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Authors: Nan Li and Bing-Tao Guan

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Yttrium–Benzyl Complexes Bearing Chiral Iminophosphonamide Ligands: Synthesis and Application in Catalytic Asymmetric Amine–Silane Dehydrocoupling Reactions

Nan Li[a] and Bing-Tao Guan*[a,b]

[a] State Key Laboratory and Institute of Elemento-Organic Chemistry
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.
E-mail: guan@nankai.edu.cn

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Abstract. A series of novel iminophosphonamide ligands with chiral diamine moieties were designed and synthesized. Yttrium–benzyl compounds bearing these chiral iminophosphonamide ligands showed high reactivity and selectivity on the first catalytic asymmetric cross-dehydrogenative coupling of amines with prochiral silanes under mild conditions. A stable silylamine–boron derivative was synthesized in up to 23% *ee*, as determined by chiral HPLC analysis. By employing this catalyst system, catalytic kinetic resolution of an axially chiral silane and further in situ allylation were achieved in good yields and enantioselectivities.

Keywords: Yttrium catalyst; iminophosphonamide ligand; amine–silane dehydrocoupling reaction; kinetic resolution; axially chiral silane

The past decades have witnessed the development of organosilane compounds, which have been widely used in organic functional materials and bioactive drugs.[1] Optically active silicon stereogenic compounds, however, are not available in nature, probably due to the Berry pseudorotation (BPR) of the higher-coordinate silicon atom.[2] Significant progress has been made in creating silicon stereocenters utilizing chiral resolution and asymmetric induction.[3] However, the development of catalytic asymmetric methods using transition-metal catalysts has rarely been explored. Inventive catalytic desymmetrization reactions of prochiral silicon compounds have been developed, such as hydrosilylation of ketones,[4] alkenes[5] and alkynes,[6] carbon silylation of alkynes,[7] and [2+2+2] cycloaddition.[8] Additionally, enantioselective carbene insertion,[9] alcoholysis,[10] Si-C cross-coupling,[11] and other desymmetrization reactions[12] have also been established.

Silylamines, serving as bases, ligands, silylation agents and polymer precursors, play an important role in synthetic chemistry.[13] In contrast with traditional silylamine synthesis from chlorosilanes and amines, catalytic cross-dehydrogenative coupling of amines and silanes presents an atom-economic approach, with the generation of hydrogen as the only byproduct. Extensive studies have been carried out

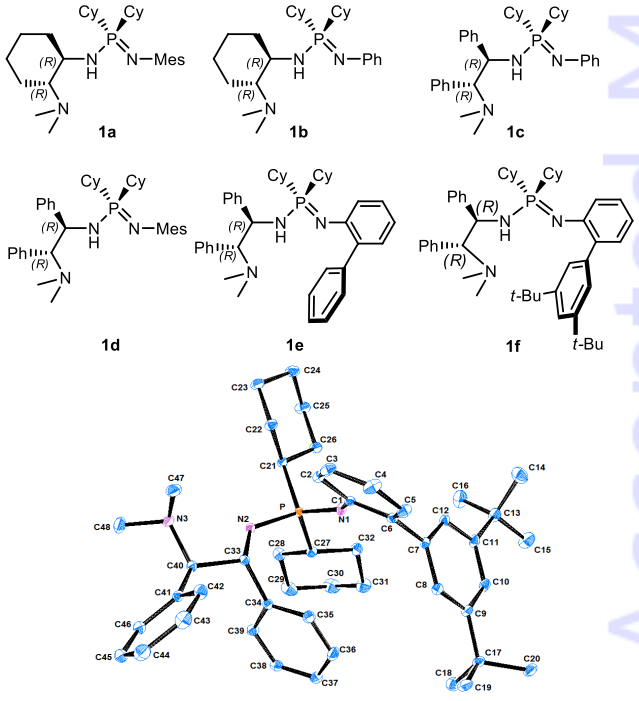

Figure 1 New Chiral Iminophosphonamide Ligands **1a-1f** and ORTEP Drawing of Ligand **1f**, 30% Thermal Ellipsoids are Shown, All Hydrogen Atoms are Omitted For Clarity.

using metal catalysts, including metal carbonyls,[14] alkali metal complexes,[15] alkaline-earth complexes,[16] rare-earth complexes,[17] group IV metal complexes[18] and other catalysts.[19] However, an asymmetric version has not been introduced into the catalytic cross-dehydrogenative coupling of amines and silanes so far. Herein, we synthesized a series of novel rare-earth

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and alkaline-earth alkyl complexes bearing non-C_2-symmetric chiral iminophosphonamide ligands, among which yttrium complexes showed good reactivity and selectivity on the first catalytic asymmetric amine−silane dehydrogenative coupling reactions.

