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## Hydrosilylation of Ketone and Imine over Poly-N-Heterocyclic Carbene Particles

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**Abstract:** N-Heterocyclic carbene (NHC)-catalyzed ketone/imine hydrosilylation, silane alcohol condensation and asymmetric ketone hydrosilylation reactions were demonstrated for the first time over solid, main-chain poly-NHC particles. The stable and robust poly-NHC particles were easily recovered, and exhibited good catalytic recyclability. A novel

## Introduction

Although organocatalysis has developed rapidly in recent years, relatively little effort has been devoted towards heterogeneous organocatalysis.<sup>[1,2]</sup> In general, active sites in polymeric catalysts are derived *via* immobilization or polymerization at a side chain. It is quite common in nature for a main-chain polymer to function as a catalyst, but this is rarely designed in synthetic polymers.<sup>[3]</sup> We recently created main-chain poly-*N*-heterocyclic carbene (poly-NHC) polymer materials and their poly-organometallic derivatives were demonstrated to be excellent heterogeneous catalysts.<sup>[4]</sup> Herein, the catalytic applications of the stable free carbene polymer materials were studied.

Ketone or imine reduction by hydrogenation, hydroboration and hydrosilylation is one of the most ubiquitous protocols in organic synthesis.<sup>[5]</sup> Although hydrogenation is widely practiced industrially, it faces shortcomings such as, metal leaching, high-pressure requirements, expensive catalysts, and difficulty in catalyst recycling.<sup>[6]</sup> Developing effective metal-free organocatalysts for the hydrosilylation of ketones and imines has attracted great interest.<sup>[7]</sup> In comparison, a robust and simple heterogeneous organocatalyst for ketone hydrosilylation would be even more desirable since it could be both environmentally friendly and more economical. NHCs have been known as powerful nucleophilic organocatalysts, and are used in catalyzing the silylcyanation reactions of ketones.<sup>[8,9]</sup> In this article, we demonstrated for the first time NHCcatalyzed ketone and imine hydrosilylation, silane alchiral induction protocol with a cheap and easily accessible secondary alcohol as the chiral source was also developed in this catalytic system.

**Keywords:** heterogeneous catalysis; hydrosilylation; N-heterocyclic carbenes; organocatalysis

cohol condensation and asymmetric ketone hydrosilylation reactions using solid poly-NHC particles.

## **Results and Discussion**

As shown in Scheme 1, poly-imidazolium salt 1 was synthesized by condensation of bisimidazole and 2,4,6-tris(bromomethyl)mesitylene in dimethylformamide (DMF) at 110 °C for 24–72 h. Spherical particles (1.2  $\mu$ m in diameter) of poly-imidazolium 1 were obtained in 82% yield.<sup>[4]</sup> Longer reaction times resulted in more stable and robust polymer particles with a higher imidazolium component (less terminal groups) in the polymer network structure. NHC solid particles 2 were generated by a basic treatment of 1 (see



Scheme 1. Synthesis of poly-NHC particles.

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Scheme 1).<sup>[4]</sup> Typically, NaO-t-Bu (40 mg, 0.5 mmol) was added to a DMF (10 mL) suspension of 1 (150 mg) in a reaction flask. The reaction mixture was stirred for 16 h. The solid product was filtered, and washed with DMF to remove NaBr salt to obtain a yellowish brown powder 2 (95 mg). The poly-NHC particles 2 were characterized by <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, and elemental analysis.<sup>[4]</sup> The average carbene content in polymer 2 was  $\sim 2 \text{ mmol g}^{-1}$  based on elemental analysis and metal coordination experiments.<sup>[4]</sup>

Solid particles 2 were first tested as a novel heterogeneous organocatalyst for the cyanation reaction between trimethylsilyl cyanide (TMSCN) and carbonyl compounds. Catalyst 2 generated in situ and used as isolated particles demonstrated excellent catalytic activities in this reaction at room temperature. Full conversions were achieved in 10 min for aldehyde substrates with 1 mol% of catalyst loading in tetrahydrofuran (THF), and the colloidal particles were also easily recovered and reused (Table 1, entries 1–3). The reaction for ketone substrates in THF was much

 Table 1. Heterogeneous TMS cvanation reactions over 2.<sup>[a]</sup>

	0	Me₃Si-CN	$\mathbb{R}^2$	 3i
	R' `R <sup>2</sup>	2		
Entry	Substrate	Solvent	Time [min]	Yield [%] <sup>[b</sup>
1	ОН	THF	10	99
2	ОН	THF	10	99 <sup>[c]</sup>
3	ОН	THF	10	99 <sup>[d]</sup>
4	O C	DMF	30	99
5	0 C	DMF	45	99
6	° L	DMF	45	99 <sup>[e]</sup>

- [a] Typical reaction conditions: 1 mol% of catalyst, 1.2 mmol of TMSCN, 1 mmol of substrate in THF or DMF (1 mL), room temperature.
- [b] Yields were determined by GC and GC-MS.
- [c] Recycled catalyst of entry 1.
- [d] Recycled catalyst of entry 2.

