup>5b</sup> Co(Cy) did not catalyze this reaction at all.

We reported that **Co(Mes)** shows a unique catalytic property in terms of chemoselective hydrosilylation with  $Ph_2SiH_2$  of 3acetylstylene having both olefin and ketone moieties in the molecule: olefin selective hydrosilylation in neat conditions and ketone selective hydrosilylation in pyridine.<sup>8</sup> Therefore, we investigated whether **Co(Cy)** also exerts its selectivity, and found that the olefin selective reaction took place in neat reaction conditions to give **7a** in 51% yield and the ketone selective reaction occurred in pyridine to produce **7b** in 67% yield (Scheme 5).

As comparison, hydrosilylation of sterically encumbered olefins was conducted in the presence of Co(Mes). When vinylcyclohexane was used, anti-Markovnikov selective product 3 was obtained in 95% yield. Styrene was also converted to 4 in 88% yield. For the hydrosilylation of 1,2-epoxy-5hexene and N,N-dimethylallylamine, mixtures of a few products were obtained; the mixtures from both olefins probably contained anti-Markovnikov and Markovnikov compounds, but Markovnikov products were not identified, since both Markovnikov samples were not isolated yet. 5-Hexene-2-one underwent not olefin hydrosilylation but ketone hydrosilylation quantitatively as well as Co(Cy) did. In a previous report,<sup>8</sup> we conducted hydrosilylation of 3-acetylstyrene in neat conditions and in pyridine, which resulted in the production of 8a and 8b in 93% and 90% yields, respectively. Overall, Co(Mes) showed higher reactivity and less regioselectivity than Co(Cy) probably due to relatively large active space of Co(Mes).

Substrate Scope of Hydrosilanes. We finally studied the substrate scope of hydrosilanes using 1-octene as an olefin substrate. Primary, secondary and tertiary silanes were employed for Co(Cy) system (Scheme 6). In most cases of hydrosilanes except Et<sub>3</sub>SiH and Me<sub>3</sub>SiOMe<sub>2</sub>SiH, anti-Markovnikov products were obtained selectively. PhSiH<sub>3</sub> could be applied to this reaction system to give the quantitative amount of the corresponding product, 9. As secondary silanes, PhMeSiH<sub>2</sub> and Et<sub>2</sub>SiH<sub>2</sub> were applicable to this catalytic system giving **10** and 11 in 87% and 75% yields, respectively. However, tertiary silanes caused significant decrease of yields. In the reaction using  $Et_3SiH$ , the corresponding product (12) was not obtained. Me<sub>2</sub>PhSiH and MePh<sub>2</sub>SiH gave the corresponding products, 13 and 14, but the yields were quite low even in the long-time reaction (72 h). Pentamethyldisiloxane was also employed as a substrate, but the hydrosilylated product (15) was not obtained at all. These results can be understood to reflect that Co(Cv)hardly serves as a catalyst in the reaction of bulky hydrosilanes because the Cy substituent narrows active space for the reaction.



# 3. Conclusion

Many cobalt catalysts for hydrosilylation of olefins have been reported, but most of them produce a mixture of anti-Markovnikov and Markovnikov products. Only a limited number of Co catalysts show regioselective hydrosilylation, but an effective way to control the selectivity has not been reported.

We found that a Co-iminobipyridine complex with a Mes substituent on the imino nitrogen (Co{Mes}) shows a catalytic activity for hydrosilylation of olefins to give a mixture of anti-Markovnikov and Markovnikov products whereas a Coiminobipyridine complex with a Cy substituent (Co{Cy}) produces the anti-Markovnikov product selectively. The X-ray structures of Co{Mes} and Co{Cy} suggest that the Cy substituent narrows active space around the Co more than the Mes substituent but these two substituents did not give a large difference in the Co-Br bond lengths. Therefore, we proposed that the steric demand rather than the electronic effect of the Cy substituent plays a dominant role to show the regioselective hydrosilylation.