The iminophosphonamide ligands, being versatile in tuning steric and electronic properties around rare-earth metal centers, [20] have found their applications in catalytic polymerization and hydroamination reactions. In order to further explore the catalytic asymmetric potentiality, a chiral diamine moiety (1*R*, 2*R*)-diaminocyclohexane or (1*R*,2*R*)-diphenylethylenediamine was introduced into the iminophosphonamide structure, thus a series of novel chiral ligands were synthesized (**Figure 1, 1a**-**1f**). X-ray crystallographic analysis of the most complicated ligand **1f** was achieved, which unambiguously verified the chiral iminophosphonamide structure. Treating the chiral iminophosphonamide ligands with alkaline-earth or rare-earth metal benzyl compounds, the quick, complete deprotonation reactions could be observed with the ^{1}H NMR analysis. In this manner, a class of alkyl metal complexes (**Figure 2, 2a**-**2i**) bearing chiral iminophosphonamide ligands were obtained in quantitative yields.

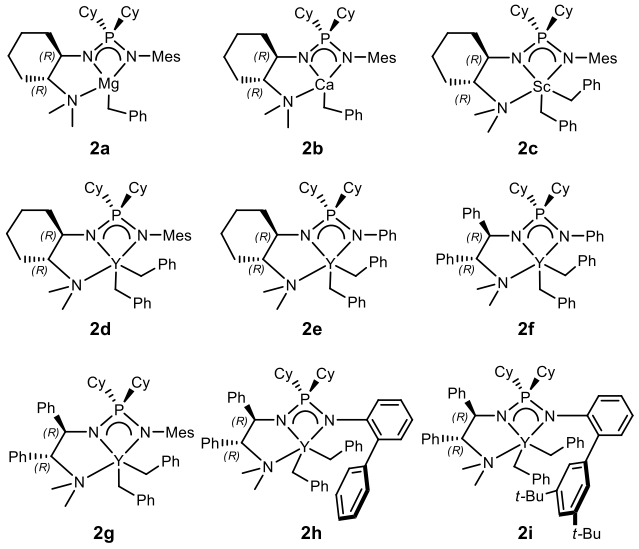
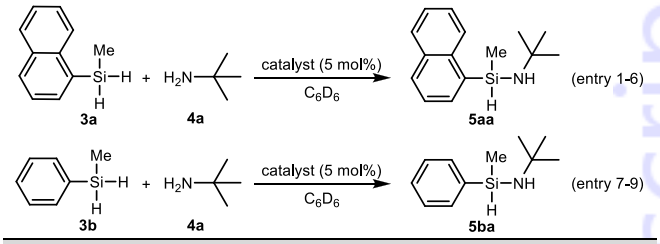


Figure 2 Alkyl Metal Complexes (**2a**-**2i**) Bearing Chiral Iminophosphonamide Ligands

With these chiral alkaline-earth and rare-earth metal benzyl complexes in hand, we began our studies by investigating the cross-dehydrogenative coupling reaction between methyl(naphthalen-1-yl)silane (**3a**) and *tert*-butylamine (**4a**) (Table 1). Using magnesium (**2a**), calcium (**2b**) or scandium (**2c**) alkyl complexes as catalysts, there were little dehydrogenative coupling products detected after heating at 50 ˚C for 3 hours (Table 1, entries 1-3). Gratifyingly, the dehydrogenative coupling reaction with yttrium complex (**2d**) as catalyst proceeded efficiently at room temperature to give the desired silylamine **5aa** in 93% NMR yield (Table 1, entry 4). As a contrast, tribenzylyttrium complex without an auxiliary ligand was also investigated, which failed to achieve the catalytic dehydrogenative coupling reaction even at elevated temperature (Table 1, entries 5-6). Similar ligand accelerating effect was also reported by Crimmin and Cui using a phosphorus based ligand and a NHC ligand. [17b,c] Using the yttrium complex (**2d**) as catalyst, we further carried out the silylamination reaction of methylphenylsilane (**3b**) and *tert*-butylamine. The reaction finished in 2 hours at room temperature, and the desired product silylamine 5b was isolated in 80% yield (Table 1, entry 7). To further explore the ligand effects, the methylphenylsilane and *tert*-butylamine was tested with yttrium complexes (**2e-2f**) as catalysts, and silylamine **5ba** was obtained with even better yields (Table 1, entries 8-9). These results revealed that the yttrium complex bearing 1,2-diphenylethylenediamine moiety showed better catalytic reactivity than the one with the 1,2-diaminocyclohexane moiety.

