ORGANOMETALLICS
Communication
Cite This: Organometallics XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

# Cobalt-Catalyzed Asymmetric Hydrogenation of Vinylsilanes with a Phosphine−Pyridine−Oxazoline Ligand: Synthesis of Optically Active Organosilanes and Silacycles

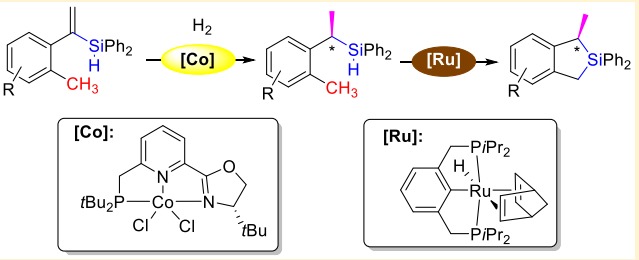
Ziqing Zuo,[†] Songgen Xu,[†] Lei Zhang,[†] Lan Gan,[†] Huaquan Fang,[†] Guixia Liu,*[,†] and Zheng Huang*[,†,‡]

[†]State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[‡]Chang-Kung Chuang Institute, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, People's Republic of China

Supporting Information

**ABSTRACT:** The asymmetric hydrogenation of vinylsilanes catalyzed by a new $C_1$-symmetric phosphine−pyridine−oxazoline cobalt complex is described. The method provides an efficient approach to chiral tertiary silanes with enantioselectivities up to 99% ee. Furthermore, the *o*-methyl-substituted benzylic silane products undergo ruthenium-catalyzed dehydrogenative silylation to produce chiral benzosilolanes in high yields without racemization of the stereogenic center $\alpha$ to the quaternary Si atom.






Asymmetric hydrogenation of alkenes offers a powerful approach to optically active compounds due to atom economy and operational simplicity and has been widely used in the pharmaceutical, agrochemical, and fine-chemical industries.[1] While this area has been dominated by precious-metal catalysts,[2−4] the demand for low-cost and sustainable catalysts has recently inspired many efforts on the development of base-metal catalysts.[5] Perhaps more importantly, the distinct electronic structures and redox properties of base-metals may provide new opportunities for catalyst development with novel reactivity and selectivity.[6] Over the past decades, remarkable progress has been achieved in the asymmetric hydrogenation of alkenes using cobalt catalysts (Figure 1).[7] The pioneering work of Ohgo showed that the asymmetric hydrogenation of $\alpha,\beta$-unsaturated carbonyl derivatives with (dimethylglyoximato)cobalt(II) catalysts led to moderate enantioselectivity.[7a] By utilizing chiral semicorrin cobalt catalysts, Pfaltz reported the enantioselective hydrogenation of $\alpha,\beta$-unsaturated esters with ee values up to 97%.[7b] More recently, Chirik disclosed that Co(II) complexes of chiral bidentate phosphines effected highly enantioselective hydrogenation of amino acid and enamide derivatives.[7e] Beyond chelating alkenes, unfunctionalized alkenes could also be hydrogenated under cobalt catalysis.[7c,d] Chirik developed $C_1$-symmetric bis(imino)pyridine (PDI) cobalt complexes for asymmetric hydrogenation of $\alpha$-substituted styrene derivatives[7f] and benzo-fused cyclic alkenes.[7g] Lu demonstrated that iminopyridine−oxazoline (IPO) cobalt complexes enabled highly enantioselective asymmetric hydrogenation of 1,1-diarylethenes.[7h]

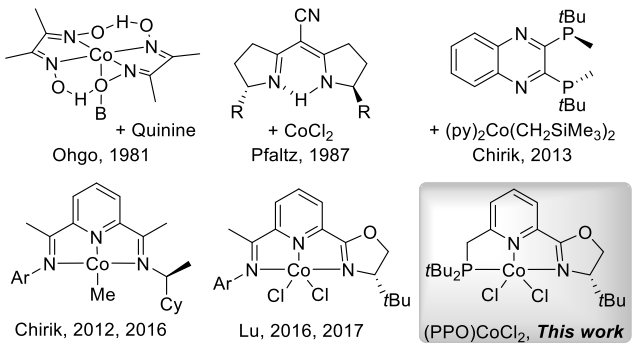



**Figure 1.** Chiral cobalt catalysts for asymmetric alkene hydrogenation.

Despite the achievements in cobalt-catalyzed asymmetric hydrogenation of chelating olefins and unfunctionalized olefins, the asymmetric hydrogenation of vinylsilanes still remains rare.[4e] In 2017, Lu and co-workers developed a highly regio- and enantioselective (IPO)Co-catalyzed sequential Markovnikov hydrosilylation/hydrogenation of terminal aryl alkynes, where highly enantioselective asymmetric hydrogenation of 1,1-arylsilyl substituted alkenes was involved.[7i]

**Special Issue:** Asymmetric Synthesis Enabled by Organometallic Complexes

**Received:** January 31, 2019



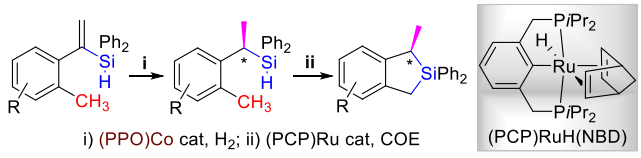

DOI: 10.1021/acs.organomet.9b00067
Organometallics XXXX, XXX, XXX−XXX

However, the scope in this work was restricted to substrates without ortho substituents in the aryl groups. From a synthetic point of view, the introduction of *o*-methyl substituents is desired because the dehydrogenative silylation between the *o*-methyl C−H bond and a Si−H bond can potentially produce novel chiral silolanes.