[e] The products were a mixture of 1,2-addition (70%) and 1,4-addition (30%).



Me<sub>3</sub>Si-CN

Ph<sub>2</sub>HSi-H

Scheme 2. Poly-NHC-catalyzed cyanation and hydrosilyla-

2

tion reactions.

Firstly, the hydrosilylation of acetophenone with triethylsilane was tested and, unfortunataly, no reaction was observed in THF at room temperature in 24 h. When the more active diphenylsilane was employed, the hydrosilylation reaction proceeded smoothly under ambient conditions in THF. Full conversions were achieved in 10-36 h at room temperature for a wide range of ketone substrates with 10 mol% of solid **2** particles (Table 2). The poly-NHC catalyst was easily recycled by filtration. The washed and reused catalyst showed similar activity as the fresh catalyst (Table 2, entries 1-3). Both aryl ketones and alkyl ketones were found to be active for this reaction (Table 2). When DMF was used as the solvent instead of THF, the reaction proceeded very rapidly, and a product mixture of 1-phenylethanol, diphenyl(1-phenylethyloxy)silane and diphenyldi(1-phenylethyloxy)silane was obtained. This suggested that the polar solvent DMF increased the activity of NHC, causing part of the product to be over-reduced by silane. On the other hand, the reaction did not work in dichloromethane (DCM) and toluene. Furthermore, the system was successfully extended to imine hydrosilylation (Table 2, entry 10). In most hydrosilylation systems, excess silane (2–5 equiv. to substrate) was required for the metal complexes or organocatalysts employed. In our case, only 1 equiv. of silane was needed, and a quantitative yield of product was attained. Since this reaction worked under mild conditions and in a well-controlled manner, its extension to asymmetric reactions could be promising.

In asymmetric organic reactions, the chirality of products could be derived from the chiral starting materials or chiral catalysts. Almost all asymmetric hydrosilylation reactions were catalyzed by chiral catalysts.<sup>[6]</sup> A chiral silane was very rarely used due to the difficulty in its preparation.<sup>[10]</sup> Scheme 3 illustrates a novel chiral induction protocol for asymmetric hydrosilvlation over non-chiral poly-NHC particles. The chirality of the products was transferred from a chiral

 Table 2. Heterogeneous ketone and imine hydrosilylation

 with diphenylsilane over 2.<sup>[a]</sup>

Entry	Substrate	Product	Yield [%] <sup>[b]</sup>
1		Ph, Ph O <sup>Si</sup> H	99
2		Ph O <sup>Si</sup> H	99 <sup>[c]</sup>
3		Ph, Ph OSi H	99 <sup>[d]</sup>
4		Ph, Ph O <sup>Si</sup> H	99
5		Ph Ph Si H	99
6	MeO	Ph Ph O <sup>Si</sup> H	99
7	Br	Ph O-Si H	99
8		Ph Ph O Si H	99
9	O C	Ph_Ph O <sup>Si</sup> H	99
10	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		99

 [a] Reaction conditions for ketone: 10 mol% of poly-NHC, 0.2 mmol of ketone, 0.2 mmol of diphenylsilane, 1 mL of THF, room temperature, 10–36 h. DMF was used for imine hydrosilylation.

- <sup>[b]</sup> Products were confirmed by <sup>1</sup>H NMR spectroscopy and GC-MS. Yield was determined by GC and GC-MS.
- <sup>[c]</sup> Recycled catalyst of entry 1.
- <sup>[d]</sup> Recycled catalyst of entry 2.

secondary alcohol such as menthol (which is inexpensive and easily obtained from natural products) through the silane. In this proposed approach, a chiral silane intermediate was generated through silane/alcohol condensation *in situ*; this was then used to induce the asymmetric hydrosilylation.