Table 1 Catalytic Amine-Silane Dehydrocoupling Reactions[a]



entry	Cat.	time	Temp.	Conv. [b]	yield[b]
1	**2a**	3 h	50 ˚C	4%	**5aa** <5%
2	**2b**	3 h	50 ˚C	7%	**5aa** <5%
3	**2c**	3 h	50 ˚C	0%	**5aa** 0%
4	**2d**	3 h	25 ˚C	100%	**5aa** 93%
5	$YBn_3(thf)_3$	3 h	25 ˚C	0%	**5aa** 0%
6	$YBn_3(thf)_3$	3 h	50 ˚C	10%	**5aa** 6%
7	**2d**	2 h	25 ˚C	98%	**5ba**(+) 80% [c]
8	**2e**	2 h	25 ˚C	100%	**5ba**(-) 87%[c]
9	**2f**	2 h	25 ˚C	100%	**5ba**(-) 89% [c]

[a] Reaction conditions: methyl(naphthalen-1-yl)silane (**3a**) or Methylphenylsilane (**3b**) (0.21 mmol), amine **4a** (0.25 mmol), catalyst (5.0 mol%), C_6D_6 (1 mL).

[b] Conversion and yields were recorded by ^{1}H NMR analysis using hexamethylbenzene as an internal standard if without further notes.

[c] Isolated yields after distillation. Sign of $[\alpha]_D$ at 30 ˚C in parentheses.

Displaying better catalytic activity, complex **2f** as catalyst was then subjected to investigate the substrate scope of the dehydrogenative coupling reactions (Table 2). Silane **3b**, combined with benzylamine (**4b**) or isobutylamine (**4c**), was submitted to the catalytic silylamination reaction. To our delight, the reactions took place smoothly with excellent NMR yields. After distillation, the corresponding silylamine products **5bb** and **5bc** were obtained in moderate to good isolated yields. Besides primary amines, secondary amines such as diethylamine (**4d**), piperidine (**4e**) and morpholine (**4f**) could also undergo the silylamination reactions efficiently to afford silylamines (**5bd, 5be, 5bf**) in good yields. Furthermore, ethyl(phenyl)silane (**3c**), isopropyl(phenyl)silane (**3d**) and methyl(naphthalen-1-yl)silane (**3a**) were subjected to the dehydrogenative coupling reactions with amine **4a** and **4d** , and the desired products **5ca, 5cd, 5da, 5dd, 5aa, 5ad** were obtained efficiently. Phenyl(naphthalen-1-yl)silane (**3e**), a silane with extremely bulky groups, also underwent the dehydrogenative coupling reaction smoothly

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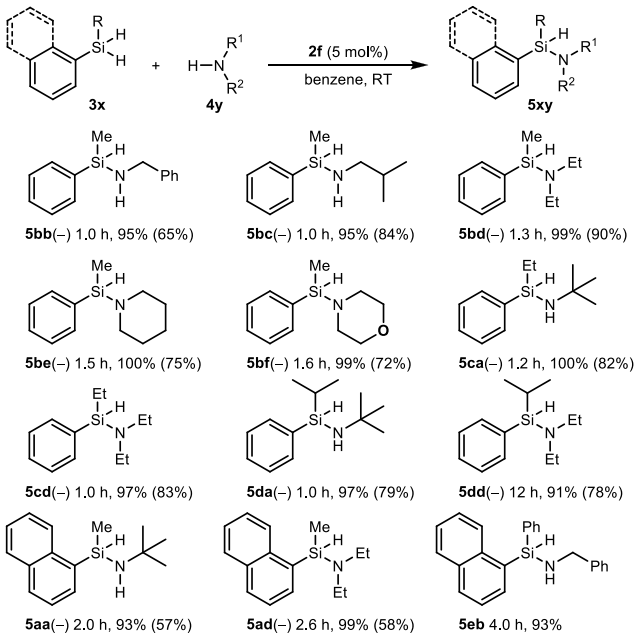
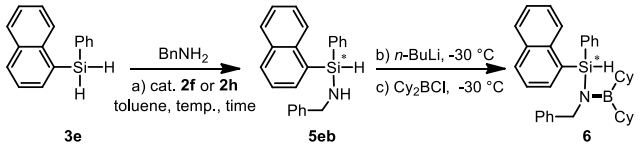
with benzylamine to afford silylamine **5eb** in 93% yield. It is remarkable that catalyst **2f** displayed nice chemoselectivity, which providing only monoamination products. All the isolated silylamines in Table 2 showed negative specific optical rotation.