Chiral organosilanes are valuable building blocks in organic synthesis and materials science as well as medicinal chemistry. In addition, a carbon to silicon switch (sila substitution) is a potentially useful tool for the development of silicon-based drugs,[8] luminescent materials,[9] and odorant compounds.[10] The fundamental difference between C and Si atoms (e.g., covalent radius and electronegativity) could impart, ideally, enhanced physicochemical and biological properties to the sila congeners.[11] Given the prevalence of chiral carbon-based cyclic units in bioactive molecules, it is significant to develop an efficient way to synthesize the silacycles with high enantiopurity.

On the basis of our continuous interest in development of chiral tridentate ligands for transition-metal catalysis,[12] we report herein the synthesis of a new chiral phosphine−pyridine−oxazoline (PPO) ligand and their application in Co-catalyzed asymmetric hydrogenation of vinylsilanes to afford optically active organosilanes. High activity and enantioselectivity can be achieved for a broad range of substrates with various substitution patterns on the aryl groups. Importantly, when sterically hindered 1-(*o*-tolyl)vinylsilanes were used, the hydrogenation products could be further transformed to chiral silolanes with excellent enantiopurity by Ru-catalyzed intramolecular C($sp^3$)−H bond dehydrogenative silylation (Scheme 1).[13]

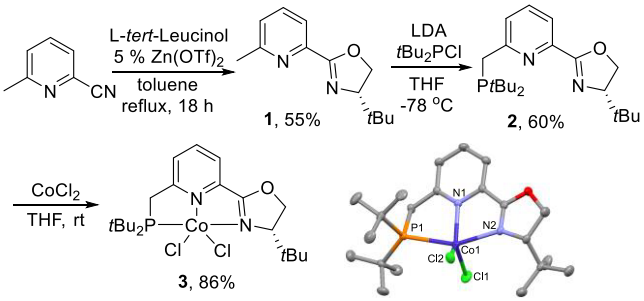
**Scheme 1. Synthesis of Chiral Benzosilolanes**




Our initial efforts were focused on the development of a cobalt catalyst for asymmetric hydrogenation of α-vinylsilanes. During this endeavor, a new type of phosphine-containing tridentate chiral ligand, phosphine−pyridine−oxazoline (PPO), was designed. In comparison with the iminopyridine−oxazoline (IPO) ligands initially developed by our group[12a] and Lu's[14] group independently for cobalt-catalyzed asymmetric alkene hydroboration, the $C_1$-symmetric PPO ligand retains the pyridine−oxazoline part for enantiocontrol but substitutes the π-accepting imino subunit with a more electron donating di-*tert*-butylphosphine group.

The synthesis of the enantiopure (PPO)$CoCl_2$ is outlined in Scheme 2. Treatment of 6-methylpicolinonitrile with L-*tert*-leucinol in the presence of $Zn(OTf)_2$ gave the pyridine−oxazoline complex **1**. Deprotonation of the methyl group at the 6-pyridyl position in **1** with LDA, followed by addition of electrophilic $tBu_2PCl$ reagent, generated phosphine−pyridine−oxazoline ligand **2** in moderate yield. The Co(II) dichloride complex **3** was formed in high yield by reaction of complex **2** with anhydrous $CoCl_2$. The Co(II) complex **3** shows broadened and paramagnetically shifted resonances in the $^1H$ NMR spectra. Single-crystal X-ray diffraction analysis of

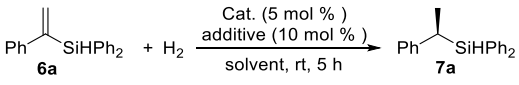
**Scheme 2. Synthesis and Molecular Structure of (PPO)$CoCl_2$ 3**



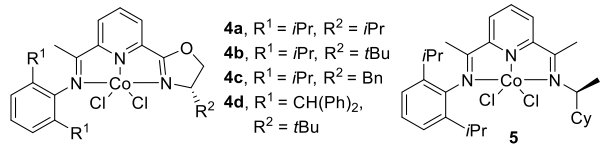

complex **3** reveals a distorted-square-pyramidal geometry around the Co center.[15]

We commenced our study by examining a series of Co catalysts with chiral tridentate ligands for the asymmetric hydrogenation of diphenyl(1-phenylvinyl)silane **6a** (Table 1). The IPO cobalt complexes **4a**−**d**, upon activation with $NaBHEt_3$, effected the hydrogenation of **6a** with quantitative conversion under 50 bar of $H_2$ in toluene (entries 1−4). The outcomes from the runs using different IPO Co catalysts reveal that the enantioselectivity generally improves as the size of