The key challenge for this approach was to generate the chiral silane intermediate efficiently and easily. Silane/alcohol dehydrogenative condensation reactions can be catalyzed by base, Lewis acid and many organometallic complexes.<sup>[11]</sup> Silanolysis of alcohol with R<sub>2</sub>SiH<sub>2</sub> was of particular interest to us since it could generate chiral silane  $R_2(R'O)SiH$  when a chiral secondary alcohol was employed. However, the selective production of mono-substituted silane  $R_2(R'O)$ SiH was still a great challenge. Herein, poly-NHC was developed as a heterogeneous organocatalyst for the silanolysis of secondary alcohols with Ph<sub>2</sub>SiH<sub>2</sub> under very mild conditions. The reaction was highly selective in producing the mono-substituted silane Ph<sub>2</sub>(R'O)SiH in quantitative yield with dihydrogen as the only by-product. The chiral silane product of this silane/alcohol condensation reaction could proceed directly to the ketone hydrosilylation reaction over poly-NHC upon the addition of a ketone substrate. As (-)-menthol was used as the chiral alcohol, the hydrosilylation of acetophenone with diphenylsilane over 2 produced (R)-1-phenylethanol in 40% ee. When (+)-menthol was used in this reaction, the product was in the (S) form with a similar ee value.

The proposed reaction mechanism is shown in Scheme 4. In cycle **A**, silane was activated by nucleophilic NHCs, and then reacted with a secondary alcohol to generate siloxane **3** and dihydrogen. The high selectivity for forming mono-substituted silane **3** might be due to the steric requirements of the bulky alcohol and solid polymer catalyst. In cycle **B**, the ketone might be activated by the poly-NHC to form intermediate **4**, and further reacted with chiral diphenylsiloxane **3** to form product **6**.

### Conclusions

In conclusion, this study has demonstrated that ketone and imine hydrosilylation reactions could proceed very smoothly and cleanly over poly-NHC particles. This novel heterogeneous catalyst was easily recycled for reuse. Only 1 equiv. of silane was needed, and a quantitative product yield was attained under mild conditions. Poly-NHC was also an excellent cata-



Scheme 3. Asymmetric hydrosilylation reactions over 2.

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Scheme 4. Proposed mechanism for asymmetric hydrosilylation reactions.

lyst for the dehydrogenative condensation between silanes and alcohols. The reaction could be extended to an asymmetric version with inexpensive and readily accessible secondary alcohols as the chiral source.

## **Experimental Section**

#### **General Information**

All solvents and chemicals were used as received from commercial suppliers, unless otherwise indicated. Centrifugation was performed on an Eppendorf Centrifuge 5810R (4000 rpm, 10 min). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AV-400 (400 MHz) instrument. Photoacoustic FT-IR (PA-FT-IR) spectra were recorded on a Digilab FTS 7000 FTIR spectrometer equipped with a MTEC-300 photoacoustic detector. Data for PA-FT-IR are reported in wavelength (cm<sup>-1</sup>) and intensity (s=strong, m=medium, w= weak). GC-MS was performed on a Shimadzu GCMS QP2010. Gas liquid chromatography (GLC) was performed on an Agilent 6890N gas chromatographs equipped with split-mode capillary injection system and flame ionization detector. Elemental analysis (C, H, N) was performed on an EAI CE-440 Elemental Analyzer. SEM images were obtained on a JEOL JSM-7400F electron microscope (10 kV).

#### **Preparation of Bisimidazole A**

NaH (60% in oil, 440 mg, 11 mmol) was added to a DMF solution of imidazole (680 mg, 10 mmol), and the resulting



suspension was stirred at room temperature for 2 h. *a,a*'-Dichloro-*p*-xylene (5 mmol) was added to the residue. The resulting solution was stirred at room temperature for another 4 h. The solvent was removed under vacuum. The product was extracted with DCM, and **A** was obtained in quantitative yield after removing the solvent. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta =$ 7.55 (s, 2H), 7.13 (s, 4H), 7.10 (s, 2H), 6.89 (s, 2H), 5.12 (s, 4H); MS (GC-MS): m/z = 238 (M<sup>+</sup>).

#### **Preparation of 1**

In a pressure flask, 2,4,6-tris(bromomethyl)mesitylene (399 mg, 1 mmol) and **A** (357 mg, 1.5 mmol) were dissolved in 100 mL of DMF. The flask was capped and placed in an oven at 110 °C for 24 h. A white solid product was precipitated in the reaction flask, filtered, washed with DMF and ether, and dried under vacuum. It was collected as a white powder; yield: 620 mg (82%). Elemental analysis, found: C 48.17, H 4.97, N 9.85. These results corresponded to a polymer with bromo-dominated end group (calcd.: C 50.48, H 4.64, N 9.81); <sup>13</sup>C NMR (solid):  $\delta = 18$  (CH<sub>3</sub>), 48–52 (CH<sub>2</sub>), 115–145 (C=C, C=N); PA-FT-IR n=1150 (s, NR<sub>4</sub><sup>+</sup>), 1558 cm<sup>-1</sup> (s, C=N, C=C).