Table 2 Substrates Scope[a]



[a] Yields were recorded by ^{1}H NMR analysis using hexamethylbenzene as an internal standard and the values in parentheses refer to the yields of isolated product.

Table 3 Synthesis and *ee* Value Determination of Compound **6**

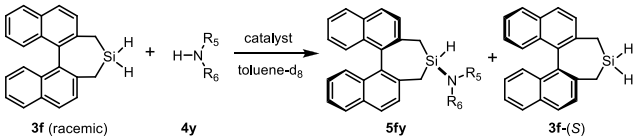


entry	Cat.	Temp.	time	yield of **6**	*ee* of **6**
1	**2f**	25 ˚C	4 h	70%	17%
2	**2f**	-30 ˚C	8 h	69%	21%
3	**2h**	25 ˚C	4 h	72%	17%
4	**2h**	-30 ˚C	12 h	71%	23%

[a] Reaction conditions: silane **3e** (0.17 mmol), amine **4b** (0.17 mmol, 1,0 equiv.), catalyst (5.0 mol%), toluene (1.5 mL). [b] *n*-BuLi (0.17 mmol), -30 ˚C to RT. [c] Cy_2BCl (0.17 mmol), -30 ˚C to RT, 1 hour.

The direct *ee* values analyses by conventional chiral HPLC or GC analyses met limited success mainly due to the high moisture sensitivity of silylamines (Table 2). The transformation of silylamines into more stable derivatives thus appears to be particularly important for the further analysis. After various attempts, we found that silylamine-boron derivative **6**, which was synthesized from silylamine **5eb** via a one-pot deprotonation/boronation procedure, was stable and could be successfully separated by chiral HPLC analysis. Following a two-step process showed in table 3, derivative **6** was obtained in 70% yield and 17% *ee* (at 25 °C) by using catalyst **2f**. The *ee* value was improved to 21% by using the same catalyst at -30 °C. When catalyst **2h** was employed, derivative **6** could also be obtained in 71% yield and 23% *ee* (at -30 °C).

Table 4 Kinetic Resolution of Racemic Axially Chiral Silane **3f**[a]



entry	Cat.	**4y**	Temp.	Conv.[b]	yield[b] **5fy**	yield[c] (*ee*)[d] **3f**
1	**2f**	**4a**	20 ˚C	52%	**5fa** 49%	43% (16%)(+)
2	**2g**	**4a**	20 ˚C	50%	**5fa** 48%	44% (24%)(+)
3	**2h**	**4a**	20 ˚C	50%	**5fa** 47%	45% (70%)(+)
4	**2i**	**4a**	20 ˚C	51%	**5fa** 50%	42% (50%)(+)
5	**2h**	**4a**	-30 ˚C	50%	**5fa** 49%	46% (80%)(+)
6	**2h**	**4g**	-30˚C	52%	**5fg** 46%	41% (26%)(+)
7	**2h**	**4h**	-30 ˚C	51%	**5fh** 50%	46% (50%)(+)
8	**2h**	**4e**	-30 ˚C	56%	**5fe** 51%	39% (14%)(-)

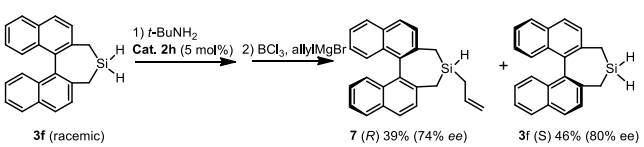
[a] Reaction conditions: silane **3f** (0.26 mmol, 1.0 equiv.), amine (0.13 mmol, 0.5 equiv.), catalyst (5.0 mol%), toluene-d_8 (1.3 mL). **4g**: *tert*-amylamine. **4h**: amantadine. **4e**: piperidine.

[b] Conversions and yields were recorded by ^{1}H NMR analysis using tetramethylsilane as an internal standard.

[c] Isolated yields.

[d] Determined by chiral HPLC analysis.