**Table 1. Optimization for Asymmetric Hydrogenation of α-Vinylsilanes**[a]




| entry | solvent | $H_2$ (bar) | Cat | additive | yield (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | toluene | 50 | **4a** | $NaBHEt_3$ | 96 | -6 |
| 2 | toluene | 50 | **4b** | $NaBHEt_3$ | 98 | -11 |
| 3 | toluene | 50 | **4c** | $NaBHEt_3$ | 96 | -10 |
| 4 | toluene | 50 | **4d** | $NaBHEt_3$ | 98 | -50 |
| 5 | toluene | 50 | **5** | $NaBHEt_3$ | 98 | -34 |
| 6 | toluene | 50 | **3** | $NaBHEt_3$ | 94 | 62 |
| 7 | toluene | 10 | **3**[b] | $NaBHEt_3$ | 97 | 80 |
| 8 | toluene | 4 | **3** | $NaBHEt_3$ | 95 | 83 |
| 9 | toluene | 2 | **3** | $NaBHEt_3$ | 94 | 83 |
| 10 | toluene | 2 | **3** | MeLi | 93 | 82 |
| 11 | toluene | 2 | **3** | $TMSCH_2Li$ | 95 | 81 |
| 12 | benzene | 2 | **3** | $NaBHEt_3$ | 92 | 82 |
| 13 | $n$-$C_5H_{12}$ | 2 | **3** | $NaBHEt_3$ | 91 | 87 |
| 14 | THF | 2 | **3** | $NaBHEt_3$ | 92 | 85 |

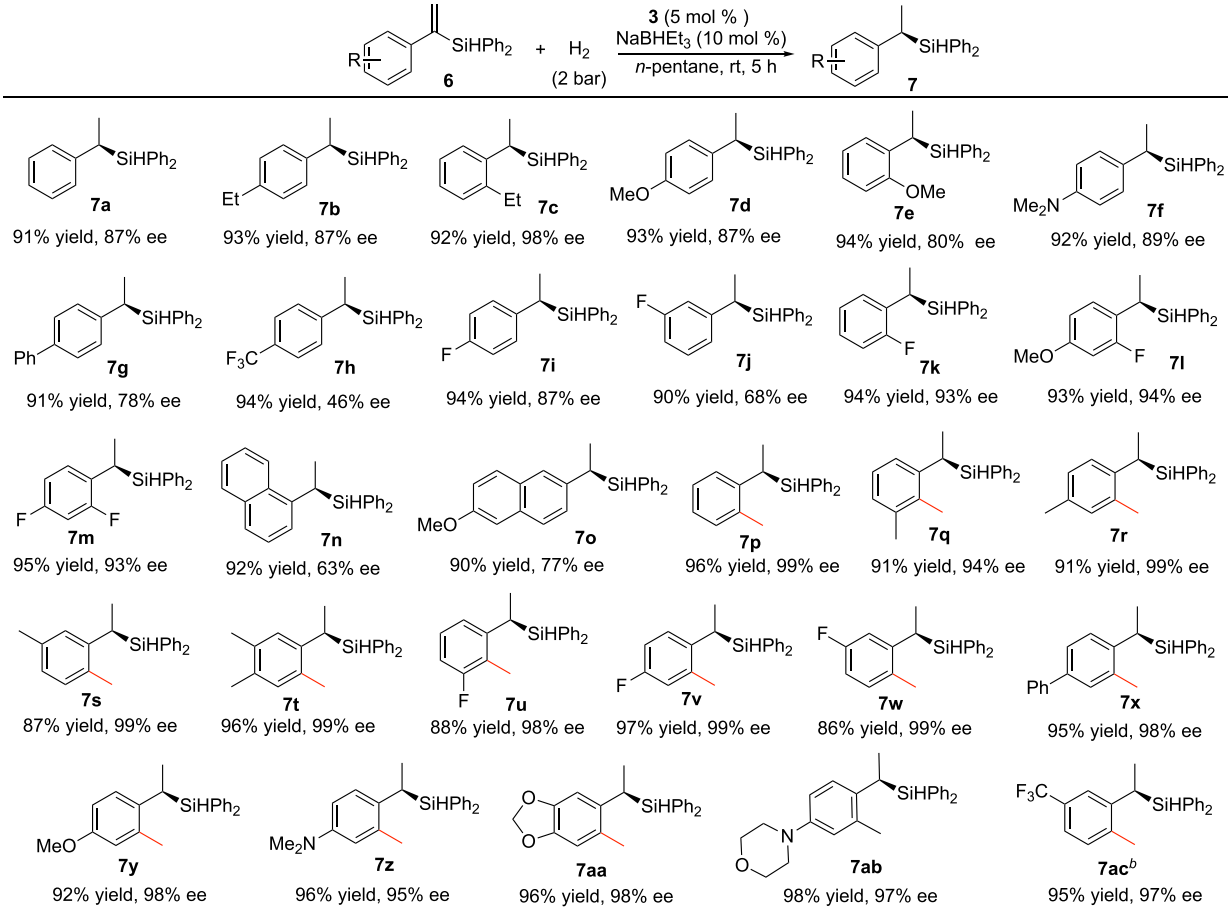



[a]Reaction conditions: **6a** (0.2 mmol), $H_2$, Cat. (5 mol %), and additive (10 mol %) in solvent (2 mL) at room temperature for 5 h. The yield of isolated product is given unless otherwise noted. ee values were determined by chiral HPLC analysis. The absolute configurations were assigned by comparison with reported optical rotations after oxidation to the related alcohols. [b]With 2.5 mol % of **3**.