## 4. Experimental Section

General Information. All reactions were carried out under N<sub>2</sub> using Schlenk techniques. All solvents were dried and stored under N<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent were used as an internal standard. NMR measurement of the cobalt complexes were difficult because they were practically insoluble in common solvents. GC analyses were carried out using a Shimadzu GC-2014 equipped with an Rtx-5MS (RESTEC, 30 m, 0.25 mmID, 0.25 µm) capillary column. Product yields were determined based on the calibration curve of each authentic sample. FAB-MS measurement was conducted using JEOL JMS-700(2).

**Materials.** La and Lb in Scheme 1 were synthesized according to literature methods.<sup>5</sup> Hydrosilylation products, 1,<sup>91</sup> 2,<sup>6</sup> 3,<sup>90</sup> 4,<sup>6</sup> 6,<sup>15</sup> 7,<sup>20</sup> 8a,<sup>8</sup> 8b,<sup>8</sup> 9,<sup>6</sup> 10,<sup>21</sup> 11,<sup>16e</sup> 13<sup>22</sup> and 14<sup>23</sup> were

synthesized as authentic samples according to the literature. All other chemicals were purchased from commercial sources and used as received.

Typical Procedure for the Catalytic Hydrosilylation of Olefins Using a Co Precatalyst. Co{Mes} (2.0 mg,  $3.7 \mu \text{mol}$ ) or Co{Cy} (1.8 mg,  $3.7 \mu \text{mol}$ ) was placed in a Schlenk tube. The air in the tube was replaced by N<sub>2</sub>. 1-Octene ( $571 \mu L$ , 3.74 mmol) and diphenylsilane ( $711 \mu L$ , 3.74 mmol) were added to the tube. Sodium triethylborohydride (1.0 M in toluene,  $37 \mu L$ ,  $37 \mu \text{mol}$ ) was added to the tube for the activation of the precatalyst. The homogenous wine-red solution was heated at 50 °C and stirred for 3 h. Then, the solution was exposed to air. An excess amount of hexane was added to the solvent and the catalyst was removed through short column (silica gel). After concentration, the product was subjected to GC analysis to determine the yield.

N-(1-[2,2'-Bipyridine-6-yl]ethylidene)-cyclohexylamine A mixture of cyclohexylamine (1.8 mL, 15 mmol), La (Lc). (2.0 g, 10 mmol), and p-toluene sulfonic acid monohydrate (53 mg, 0.30 mmol) in toluene (22 mL) was heated to reflux temperature for 15 h using a Dean-Stark apparatus. After the mixture was cooled to room temperature, K<sub>2</sub>CO<sub>3</sub> (41 mg, 0.60 mmol) was added to the mixture and stirred for 1 h. After filtration, volatile materials were removed from the filtrate under reduced pressure, and the residue was washed with hexane  $(4 \text{ mL} \times 3)$ and dried to obtain c as a yellow powder (0.76 g, 27%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.25–1.62 (m, 5H), 1.68– 1.78 (m, 3H), 1.82–1.88 (m, 2H), 2.48 (s, 3H, CCH<sub>3</sub>), 3.58– 3.62 (m, 1H, NCH), 7.30 (ddd, 1H, J = 8.0, 4.8, 1.2 Hz), 7.82 (dd, 1H, J = 8.0, 8.0 Hz), 7.83 (ddd, 1H, J = 8.0, 8.0, 1.2 Hz), 8.11 (dd, 1H, J = 8.0, 0.8 Hz), 8.39 (dd, 1H, J = 8.0, 0.8 Hz), 8.52 (d, 1H, J = 8.0 Hz), 8.68 (d, 1H, J = 4.8 Hz).  $^{13}C{^{1}H} NMR$  (100.4 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 13.75, 24.99, 25.98, 33.62, 60.43, 121.11, 121.19, 121.21, 123.75, 136.96, 137.36, 149.24, 154.50, 156.48, 157.81, 164.07. Elemental analysis. Calcd. for C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>: C, 77.38; H, 7.58; N, 15.04; Found: C, 77.08; H, 7.54; N, 14.83. HRMS (DART):  $[M + H]^+$  Calcd. for  $C_{18}H_{22}N_3$ : 280.18137; Found: 280.18191.

