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Rhodium-catalyzed Decarbonylation of Acylsilanes

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Dedicated to Professor Keiji Maruoka on the occasion of his 70th birthday

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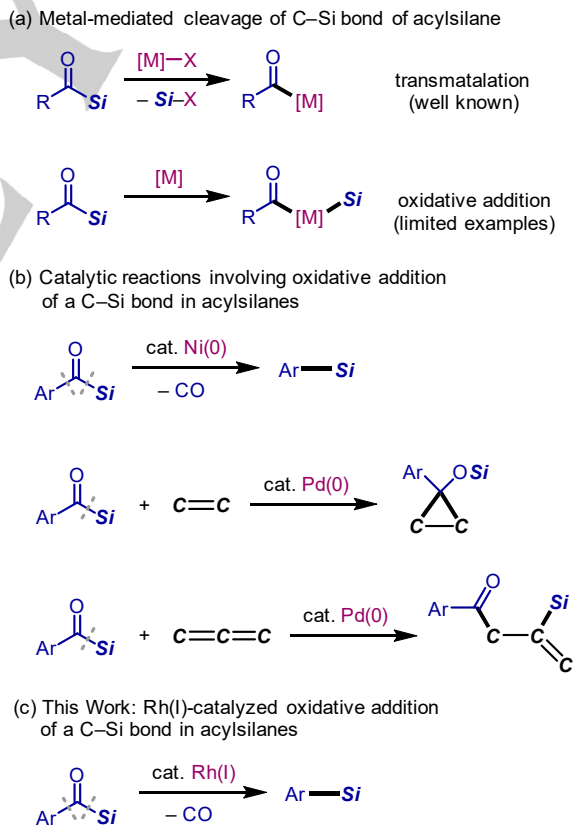
Abstract: We report herein on the rhodium-catalyzed decarbonylation of acylsilanes. This reaction proceeds through the cleavage of a carbon–silicon bond in acylsilanes.

Introduction

The transition metal-catalyzed decarbonylation of aldehydes, or Tsuji-Wilkinson decarbonylation, has been used extensively in organic synthesis.[1] If such a decarbonylation process could be applied to other carbonyl compounds, it would provide a powerful method for forging new chemical bonds other than C–H bonds.[2] Although the scope of the reaction is somewhat limited, catalytic decarbonylation reactions of ketones,[3] esters,[4] amides,[5] and some other carbonyl compounds[6,7] have been reported to date. We[8a] and Rueping[8b] independently reported that acylsilanes[9] can also be decarbonylated with the aid of nickel catalysts via the cleavage of C–C and C–Si bonds.

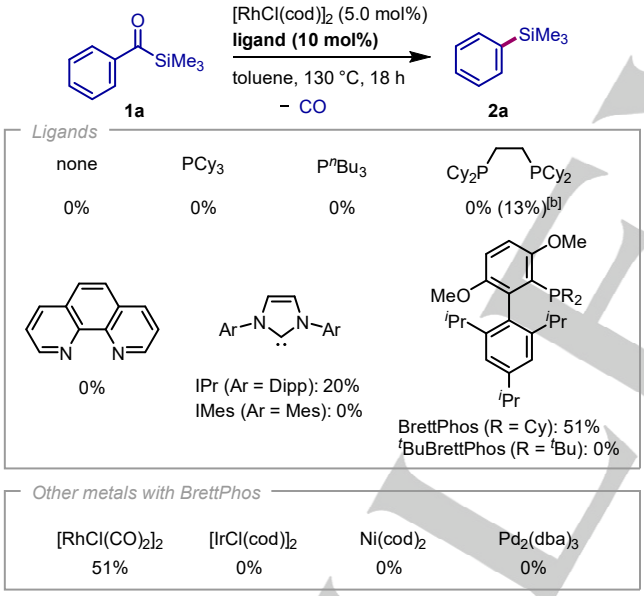
Regarding the cleavage of a carbon–silicon bond in acylsilanes, two mechanistic modes appear to be involved. One is a transmetallation reaction, in which a silyl group serves as a leaving group to generate an acylmetal species (Scheme 1a, top).[10] In this process, the oxidation state of the metal center remains unchanged. The other mode is oxidative addition, in which an (acyl)(silyl)metal species is formed with the increase of the oxidation state of the metal center by two (Scheme 1a, bottom). The transmetallation process has been successfully applied to cross-coupling type reactions using acylsilanes.[10] In contrast, there are only a limited number of reports of catalytic reactions that involve the oxidative addition of acylsilanes, despite the potential utility of such reactions in the synthesis of organosilicon compounds by incorporating both an acyl and a silyl group of acylsilanes into the product. Narasaka reported that bis(silyl)ketones can be decarbonylated in the presence of a catalytic amount of a palladium complex, a reaction that likely involves oxidative addition of a C–Si bond.[11] This process was further applied to decarbonylative addition across electron-deficient alkynes. However, the applicability of these reactions to acylsilanes was not mentioned. As described above, we[8a] and Rueping's group[8b] independently developed the nickel-catalyzed decarbonylation of acylsilanes, which suggests that a nickel(0) complex can mediate the oxidative addition of acylsilanes (Scheme 1b, top). We also recently reported on the palladium-catalyzed siloxycyclopropanation of alkenes[12] and silylacylation of allenes[13] using acylsilanes, in which the oxidative addition of a C–Si bond in acylsilanes to a palladium(0) complex is involved (Scheme 1b, middle and bottom). We report herein that the decarbonylation of acylsilanes can also be catalyzed by a rhodium(I) complex, which suggests that carbon–silicon bond of acylsilanes can oxidatively add to a rhodium(I) center (Scheme 1c).[14]