DOI: 10.1021/acs.organomet.9b00067
*Organometallics* XXXX, XXX, XXX−XXX

**Scheme 3. Asymmetric Hydrogenation of Vinylsilanes**[a]




[a]Reaction conditions: **6** (1.0 equiv), $H_2$ (2 bar), **3** (5 mol %), and $NaBHEt_3$ (10 mol %) in *n*-pentane (0.1 M) at room temperature for 5 h. The yield of isolated product is given unless otherwise noted. ee values were determined by chiral HPLC analysis. The absolute configurations were assigned by comparison with reported optical rotations after oxidation to the related alcohols. [b]Under 4 bar of $H_2$.

substituents on the *N*-aryl group and the oxazoline increases, and the complex **4d** containing $(Ph)_2CH-$ at the 2,6-positions of the *N*-aryl group and *t*Bu on the oxazoline ring gave the hydrogenation product **7a** in 98% isolated yield with −50% ee (entry 4). The use of the enantiopure (PDI)Co complex **5**, which was successfully developed by Chirik in the asymmetric hydrogenation of $\alpha$-substituted styrenes, resulted in a low enantioselectivity (entry 5). To our delight, the newly developed cobalt complex **3** of the PPO ligand afforded the best enantioselectivity (62% ee) (entry 6). Reducing the pressure of $H_2$ to 10 bar led to a substantial increase in enantioselectivity (80% ee) without a detrimental effect on yield (entry 7). Performing the reactions at 4 and 2 bar of $H_2$ gave 83% ee (entries 8 and 9).

The catalyst activator is not limited to $NaBHEt_3$; the reactions with MeLi and $TMSCH_2Li$ (2 equiv relative to Co) gave **7a** with similar yield and enantioselectivity (Table 1, entries 10 and 11). However, no reaction happened with zinc as the catalyst activator.[7j] *n*-Pentane proved to be the optimal medium among the solvents investigated, furnishing **7a** in 91% isolated yield with 87% ee (entries 12−14).

With $(PPO)CoCl_2$ (**3**) as the precatalyst, we examined a wide range of vinylsilanes for enantioselective hydrogenations (Scheme 3). All substrates were prepared by Markovnikov hydrosilylation of terminal alkynes with $Ph_2SiH_2$ using the Co catalyst supported by a PyBox ligand, a procedure developed by our group.[16] All hydrogenation reactions proceeded smoothly at room temperature under 2 bar of $H_2$ with 5 mol % catalyst loading, providing the corresponding tertiary silanes in high yields with moderate to high enantioselectivities. Substrates bearing either electron-donating or -withdrawing groups were effectively hydrogenated to afford the desired products. A variety of functional groups, such as methoxy (**7d**,**e**), dimethylamino (**7f**), trifluoromethyl (**7h**), fluorine (**7i**−**k**), naphthyl (**7n**,**o**), dioxolyl (**7aa**), and morpholino (**7ab**), were all well tolerated, giving benzylsilanes in high isolated yields with moderate to high enantioselectivities. However, the current catalytic system could not tolerate some functional groups, such as ester, aryl chloride, and aryl bromide, which resulted in low conversion. It is noteworthy that the position of the substituents on the aryl ring has a significant effect on enantioselectivity. Normally, higher enantioselectivities were obtained from substrates bearing ortho-substituted aryl rings. For example, *o*-ethyl and *o*-fluoro groups on the phenyl rings yielded the hydrogenation products in 98% ee (**7c**) and 93% ee (**7k**), respectively. In contrast, substrates with *p*-ethyl and *p*-fluoro groups gave the desired products in 87% ee (**7b**,**i**). However, such an ortho effect was not observed for the methoxy substituent. While the substrate with a *p*-MeO group gave the hydrogenation product in 87% ee (**7d**), the *o*-methoxy-substituted substrate yielded the product **7e** with a relatively low enantioselectivity (80% ee).