*N*-(1-[2,2'-Bipyridine-6-yl]ethylidene)-cyclohexylamine Cobalt(II) Bromide (Co(Cy)). CoBr<sub>2</sub> (0.297 g, 1.36 mmol) and Lc (0.379 g, 1.36 mmol) were placed in a Schlenk tube. The air in the tube was replaced by N<sub>2</sub>. THF (12 mL) was added to the tube and the mixture was stirred for 15 h. The precipitate formed during the reaction was collected by filtration and washed with THF (4 mL × 2) and hexane (4 mL × 2) and dried to obtain Co(Cy) as a yellowish powder (0.51 g, 76%). Elemental analysis. Calcd. for C<sub>40</sub>H<sub>52</sub>Br<sub>4</sub>Co<sub>2</sub>N<sub>6</sub>O<sub>2</sub> [2M + THF + H<sub>2</sub>O]: C, 44.22; H, 4.82; N, 7.74; Found: C, 44.34; H, 4.25; N, 7.77. HRMS (FAB): calcd for C<sub>21</sub>H<sub>18</sub>BrF<sub>3</sub>N<sub>3</sub>Co [M - Br]<sup>+</sup>, 417.0251; found, 417.0266.

X-ray Diffraction Data Collection and Determination of the Structure. The single crystals of Co-iminobipyridine complexes were obtained from slow diffusion of ether into an acetone solution of Co complexes. Data for Co(Mes) were collected at 150(2) K with a Rigaku AFC11 with Saturn 724+ CCD diffractometer using monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.710747$  Å). Data for Co(Cy) were collected at 220(2) K with a Rigaku/MSC Mercury CCD diffractometer using graphite monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71070$  Å). Those

Table 4. Crystallographic data for Co(Mes) and Co(Cy)

	Co(Mes)	Co(Cy) •0.5 acetone			
Formula	C <sub>21</sub> H <sub>21</sub> Br <sub>2</sub> CoN <sub>3</sub>	C <sub>19.50</sub> H <sub>24</sub> Br <sub>2</sub> CoN <sub>3</sub> O <sub>0.5</sub>			
Formula weight	534.16	527.17			
Crystal size/mm	$0.120 \times 0.090 \times 0.070$	0.320 × 0.320 × 0.050			
Crystal system	Orthorhombic	Monoclinic			
Space group	Pbca	C2/c			
a/Å	16.071(5)	18.1759(11)			
b/Å	16.266(5)	13.0093(6)			
c/Å	16.019(5)	18.6602(10)			
$\alpha/^{\circ}$	90	90			
$eta/^\circ$	90	107.864(2)			
γ/°	90	90			
$V/Å^3$	4187(2)	4199.6(4)			
Ζ	8	8			
T/K	150(2)	220(2)			
$D_{calcd}/\mathrm{gcm^{-3}}$	1.695	1.668			
F(000)	2120	2104			
Total reflections	55050	24333			
Unique reflections $(R_{int})$	4786 (0.0584)	4827 (0.0332)			
Refln./Param. ratio	19.298	14.991			
$R_1^a [I > 2\sigma(I)]$	0.0379	0.0348			
$wR_2^{b}$ (all data)	0.0912	0.0851			
GOF on $F^2$	1.127	1.069			
${}^{a}R_{1} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} . {}^{b}wR_{2} = [\Sigma \{w(F_{o}^{2} - F_{c}^{2})^{2}]^{1/2}.$					

data were processed using CrystalClear program (Rigaku). The structures were solved by direct methods using SIR97 and refined using SHELXL-2018/3 (Sheldrick, 2018).<sup>24</sup> These crystallographic data are shown in Table 4.

**Visualization of Catalytic Pockets of Co Complexes.** The topographic steric map of each Co complex shown in Figure 2 was calculated by SambVca.<sup>19</sup> Atomic coordinates based on X-ray structures of the Co complexes were used for the calculation. The coordination sphere was set the radius which was 3.5 Å centered at Co atom. From the structure obtained by X-ray structural analysis, Co and two Br atoms were removed, and the topographic steric map and occupancy of the ligand were obtained.

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## **Supporting Information**

 $^1HNMR$  and  $^{13}C\{^1H\}$  spectra of c and 5. This material is available on http://dx.doi.org/10.1246/bcsj.

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