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# NHC-catalyzed dehydrogenative self-coupling of diphenylsilane: a facile synthesis of octaphenylcyclotetra(siloxane)

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#### ARTICLE INFO

#### ABSTRACT

significant polymers.

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# Introduction

Siloxane polymers can be synthesized as fluids, gels, elastomers, and resins and have a wide variety of applications in both industry and academia (Fig. 1).<sup>1</sup> Straight chain poly(dimethyl-siloxane) (PDMS) is a representative silicone polymer with a number of useful properties including high gas permeability, a small dielectric constant, a very flexible backbone, and general chemical and physiological inertness.<sup>2</sup> Replacement of the methyl groups of PDMS with alternate organic substituents is of interest because it allows for fine-tuning of the properties of the polymer.<sup>3</sup> Octaphenylcyclotetra(siloxane) or (Ph<sub>2</sub>SiO)<sub>4</sub>, is a common reagent for the introduction of the diphenylsiloxane moiety into a variety of copolymers or it can be polymerized independently to yield polydiphenylsiloxane (PDPS). Recent work has shown that the incorporation of diphenvlsiloxane groups into polvimidesiloxane (PIS) polvmers provides for significantly improved compatibility between the segments of the copolymer and allowed for manipulation of the thermal stabilities and mechanical properties.<sup>4</sup>

Most of the previously published syntheses of octaphenylcyclotetra(siloxane), **1**, require lengthy reaction times and high temperatures.<sup>5</sup> These syntheses, as well as the typical industrial preparation of **1**, involve either the hydrolysis of diphenyldichlorosilanes or diphenyldialkoxysilanes. The general reaction is depicted in Scheme 1, with the best-reported reaction conditions included.<sup>6</sup> In addition to their application in polymer chemistry, silanols such as the one depicted in Scheme 1 are useful in their own right as reagents in cross coupling reactions.<sup>7</sup> Strict pH control prevents self-condensation to disiloxanes and higher order oligomers.<sup>8</sup> Although still widely prepared by the hydrolysis of the chlorosilanes, recent efforts have focused on the metal-catalyzed conversion of organosilanes to silanols. A number of promising systems employing rhenium, ruthenium, iridium, and silver have been developed,<sup>9</sup> most of which employ water or hydrogen peroxide as the oxygen source. Comparatively few methods employing

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A unique application of the CuIPr N-heterocyclic carbene (NHC) to the dehydrogenative self-coupling of

diphenylsilane has been discovered. This transformation is carried out open to air at room temperature,

vielding octaphenylcyclotetra(siloxane) quantitatively in 1 h. This preparation constitutes a significant

improvement over existing methods for the preparation of this compound and demonstrates a novel

mode of reactivity for CuIPr. The diphenylsilanone tetramer is the precursor to a number of industrially

molecular oxygen have been reported.<sup>10</sup>

## Results

The copper *N*,*N*'-bis(2,6-diisopropylphenyl)imidazol-2-ylidine (CuIPr) NHC is an air and moisture stable catalyst that has been applied in a wide variety of reactions,<sup>11</sup> but its application to silane oxidation has not, to our knowledge, been reported previously. During an investigation into the NHC–CuH mediated hydrosilylation of ketones,<sup>14</sup> we observed the formation of a highly crystalline



Figure 1. Representative siloxane polymers.





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Scheme 1. Prior synthesis of compound 1.

byproduct when rigorous exclusion of air was neglected. Indeed, our first observation of the byproduct occurred upon its precipitation from the crude hydrosilylation reaction mixture as a diamond shaped crystal over 2 cm in length! Upon isolation and characterization, we discovered it to be octaphenylcyclotetra(siloxane), **1**. Formation of the siloxane tetramer can be avoided by carrying out hydrosilylation under inert atmosphere. Alternatively, siloxane **1** can be obtained exclusively by simply stirring diphenylsilane and NaOt-Bu in THF containing 3 mol % CuIPr-Cl, open to air, under which conditions diphenyl silane is completely consumed in 1h at room temperature and siloxane **1** is produced quantitatively (Scheme 2). The evolution of gas, presumably hydrogen, is observed.

