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Synthesis of dialkoxydiphenylsilanes *via* the rhodium-catalyzed hydrosilylation of aldehydes

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Abstract

The commercially available rhodium(I) complex $[\text{RhCl}(\text{CO})_2]_2$ (**1**) was shown to be an effective catalyst for the reduction of carbonyls with organosilanes under mild conditions. This study will focus on the hydrosilylation of aldehydes with diphenylsilane leading to the isolation of a series of dialkoxydiphenylsilanes with low catalytic loading of **1**.

Introduction

The chlorodicarbonylrhodium(I) dimer $[\text{Rh}(\mu\text{Cl})(\text{CO})_2]_2$ (**1**) has been extensively used in catalysis, and aside from its role as a precursor of a plethora of other catalytic species, this commercially available compound has served directly in many important catalytic processes. Foremost, complex **1** is a well-known active catalyst in carbocyclization reactions of polyunsaturated hydrocarbons; a topic that has recently led to significant achievements.¹ Indeed these cascade cycloadditions (or cycloisomerizations) catalyzed by **1** can give access to complex polycyclic systems which are key intermediates in the total synthesis of important fused-ring natural products.^{1a,g,m,n} Other cycloaddition reactions promoted by **1** involving the participation of a functional group were also described, and have allowed the construction of diverse *O*- and *N*-heterocycles.² In addition, the ready-to-use catalyst **1** has been utilized in miscellaneous synthetic transformations, including cross-coupling reactions such as the direct arylation of *N*-heteroaromatic substrates,³ Claisen rearrangements of propargyl vinyl ethers,⁴ allylic alkylations of allylic carbonates,⁵ and the Narasaka desilylation-acylation coupling.⁶ Less recently, several studies also reported the ring opening of strained rings such as epoxides or cyclopropanes mediated by **1**.⁷

On the other hand, very little has been reported regarding the catalytic ability of **1** in the presence of hydrosilanes. In 1992, the hydrosilylation of vinyl acetate was briefly described and showed poor regioselectivity,⁸ whereas the carbonylation of enamines *via* their reaction with silanes under a pressure of CO (50 atm) provided an efficient route to various α -(siloxymethylene)amines.⁹ In 2018, the synthesis of β -silylated (*Z*)-enamides was achieved *via* the hydrosilylation of internal ynamides with bulky silanes as reactants.¹⁰ Very recently, we have disclosed that complex **1** is also an efficient catalyst for the deoxygenation of ketones to alkanes in the presence of hydrosilanes.¹¹ Finally, $[\text{RhCl}(\text{CO})_2]_2$ was used for the catalytic hydrolysis of silanes to generate silanols and dihydrogen.¹²

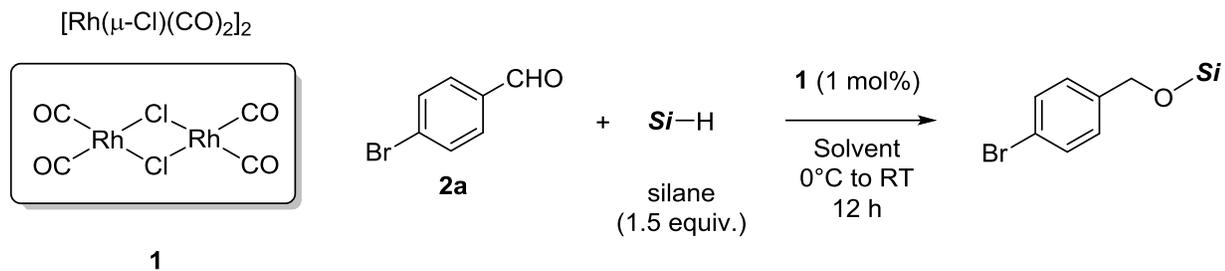
Over the years, the rhodium-catalyzed hydrosilylation of carbonyl compounds has been extensively studied and has emerged as a classical method for the synthesis of alcohols.¹³ Inspired by these studies and in line with our interest in utilising metal carbonyls in catalysis,¹⁴ we present herein the catalytic properties of **1** in the hydrosilylation of aldehydes which has resulted in the development of a new method for the synthesis of dialkoxydiphenylsilane derivatives.

Results and Discussion

Initial experiments exploring the catalytic performance of **1** in the reduction of carbonyls were carried out with 4-bromobenzaldehyde (**2a**) as the model substrate (Table 1). In the presence of HSiEt_3 as the hydride source and with a catalytic loading of 1 mol%, several solvents were screened (Table 1, entries 1-5). Chlorinated solvents were clearly the best suited since full conversions of **2a** were only reached in CHCl_3 and CH_2Cl_2 over 12 h at room temperature. Other common hydrosilanes were then tested in CH_2Cl_2 . If conversions were around 50% with dialkoxymethylsilanes, polymethylhydrosiloxane (PMHS) gave a good conversion of 95% (Table 1, entries 6-8).