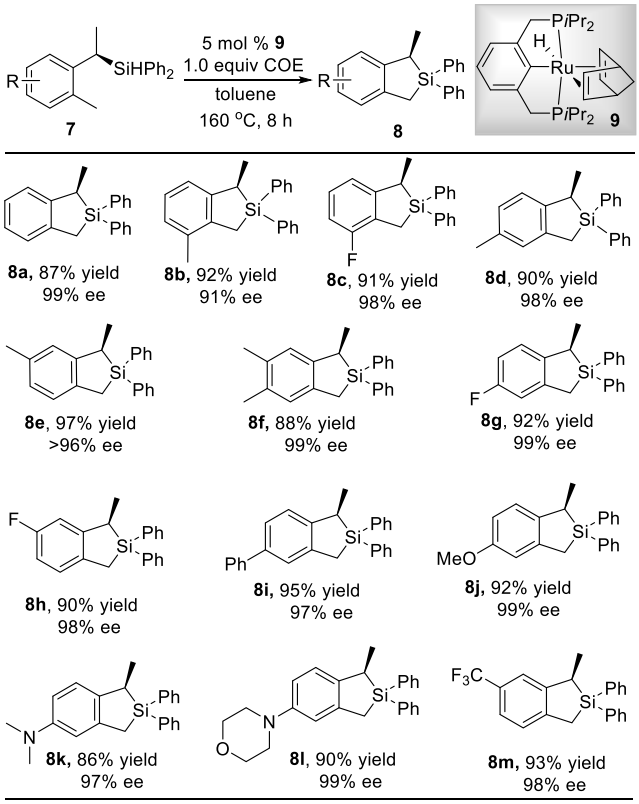


DOI: 10.1021/acs.organomet.9b00067
*Organometallics* XXXX, XXX, XXX−XXX

Furthermore, sterically hindered substrates with an *o*-methyl group on the aryl ring (**7p**–**z** and **7aa**–**ac**) underwent asymmetric hydrogenation smoothly, resulting in excellent enantioselectivities (>94%) and high isolated yields (>88%). Significantly, these substrates with *o*-Me substituents are of particular interest because the hydrogenation products could be potentially applied in subsequent dehydrogenative silylation reactions.

By using a pincer-type ruthenium complex **9** developed by our group for alkane dehydrogenation[17a] and C–H silylation,[13,17b] here we also realized the intramolecular dehydrosilylation reaction of *o*-methyl-substituted chiral benzyl silanes, providing an efficient access to five-membered silolanes with high enantiopurity (Scheme 4). Diverse silolanes were

**Scheme 4. Synthesis of Optically Active Silolanes by a Ruthenium Catalyst**[a]




[a]Reaction conditions: **7** (1.0 equiv), COE (1.0 equiv), **9** (5 mol %), toluene at 160 °C for 8 h. Isolated yields. ee values were determined by chiral HPLC analysis.

obtained with high yields (up to 97%) and excellent enantioselectivities (up to 99%), tolerating functional groups such as fluorine (**8c**,**g**,**h**), methoxy (**8j**), dimethylamino (**8k**), morpholino (**8l**), and trifluoromethyl (**8m**). Considering that the methods for preparing optically active Si-containing heterocycles are extremely limited,[18] the Co-catalyzed asymmetric hydrogenation of $\alpha$-vinylsilanes coupled with the Ru-catalyzed dehydrosilylation process represents a promising approach for the enantioselective synthesis of silacycles.

In summary, a highly efficient and enantioselective hydrogenation of 1,1-disubstituted vinylsilanes was achieved by the newly developed (PPO)Co catalyst system with broad substrate scope. This novel cobalt catalyst system represents a complement to base-metal-catalyzed asymmetric hydrogenation of minimally functionalized alkenes. In addition, the *o*-methyl-substituted chiral benzylsilanes obtained in the asymmetric hydrogenation can further undergo ruthenium-catalyzed intramolecular dehydrogenative silylation reactions to construct an optically active silolane class without racemization of the stereogenic center $\alpha$ to the quaternary Si atom.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00067.

Experimental details, characterization data, crystallographic data, NMR spectra, and HPLC data (PDF)

### Accession Codes

CCDC 1887309–1887310 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail for G.L.: guixia@sioc.ac.cn.
*E-mail for Z.H.: huangzh@sioc.ac.cn.

### ORCID

Guixia Liu: 0000-0001-7565-2183
Zheng Huang: 0000-0001-7524-098X


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the National Key R&D Program of China (2016YFA0202900, 2015CB856600), National Natural Science Foundation of China (21825109, 21821002, 21732006, 21572255, 21432011), Chinese Academy of Sciences (XDB20000000, QYZDB-SSW-SLH016), and Science and Technology Commission of Shanghai Municipality (17JC1401200).

## ■ REFERENCES

(1) (a) Knowles, W. S. Asymmetric hydrogenations (Nobel Lecture). *Angew. Chem., Int. Ed.* **2002**, *41*, 1998–2007. (b) Noyori, R. Asymmetric catalysis: science and opportunities (Nobel Lecture). *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022. (c) Knowles, W. S.; Noyori, R. Pioneering perspectives on asymmetric hydrogenation. *Acc. Chem. Res.* **2007**, *40*, 1238–1239. (d) Johnson, N. B.; Lennon, I. C.; Moran, P. H.; Ramsden, J. A. Industrial-scale synthesis and applications of asymmetric hydrogenation catalysts. *Acc. Chem. Res.* **2007**, *40*, 1291–1299. (e) Shultz, C. S.; Krska, S. W. Unlocking the potential of asymmetric hydrogenation at Merck. *Acc. Chem. Res.* **2007**, *40*, 1320–1326.

(2) (a) Ohta, T.; Ikegami, H.; Miyake, T.; Takaya, H. J. BINAP-Ru(II) and BINAP-Rh(I)-catalyzed asymmetric hydrogenation of olefins without heteroatom-functionalities. *J. Organomet. Chem.* **1995**, *502*, 169–176. (b) Forman, G. S.; Ohkuma, T.; Hems, W. P.; Noyori, R. Asymmetric hydrogenation of $\alpha$-ethylstyrenes catalyzed by chiral ruthenium complexes. *Tetrahedron Lett.* **2000**, *41*, 9471–9475. (c) Wu, S.; Wang, W.; Tang, W.; Lin, M.; Zhang, X. Highly