Since the polymer products were insoluble in common solvents, their molecular weights could not be determined definitively. When water/methanol (volume ratio=4:1) was used to extract polymer 1, only 5% of the polymer was dissolved. Gel permeation chromatography (GPC) indicated an average molecular weight (MW) of 31,000 for the soluble portion.

#### **Preparation of 2**

NaO-t-Bu (40 mg, 0.5 mmol) was added to a DMF (10 mL) suspension of 1 (150 mg) in a reaction flask. The reaction

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mixture was stirred for 16 h. The solid product was filtered, and washed with DMF (20 mL) 5 times at room temperature to remove NaBr salt to obtain a yellow powder **2**; yield: 95 mg. Elemental analysis found: C 58.01, H 6.05, N 12.25. These results corresponded to a polymer whereby the imidazolium salt in **1** was transformed to the carbene form (calcd.: C 58.71, H 6.62, N 12.84); <sup>13</sup>C NMR (solid):  $\delta = 16.4$ (CH<sub>3</sub>), 48.2 (CH<sub>2</sub>, C–O), 128–163 (C=C), 218 (C<sub>2</sub> carbene); PA-FT-IR: n = 1558 cm<sup>-1</sup> (s, C=C).

#### Procedure for Trimethylsilyl (TMS) Cyanation

Catalyst 2 (5 mg) was placed in a vial with 1 mL of DMF. TMSCN (119 mg, 1.2 mmol) and acetophenone (120 mg, 1 mmol) were added to the vial. The reaction mixture was stirred at room temperature. After completion of the reaction [as determined by gas chromatography-mass spectrometry (GC-MS)], the catalyst was filtered and the product was confirmed by GC-MS, and the yield was determined by GC. The reaction mixture was centrifuged, and the solution was decanted. This procedure was repeated at least three times using DMF as the washing solvent. The recovered catalyst was used directly for the next run.

#### **Procedure for Hydrosilylation Reactions of Ketones** and Imines

All reactions were conducted in an inert atmosphere. For entry 6 of Table 2, **2** (10 mg) was suspended in THF in a 10mL vial equipped with a stirrer bar in a glove box. Diphenylsilane (0.2 mmol, 37.1  $\mu$ L) and 4-methoxyacetophenone (0.2 mmol, 24.5  $\mu$ L) were then added to the reaction vial. The reaction mixture was stirred at room temperature for 24 h to afford diphenyl[1-(4-methoxyphenyl)ethoxy]silane as the only product in quantitative yield based on GC-MS and NMR analyses. MS: m/z=334 [M<sup>+</sup>]; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ = 7.7 (m, 2H), 7.2–7.4 (m, 10H), 6.9 (d, 2H), 5.85 (s, 1H), 5.1 (q, 1H), 3.4 (s, 3H), 1.6 (d, 3H),

The reaction mixture was centrifuged, and the solution was removed. This procedure was repeated at least three times using THF as the washing solvent. The recovered catalyst was used directly for the next run.

## Asymmetric Hydrosilylation of Ketones with a Chiral Silane Intermediate

Catalyst **2** (10 mg) was suspended in THF in a 10-mL vial with a stirrer bar. Diphenylsilane (0.2 mmol, 37.1  $\mu$ L) and (–)-menthol (0.2 mmol, 30.8 mg) were then added to the reaction vial. The reaction mixture was stirred at room temperature overnight, and the product was characterized by GC-MS and NMR. Diphenyl(1-menthoxyl)silane **3** was produced in quantitative yield. MS: m/z = 338 [M<sup>+</sup>]; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.2$ –7.4 (m, 10H), 5.83 (s, 1H), 3.68 (m, 1H), 2.57 (m, 1H), 2.18 (d, 1H), 1.4–1.6 (m, 7H), 0.84 (d, 3H), 0.78 (d, 3H), 0.74 (d, 3H).

Next, acetophenone (0.18 mmol, 22  $\mu$ L) was added to the reaction vial, and the reaction solution was stirred at room temperature for 72 h. Acetophenone was transformed to the hydrosilylation product in excellent yield. The enantioselectivity was measured using chiral GC ( $\gamma$ -TA) after the product had been transformed to alcohol. (*R*)-1-Phenylethanol was produced in 40% *ee*.

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