Table 1

Hydrosilylation of 4-bromobenzaldehyde (**2a**) catalyzed by **1**.



Entry	Solvent	Silane	Conversion ^a (%)
1	THF	HSiEt ₃	12
2	CH ₃ NO ₂	HSiEt ₃	3
3	CH ₃ CN	HSiEt ₃	traces
4	CHCl ₃	HSiEt ₃	>99
5	CH ₂ Cl ₂	HSiEt ₃	>99
6	CH ₂ Cl ₂	(EtO) ₂ MeSiH	50
7	CH ₂ Cl ₂	(MeO) ₂ MeSiH	54
8	CH ₂ Cl ₂	PMHS	95
9	CH ₂ Cl ₂	PhSiH ₃	>99
10	CH ₂ Cl ₂	Ph ₃ SiH	>99
11	CH ₂ Cl ₂	Ph ₂ SiH ₂	>99
12 ^b	CH ₂ Cl ₂	Ph ₂ SiH ₂	>99

^a Conversions were determined by ¹H NMR spectroscopy after evaporation of the crude products.

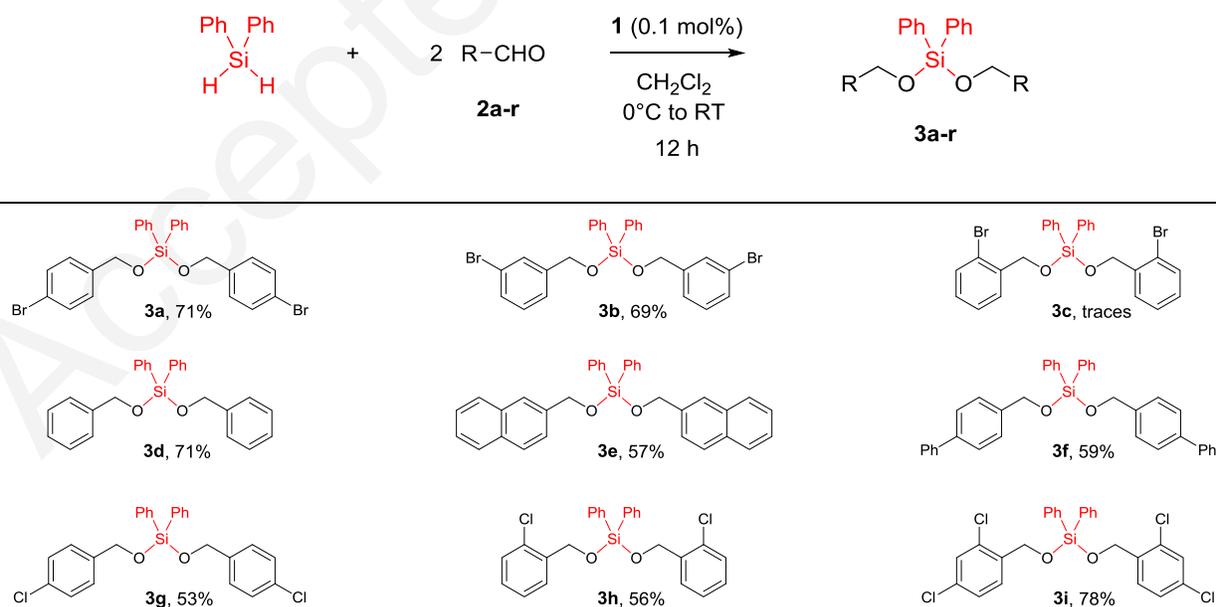
^b With 0.1 mol% of **1**.

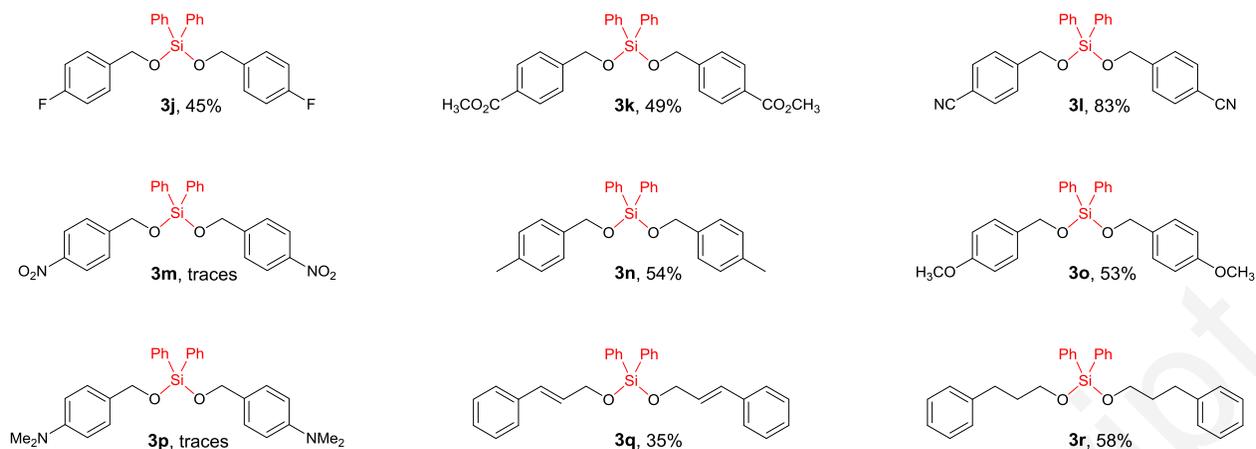
The phenylated silanes PhSiH₃, Ph₃SiH, and Ph₂SiH₂ were all highly effective in the hydrosilylation of **2a** despite their rather different reactivities (Table 1, entries 9-11). Interestingly, decreasing the catalytic amount of **1** to 0.1 mol% with Ph₂SiH₂ had no effect on the reaction (Table 1, entry 12).