Scheme 1. Metal-mediated activation of a C–Si bond in acylsilanes and its application to catalytic reactions.

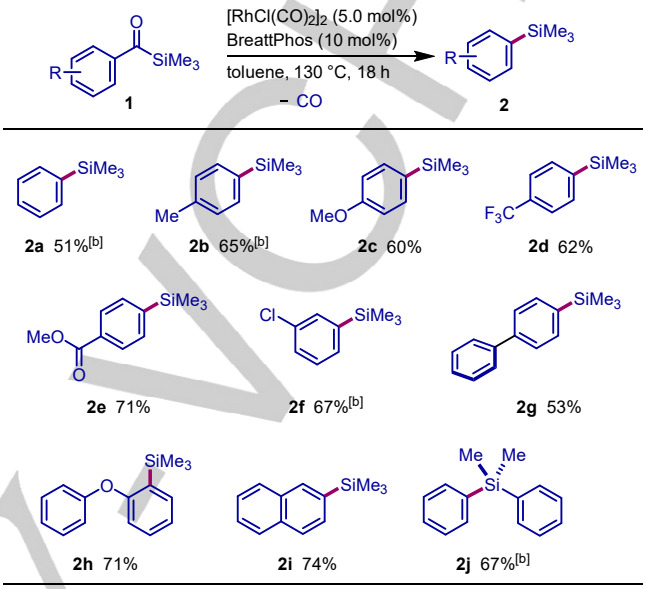
Results and Discussion

We initially investigated the reaction of acylsilane **1a** in the presence of 5.0 mol% of $[RhCl(cod)]_2$ at 130 °C for 18 h. (Scheme 2). No reaction occurred in the absence of an added ligand. The addition of monodentate phosphines, such as PCy_3 and P^nBu_3, also failed to promote the reaction. The use of a P-based bidentate ligand dcype at 160 °C led to the formation of decarbonylated product **2a**, albeit in low yield (13%). Phenanthroline (0%) and NHC ligands, such as IPr (20%) and IMes (0%), which were effective ligands for nickel-catalyzed decarbonylation of acylsilanes,[8a] were also not as effective for this rhodium system. When Brettphos was used as a ligand, the yield of **2a** was increased to 51%. When the Cy groups of Brettphos were replaced with ^{t}Bu groups (*i.e.*, ^{t}BuBrettphos), no reaction occurred. The use of $[RhCl(CO)_2]$ as a catalyst precursor resulted in the formation of **2a** in a yield comparable to that obtained with $[RhCl(cod)]_2$. This indicate that the eliminated CO does not completely deactivate the catalyst, which is in sharp contrast to nickel-catalyzed decarbonylation of carbonyl compounds.[3c,5b] When other metal catalysts such as iridium(I), nickel(0), and palladium(0), were used instead of rhodium(I), **2a** was not produced under these conditions using a BrettPhos ligand.