DOI: 10.1021/acs.organomet.9b00067
*Organometallics* XXXX, XXX, XXX–XXX

enantioselective hydrogenation of enol acetates catalyzed by Ru−TunaPhos complexes. *Org. Lett.* **2002**, *4*, 4495−4497.
(3) (a) Ojima, I.; Kogure, T.; Yoda, N. J. Asymmetric hydrogenation of prochiral olefins catalyzed by rhodium complexes with chiral pyrrolidinodiphosphines. Crucial factors for the effective asymmetric induction. *J. Org. Chem.* **1980**, *45*, 4728−4739. (b) Landis, C. R.; Halpern, J. Asymmetric hydrogenation of methyl (Z)-alpha-acetamidocinnamate catalyzed by [1,2-bis(phenyl-o-anisoyl)-phosphino)ethane]rhodium(I): kinetics, mechanism and origin of enantioselection. Rhodium-catalysed asymmetric hydrogenation as a valuable synthetic tool for the preparation of chiral drugs. *J. Am. Chem. Soc.* **1987**, *109*, 1746−1754. (c) Etayo, P.; Vidal-Ferran, A. Rhodium-catalysed asymmetric hydrogenation as a valuable synthetic tool for the preparation of chiral drugs. *Chem. Soc. Rev.* **2013**, *42*, 728−754. (d) Kita, Y.; Hida, S.; Higashihara, K.; Jena, H. S.; Higashida, K.; Mashima, K. Chloride-bridged dinuclear rhodium(III) complexes bearing chiral diphosphine ligands: catalyst precursors for asymmetric hydrogenation of Simple olefins. *Angew. Chem.* **2016**, *128*, 8439−8443.
(4) (a) Blackmond, D. G.; Lightfoot, A.; Pfaltz, A.; Rosner, T.; Schnider, P.; Zimmermann, N. Enantioselective hydrogenation of olefins with phosphinooxazoline-iridium catalysts. *Chirality* **2000**, *12*, 442−449. (b) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. Optically active iridium imidazol-2-ylidene-oxazoline complexes: preparation and use in asymmetric hydrogenation of arylalkenes. *J. Am. Chem. Soc.* **2003**, *125*, 113−123. (c) Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hörmann, E.; McIntyre, S.; Menges, F.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. Iridium-catalyzed enantioselective hydrogenation of olefins. *Adv. Synth. Catal.* **2003**, *345*, 33−43. (d) Bell, S.; Wüstenberg, B.; Kaiser, S.; Menges, F.; Netscher, T.; Pfaltz, A. Asymmetric hydrogenation of unfunctionalized, purely alkyl-Substituted olefins. *Science* **2006**, *311*, 642−644. (e) Källström, K.; Munslow, I. J.; Hedberg, C.; Andersson, P. G. Iridium-catalysed asymmetric hydrogenation of vinylsilanes as a route to optically active silanes. *Adv. Synth. Catal.* **2006**, *348*, 2575−2578. (f) Roseblade, S. J.; Pfaltz, A. Iridium-catalyzed asymmetric hydrogenation of olefins. *Acc. Chem. Res.* **2007**, *40*, 1402−1411. (g) Cheruku, P.; Diesen, J.; Andersson, P. G. Asymmetric hydrogenation of di and trisubstituted enol phosphinates with N,P-Ligated iridium complexes. *J. Am. Chem. Soc.* **2008**, *130*, 5595−5599. (h) Church, T. L.; Andersson, P. G. Iridium catalysts for the asymmetric hydrogenation of olefins with nontraditional functional substituents. *Coord. Chem. Rev.* **2008**, *252*, 513−531. (i) Cheruku, P.; Paptchikhine, A.; Church, T. L.; Andersson, P. G. Iridium-N,P-ligand-catalyzed enantioselective hydrogenation of diphenylvinylphosphine oxides and vinylphosphonates. *J. Am. Chem. Soc.* **2009**, *131*, 8285−8289. (j) Mazuela, J.; Verendel, J. J.; Coll, M.; Schäffner, B. n.; Börner, A.; Andersson, P. G.; Pàmies, O.; Diéguez, M. Iridium phosphite-oxazoline catalysts for the highly enantioselective hydrogenation of terminal alkenes. *J. Am. Chem. Soc.* **2009**, *131*, 12344−12353. (k) Tolstoy, P. i.; Engman, M.; Paptchikhine, A.; Bergquist, J.; Church, T. L.; Leung, A. W.-M.; Andersson, P. G. Iridium-catalyzed asymmetric hydrogenation yielding chiral diarylmethines with weakly coordinating or non-coordinating substituents. *J. Am. Chem. Soc.* **2009**, *131*, 8855−8860. (l) Church, T. L.; Rasmussen, T.; Andersson, P. G. Enantioselectivity in the iridium-catalyzed hydrogenation of unfunctionalized olefins. *Organometallics* **2010**, *29*, 6769−6781. (m) Mazuela, J.; Pàmies, O.; Diéguez, M. A phosphite-pyridine/iridium complex library as highly selective catalysts for the hydrogenation of minimally functionalized olefins. *Adv. Synth. Catal.* **2013**, *355*, 2569−2583. (n) Bess, E. N.; Sigman, M. S. Distinctive meta-directing group effect for iridium-catalyzed 1,1-diarylalkene enantioselective hydrogenation. *Org. Lett.* **2013**, *15*, 646−649. (o) Magre, M.; Pàmies, O.; Diéguez, M. PHOX-based phosphite-oxazoline ligands for the enantioselective Ir-catalyzed hydrogenation of cyclic $\beta$-enamides. *ACS Catal.* **2016**, *6*, 5186−5190.