As previously noted, in most studies on the hydrosilylation of aldehydes or ketones, the hydrosilylated adducts are generally converted into the corresponding alcohols, either by *in situ* hydrolysis in protic media or during aqueous work-up of the silyl ether intermediates. In an alternative approach motivated by atom economy concerns, the hydrosilylation of aldehydes catalyzed by **1** was further investigated with the aim of isolating the alkoxy silanes, which can be valuable commodity reagents,¹⁵ rather than their alcohol derivatives. The dihydrosilane Ph₂SiH₂ was used as the limiting reagent with various aldehydes in a slight excess (2.2 equiv.) according to the reaction conditions depicted in entry 12 of Table 1. Following this procedure, a series of dialkoxydiphenylsilanes **3** were obtained successfully (Table 2).

Table 2

Synthesis of dialkoxydiphenylsilanes **3** *via* the hydrosilylation of aldehydes with Ph₂SiH₂ catalyzed by **1**.^{a,b}





^a Reagents and conditions: aldehyde (1.18 mmol), diphenylsilane (0.54 mmol), complex **1** (0.1 mol%, based on the aldehyde), CH₂Cl₂ (3 mL), room temperature, 12 h, under argon.

^b Isolated yields.

The model substrate **2a** gave compound **3a** with a good yield of 71%. Its *meta* isomer **3b** was obtained in a similar yield (69%) from 3-bromobenzaldehyde (**2b**), whereas low conversion was observed with 2-bromobenzaldehyde (**2c**) giving rise to only trace amounts of **3c**, indicating that this condensation of carbonyl groups with Ph₂SiH₂ is sensitive to steric hindrance. The reaction of **2c** in the presence of 1 mol% of **1** led to the same result. With benzaldehyde (**2d**), 2-naphthaldehyde (**2e**), and 4-phenylbenzaldehyde (**2f**), the silyl ethers **3d-f** were obtained in moderate to good yields, ranging from 57% to 71%. The reactivity of benzaldehyde derivatives possessing electron-withdrawing groups was next examined. 4-Chlorobenzaldehyde (**2g**) was transformed into **3g**, which was isolated with a lower yield than its bromo analog **3a** (53% vs. 71%). In the case of 2-chlorobenzaldehyde (**2h**), and contrary to **2c**, the reaction was not hampered by steric effects and compound **3h** was isolated in 56% yield. The silyl acetal **3i** was easily prepared from 2,4-dichlorobenzaldehyde (**2i**) with a good yield of 78%, whereas the fluorinated compound **3j** was isolated with a lower yield of 45%, presumably due to the partial oxidation of 4-fluorobenzaldehyde (**2j**). This process also tolerated ester and nitrile functional groups, and **3k** and **3l** were synthesized in 49% and 83% yields, respectively. For 4-nitrobenzaldehyde (**2m**), analysis of the crude compound revealed the formation of an intractable mixture, presumably due

to competitive reduction pathways between the carbonyl and the NO₂ groups. For electron-rich aldehydes such as *p*-tolualdehyde (**2n**) and *p*-anisaldehyde (**2o**), the condensation products **3n** and **3o** were isolated in 54% and 53% yields, respectively, whereas the presence of a stronger donor group such as NMe₂ in **2p** has resulted in a severe decrease in conversion. In addition to the aromatic aldehydes, cinnamaldehyde (**2q**) was also submitted to the reaction giving **3q** with a modest yield of 35%, and 3-phenylpropionaldehyde (**2r**) gave alkoxyasilane **3r** in 58% yield. With the exception of **3d** and **3q**,¹⁶ all of the silyl acetals obtained were novel compounds and were fully characterized.

Conclusion

Chlorodicarbonylrhodium dimer (**1**) was demonstrated to be an active catalyst for the reduction of aldehydes in the presence of hydrosilanes as mild reducing agents. With low catalytic loading, the efficient hydrosilylation of aldehydes in the presence of diphenylsilane led to the synthesis of dialkoxydiphenylsilanes. Other studies on this catalytic system will be reported in due course to further enhance the long-lasting interest devoted to complex **1** as a reliable commercial tool for catalysis.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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