Scheme 2. Reaction optimization[a] [a]Yield of **2a** was determined by GC using pentadecane as an internal standard due to volatility of **2a**. [b]Run at 160 °C.

With the optimized conditions in hand, the scope of this rhodium-catalyzed decarbonylation of acylsilanes was next explored (Scheme 3). Both electron-rich (**1b**, **1c**) and electron-deficient (**1d**, **1e**) acylsilanes could be decarbonylated under these conditions with the formation of the corresponding arylsilanes **2b**, **2c**, **2d**, and **2e**, in which ether and ester groups were tolerated. A chloroarene moiety was also applicable for this reaction without loss of the chlorine atom, as exemplified by the formation of **2f**. When a substrate containing a biphenyl moiety (**1g**) was used, the corresponding arylsilane **2g** was obtained in 53% yield. Substrates bearing an ortho substituent, such as 2-phenoxybenzoylsilane (**1h**), were also good substrates for this reaction. An acylsilane having a π-extended naphthalene ring (**1i**) also participated in this decarbonylation to form 2-naphthylsilane **2i** in 74% yield. Regarding the substituents on the silicon atom, a bulkier $SiMe_2Ph$ group (**1j**) can also be used for this rhodium-catalyzed decarbonylation, with biarylsilane **2j** being produced in 67% yield.



Scheme 3. Scope of Rh-catalyzed decarbonylation of acylsilanes.[a] [a]Isolated yields are shown unless otherwise noted. [b]Yield of **2** was determined by GC using pentadecane as an internal standard due to the volatility of the product.

Several preliminary experiments were carried out to obtain mechanistic insights for this decarbonylation reactions. When $[RhCl(CO)_2)]_2$ and a BrettPhos ligand (0.50 equiv) were reacted in toluene at 80 °C, a yellow precipitate was formed. X-ray crystallographic analysis of a recrystallized sample unambiguously determined that an ion pair consisting of cationic and anionic rhodium complexes (*i.e.*, **3**) was generated, presumably by disproportionation of a neutral rhodium(I)–Cl complex (Scheme 4a). Although similar ion pair rhodium complexes are known to be formed with several ligands,[15] complexes with a Buchwald-type ligand has not been reported, to the best of our knowledge. We next examined the catalytic activity of **3** for the decarbonylation of **1a** (Scheme 4b). As a result, **2a** was obtained in a yield comparable to that obtained with a $[RhCl(CO)_2]_2$/BrettPhos catalyst, although it is unclear at this stage whether **3** is the catalytically active species or a resting-state species in this reaction. A crossover experiment using acylsilanes **1c** and **1j** resulted in the formation of crossover products **2c'** and **2a**, in addition to intramolecular decarbonylation products **2c** and **2j** (Scheme 4c). These results indicate that the aryl groups on the rhodium center are interchangeable under the catalytic conditions being used.[16]