In order to further demonstrate the enantioselectivity of the catalysts, we carried out the kinetic resolution of a racemic axially chiral silane **3f**[21] by a cross-dehydrogenative coupling reaction. Guided by our previous results, silane **3f** was allowed to react with amine **4a** in toluene-d_8 using **2f** as catalyst. Delightfully, after 3 hours at 20°C, about half amount of silane **3f** was converted, and the desired product **5fa** was detected in a yield of 49% with ^{1}H NMR analysis. The remaining silane **3f** was recovered via flash chromatography and found in 43% yield and 16% *ee* (Table 4, entry 1). Using **2g** as catalyst, bearing iminophosphonamide ligands derived from bigger steric hindrance aniline, silane **3f** was recovered with better *ee* value of 24%. When using catalyst **2i**, a better *ee* value (50%) was afforded. A breakthrough was achieved by using catalyst **2h**, giving the kinetic resolution with 70% *ee*. Carrying out the reaction at -30 °C, the kinetic resolution was improved to a higher *ee* value of 80% (Table 4, Entry 5). With the optimized reaction conditions in hand, the amine scopes of the kinetic resolution were further examined. When more steric hindered amine **4g** and **4h** were employed, comparable yields but lower *ee* values were obtained. Interestingly, inversed enantioselectivity was detected when applying amine **4e** for kinetic resolution reaction.



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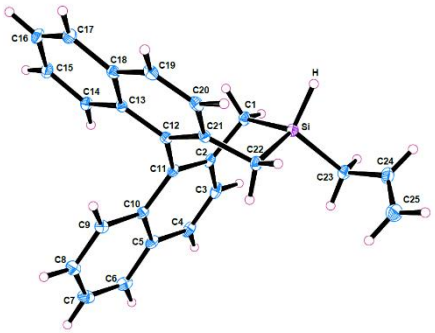

Scheme 1. Kinetic resolution of silane **3f** and in situ allylation. Reaction conditions: 1) silane 3f (0.26 mmol), amine 4a (0.13 mmol), 2h (5.0 mol%), toluene-d8 (1.3 mL), -30 °C, 12 h. 2) BCl_3 (0.042 mmol), 20 min, allylmagnesium bromide (0.13 mmol). ORTEP drawing of compound **7**, 30% thermal ellipsoids are shown

Similar to previous silylamines, this axially chiral silylamine **5fa** was also very moisture sensitive. Then an in situ transformation was proposed to further demonstrate the kinetic resolution reaction (Table 4, entry 5). As shown in scheme 1, boron trichloride and allylmagnesium bromide were added in sequence to the mixture of **5fa** and **3f**, and the in situ allylation of silylamine **5fa** was realized to produce allyl silane **7** in 39% yield and 74% *ee*. The absolute configuration of **7** was determined to be *R* by X-ray crystallographic analysis.

In summary, a series of novel chiral iminophosphonamide ligands and their alkyl metal complexes were designed and synthesized. The Yttrium complexes showed highly catalytic activity towards the enantioselective cross-dehydrogenative coupling of amines and prochiral silanes at mild conditions. In addition, this approach was also applied to the kinetic resolution process of an axially chiral silane, which could provide a useful method for the preparation of optical axially chiral silanes and related derivatives.

Experimental Section

In a glovebox, catalyst **2f** (40 mg, 0.05 mmol, 2 mol%) was dissolved in benzene (8 mL). $PhSiH_2Me$ (0.31 g, 2.53 mmol) was added to the solution, followed by *t*-$BuNH_2$ (0.22 g, 3.03 mmol). The mixture was stirred at room temperature till complete conversion (about 2 h, monitored by ^1H NMR spectroscopy), then the volatiles were removed under vacuum. The remaining residue was purified by distillation under vacuum to yield a colorless oil of PhMeSiH(NH*t*-Bu) 5b (0.42 g, 89%yield).

CCDC.1541362 (ligand **1f**) and CCDC.1531210 (compound **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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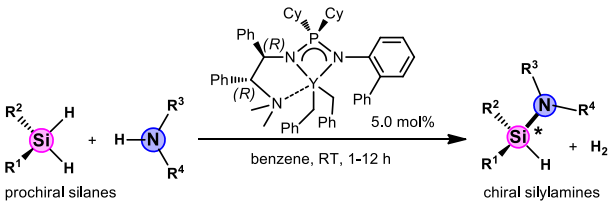
Nan Li and Bing-Tao Guan*



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