(5) (a) Bullock, R. M. Abundant metals give precious hydrogenation performance. *Science* **2013**, *342*, 1054−1055. (b) Chirik, P. J. Iron and cobalt-catalyzed alkene hydrogenation: Catalysis with both redox-active and strong field ligands. *Acc. Chem. Res.* **2015**, *48*, 1687−1695.
(6) (a) Semproni, S. P.; Milsmann, C.; Chirik, P. J. Four-coordinate cobalt pincer complexes: electronic structure studies and ligand modification by homolytic and heterolytic pathways. *J. Am. Chem. Soc.* **2014**, *136*, 9211−9224. (b) Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. W.; Chirik, P. J. Cobalt-catalyzed [$2\pi$ + $2\pi$] cycloadditions of alkenes: scope, mechanism, and elucidation of electronic structure of catalytic intermediates. *J. Am. Chem. Soc.* **2015**, *137*, 7903−7914. (c) Hoyt, J. M.; Schmidt, V. A.; Tondreau, A. M.; Chirik, P. J. Iron-catalyzed intermolecular [2 + 2] cycloadditions of unactivated alkenes. *Science* **2015**, *349*, 960−963. (d) Holland, P. L. Distinctive reaction pathways at base metals in high-spin organometallic catalysts. *Acc. Chem. Res.* **2015**, *48*, 1696−1702. (e) Zhang, Z.; Butt, N. A.; Zhou, M.; Liu, D.; Zhang, W. Asymmetric transfer and pressure hydrogenation with earth-abundant transition metal catalysts. *Chin. J. Chem.* **2018**, *36*, 443−454.
(7) (a) Ohgo, Y.; et al. Asymmetric reactions. X. asymmetric hydrogenation catalyzed by bis(dimethylglyoximato)cobalt(II)-chiral cocatalyst (amino alcohol) System. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2124−2135. (b) Leutenegger, U.; Madin, A.; Pfaltz, A. Enantioselective reduction of $\alpha$, $\beta$-unsaturated carboxylates with $NaBH_4$ and catalytic amounts of chiral cobalt semicorrin complexes. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 60−61. (c) Corma, A.; Iglesias, M.; del Pino, C.; Sánchez, F. Optically active complexes of transition metals (RhI, RuII, CoII and NiII) with 2-aminocarbonylpyrrolidine ligands. Selective catalysts for hydrogenation of prochiral olefins. *J. Organomet. Chem.* **1992**, *431*, 233−246. (d) Nindakova, L. O.; Shainyan, B. A.; Shmidt, F. K. Total synthesis of terpenes. XIX. Synthesis of 8-methoxy-4a.beta., 10b.beta., 12a.alpha.-trimethyl-3,4,4a,4b.alpha.,5,6,10b,11,12,12a-decahydrochrysen-1(2H)-one, a key intermediate in the total synthesis of (+-)-shionone. *Russ. J. Org. Chem.* **2004**, *40*, 973−975. (e) Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J. Cobalt precursors for high-throughput discovery of base metal asymmetric alkene hydrogenation catalysts. *Science* **2013**, *342*, 1076−1080. (f) Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. Enantiopure $C_1$-symmetric bis(imino)pyridine cobalt complexes for asymmetric alkene hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 4561−4564. (g) Friedfeld, M. R.; Shevlin, M.; Margulieux, G. W.; Campeau, L. C.; Chirik, P. J. Cobalt-catalyzed enantioselective hydrogenation of minimally functionalized alkenes: isotopic labeling provides insight into the origin of stereoselectivity and alkene insertion preferences. *J. Am. Chem. Soc.* **2016**, *138*, 3314−3324. (h) Chen, J.; Chen, C.; Ji, C.; Lu, Z. Cobalt-catalyzed asymmetric hydrogenation of 1,1-diarylethenes. *Org. Lett.* **2016**, *18*, 1594−1597. (i) Guo, J.; Shen, X.; Lu, Z. Regio- and Enantioselective cobalt-catalyzed sequential hydrosilylation/hydrogenation of terminal alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 615−618. (j) Friedfeld, M. R.; Zhong, H.; Ruck, R. T.; Shevlin, M.; Chirik, P. J. Cobalt-catalyzed asymmetric hydrogenation of enamides enabled by single-electron reduction. *Science* **2018**, *360*, 888−893.
(8) (a) Jachak, G. R.; Ramesh, R.; Sant, D. G.; Jorwekar, S. U.; Jadhav, M. R.; Tupe, S. G.; Deshpande, M. V.; Reddy, D. S. Silicon incorporated morpholine antifungals: design, synthesis, and biological evaluation. *ACS Med. Chem. Lett.* **2015**, *6*, 1111−1116. (b) Geyer, M.; Baus, J. A.; Fjellstrom, O.; Wellner, E.; Gustafsson, L.; Tacke, R. Synthesis and pharmacological properties of silicon-containing GPR81 and GPR109A agonists. *ChemMedChem* **2015**, *10*, 2063−2070. (c) Geyer, M.; Karlsson, O.; Baus, J. A.; Wellner, E.; Tacke, R. Si-and C-functional organosilicon building blocks for synthesis based on 4-silacyclohexan-1-ones containing the silicon protecting groups MOP (4-methoxyphenyl), DMOP (2,6-dimethoxyphenyl), or TMOP (2,4,6-trimethoxyphenyl). *J. Org. Chem.* **2015**, *80*, 5804−5811. (d) Ramesh, R.; Reddy, D. S. Quest for novel chemical entities through incorporation of silicon in drug scaffolds. *J. Med. Chem.* **2018**, *61*, 3779−3798. (e) Fujii, S.; Hashimoto, Y. Progress in the medicinal chemistry of silicon: C/Si exchange and beyond. *Future Med. Chem.* **2017**, *9*, 485−505.