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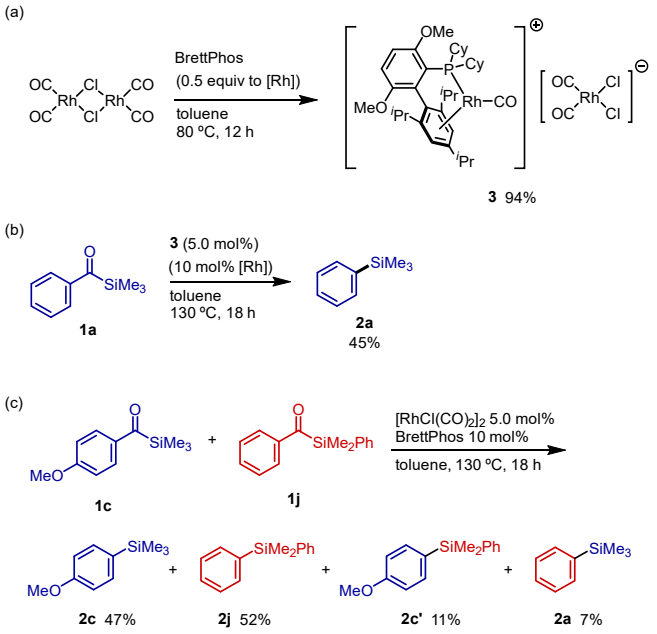
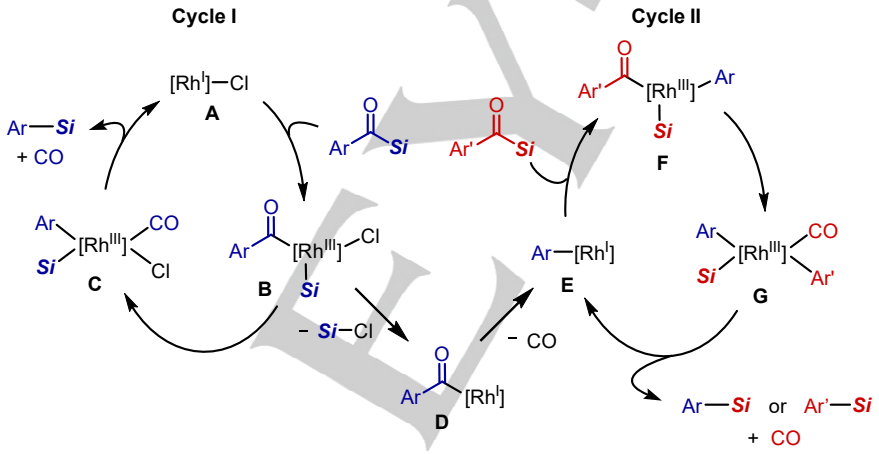


Scheme 4. Mechanistic studies.

Based on the results of a crossover experiment, proposed catalytic cycles for this reaction are depicted in Scheme 5. The reaction is initiated by the oxidative addition of a carbon–silicon bond of acylsilane **1** across Rh(I)–Cl (**A**) to give (acyl)(silyl)rhodium(III) intermediate **B**. The elimination of CO subsequently gives arylrhodium(III) species **C**, which finally leads to the formation of product **2** by reductive elimination (Cycle I). Alternatively, intermediate **B** can release chlorosilane (*Si*–Cl) by reductive elimination to generate acylrhodium(I) **D**,[17] which leads to the formation of arylrhodium(I) **E** by the extrusion of CO. This complex **E** can also catalyze the decarbonylation of acylsilane (Cycle II). Cycle II is basically the same as Cycle I, except that the chloro ligand is replaced by an aryl group. The oxidative addition of an acylsilane, followed by decarbonylation forms intermediate **G**, which bears two aryl ligands. Both of the aryl ligands can reductively eliminate with the silyl ligand to form a decarbonylated product, which explains the experimental observations of the crossover products.



Scheme 5. A possible mechanism.

Conclusion

In summary, we report on the rhodium-catalyzed decarbonylation of acylsilanes, in which BrettPhos serves as an appropriate ligand. In previously reported catalytic reactions of acylsilanes that involves the oxidative addition of a carbon–silicon bond, Ni(0) and Pd(0) catalysts were used. This work demonstrates that a rhodium(I) complex can also mediate the oxidative addition of carbon–silicon bonds of acylsilanes and can be used for the transformation of acylsilanes in which a substituent of the acyl group and the silyl group are both incorporated into the product. Further investigation of catalytic transformation of acylsilanes via oxidative addition of a carbon–silicon bond is ongoing in our laboratory.

Acknowledgements

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Keywords: Acylsilanes • Decarbonyaltion • Homogeneous catalysis • Organosilicon compounds • Rhodium catalyst

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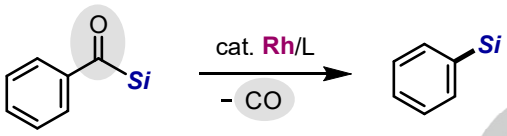

Cleavage of C–C and C–Si bonds

A carbon–silicon bond in acylsilanes can be activated by a rhodium(I) catalyst. A rhodium-catalyzed decarbonylation of acylsilane is developed for the formation of arylsilanes.

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