The identity of siloxane **1** was established by NMR, XRD, and combustion and melting point analysis. Very high quality colorless cubic crystals were obtained by slow diffusion of hexanes into dichloromethane at low temperature. The triclinic unit cell (*a* = 10.726 Å, *b* = 10.7624 Å, *c* = 19.125 Å,  $\alpha$  = 83.694°,  $\beta$  = 83.026°,  $\gamma$  = 76.213°) was determined to have the P1 space group, and after refinement, a final R value of 0.0402 was obtained. Details are found in the Supplementary data. Our crystal structure is illustrated in Figure 2, which is in complete agreement with that previously reported.<sup>5,6</sup>

It is likely that when the CuIPr is first treated with a *tert*-butoxide base it forms the copper alkoxide, which then reacts with the silane to give the corresponding copper hydride. The formation of IPr copper hydride in this manner is supported by its previously reported activity.<sup>12</sup> Notably, copper (I) hydride complexes have been reported to catalyze silicon–oxygen bond formation between organosilanes and alcohols.<sup>13</sup>

However, as this transformation proceeds smoothly even under anhydrous conditions, it apparently employs dioxygen as a reactant. The mechanism of the CuIPr-catalyzed formation of **1** is not obvious; there is precedence for the coordination of both molecular oxygen<sup>15</sup> and organosilanes<sup>16</sup> to NHCs. It is likely that the catalytic cycle yields diphenylsilanediol, which then undergoes dehydrogenative self-coupling to yield **1**.



Scheme 2. NHC-catalyzed oxidation of diphenylsilane.



Figure 2. XRD structure of compound 1.

## Conclusion

In summary, an extremely facile synthesis of octaphenylcyclotetra(siloxane) was discovered and, perhaps more notably, an interesting mode of reactivity for CuIPr NHC. The new synthesis of siloxane **1** provides a significant improvement over those currently in the literature and may be adaptable to a larger scale.

# Experimental

# General

All reagents and solvents were used as received, unless indicated below. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under N<sub>2</sub> immediately prior to use. <sup>1</sup>H NMR spectra were obtained at 300 or 400 MHz in CDCl<sub>3</sub> unless otherwise noted. Coupling constants (*J*), are reported in Hz. X-ray diffraction was carried out on a Bruker SMART X2S. The CuIPr was prepared according to literature methods.<sup>17</sup>

## Synthesis of octaphenylcyclotetrasiloxane, 1

To a scintillation vial equipped with a stir bar was added CuIPr (14.6 mg, 0.030 mmol), sodium *tert*-butoxide (11.5 mg, 0.12 mmol), and THF (5 mL). The reaction vessel was left open to air. The heterogeneous solution was stirred for 10 min before the addition of diphenyl silane (0.186 mL, 1.0 mmol). An immediate color change to bright yellow was observed and stirring was continued for 1 h, over which time the reaction solution darkened significantly. The reaction solution was then treated with charcoal, run through a plug of silica and celite, and recrystallized from dichloromethane and hexanes. The resultant highly crystalline white solid was isolated by filtration (0.25 mmol, 0.197 g, 100%). <sup>1</sup>HNMR (CDCl<sub>3</sub>): 7.23 (16H, t, *J* = 7.33), 7.39 (8H, tt, *J* = 7.49), 7.53 (16H, dd, *J* = 7.33). 13C NMR (CDCl<sub>3</sub>): 127.63 (CH), 130.04 (C), 134.40 (CH). Anal Calcd for C<sub>48</sub>H<sub>40</sub>O<sub>4</sub>Si<sub>4</sub>: C, 72.68; H, 5.08. Found: C, 72.62; H, 5.00.

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# Supplementary data

Spectroscopic data for compound **1** as well all XRD data can be found in supporting information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.09.028.

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