DOI: 10.1021/acs.organomet.9b00067
*Organometallics* XXXX, XXX, XXX−XXX

(9) (a) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. Catalytic hydrosilylation routes to divinylbenzene bridged silole and silafluorene polymers. applications to surface imaging of explosive particulates. *Macromolecules* **2008**, *41*, 1237−1245. (b) Shimizu, M.; Hiyama, T. Silicon-bridged biaryls: Molecular design, new synthesis, and luminescence control. *Synlett* **2012**, *23*, 973−989.
(10) Liu, J.; Zou, Y.; Fan, W.; Mao, J.; Chai, G.; Li, P.; Qu, Z.; Zong, Y.; Zhang, J.; Kraft, P. Synthesis and olfactory properties of silicon-containing analogs of rosamusk, romandolide, and applelide: Insights into the structural parameters of linear alicyclic musks. *Eur. J. Org. Chem.* **2016**, *2016*, 976−982.
(11) (a) Cusak, A. Temporary silicon-tethered ring-closing metathesis: Recent advances in methodology development and natural product synthesis. *Chem. - Eur. J.* **2012**, *18*, 5800−5824. (b) Shainyan, B. A.; Kleinpeter, E. Silacyclohexanes and silaheterocyclohexanes-why are they so different from other heterocyclohexanes. *Tetrahedron* **2013**, *69*, 5927−5936.
(12) (a) Zhang, L.; Zuo, Z.; Wan, X.; Huang, Z. Cobalt-catalyzed enantioselective hydroboration of 1,1-disubstituted aryl alkenes. *J. Am. Chem. Soc.* **2014**, *136*, 15501−15504. (b) Wen, H.; Wan, X.; Huang, Z. Asymmetric synthesis of silicon-stereogenic vinylhydrosilanes by cobalt-catalyzed regio-and enantioselective alkyne hydrosilylation with dihydrosilanes. *Angew. Chem., Int. Ed.* **2018**, *57*, 6319−6323. (c) Ma, X.; Qiao, L.; Liu, G.; Huang, Z. A New Phosphine-Amine-Oxazoline Ligand for Ru-Catalyzed Asymmetric Hydrogenation of N-Phosphinylimines. *Chin. J. Chem.* **2018**, *36*, 1151−1155.
(13) Fang, H.; Hou, W.; Liu, G.; Huang, Z. Ruthenium-catalyzed site-selective intramolecular silylation of primary C-H bonds for synthesis of sila-heterocycles. *J. Am. Chem. Soc.* **2017**, *139*, 11601−11609.
(14) Chen, J.; Xi, T.; Ren, X.; Cheng, B.; Guo, J.; Lu, Z. Asymmetric cobalt catalysts for hydroboration of 1,1-disubstituted alkenes. *Org. Chem. Front.* **2014**, *1*, 1306−1309.
(15) CCDC 1887310 (**3**) and CCDC 1887309 (**4d**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
(16) Zuo, Z.; Yang, J.; Huang, Z. Cobalt-catalyzed alkyne hydrosilylation and sequential vinylsilane hydroboration with markovnikov selectivity. *Angew. Chem., Int. Ed.* **2016**, *55*, 10839−10843.
(17) (a) Zhang, Y.; Fang, H.; Yao, W.; Leng, X.; Huang, Z. Synthesis of pincer hydrido ruthenium olefin complexes for catalytic alkane dehydrogenation. *Organometallics* **2016**, *35*, 181−188. (b) Fang, H.; Guo, L.; Zhang, Y.; Yao, W.; Huang, Z. A pincer ruthenium complex for regioselective C-H silylation of heteroarenes. *Org. Lett.* **2016**, *18*, 5624−5627.
(18) (a) Shintani, R.; Moriya, K.; Hayashi, T. Palladium-catalyzed enantioselective desymmetrization of silacyclobutanes: construction of silacycles possessing a tetraorganosilicon stereocenter. *J. Am. Chem. Soc.* **2011**, *133*, 16440−16443. (b) Arii, H.; Yano, Y.; Nakabayashi, K.; Yamaguchi, S.; Yamamura, M.; Mochida, K.; Kawashima, T. Regioselective and stereospecific dehydrogenative annulation utilizing silylium Ion-activated Alkenes. *J. Org. Chem.* **2016**, *81*, 6314−6319.



DOI: 10.1021/acs.organomet.9b00067
*Organometallics* XXXX, XXX, XXX−XXX