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Cobalt-Catalyzed Decarbonylation of Aromatic Acylsilanes via the Cleavage of Carbon–Silicon Bonds

Akihisa Matsuura,[a] Ryoichi Tabata,[a] and Mamoru Tobisu*[a, b]

Dedicated to the memory of Prof. Shinji Murai.

The catalytic decarbonylation of acylsilanes provides a unique entry to arylsilanes through C—Si bond activation. Here we describe a cobalt-catalyzed protocol that enables this transformation. A range of benzoylsilanes bearing trimethylsilyl, triethylsilyl, or dimethylphenylsilyl groups were converted into the corresponding arylsilanes, while functional groups such as esters, nitriles, ethers, and acetals were tolerated. Control experiments using mixed acylsilanes revealed that the cobalt catalyst operates without generating crossover products, suggesting a pathway distinct from that of rhodium catalysts and mechanistically closer to nickel. Comparative studies further demonstrated that the cobalt system exhibits higher activity than the nickel counterpart. In addition, the method allows post-modification of acylsilane directing groups, as illustrated by the sequential ortho-C—H functionalization and subsequent cobalt-catalyzed decarbonylation.

1. Introduction

Acylsilanes are a distinctive class of organosilicon compounds in which a carbonyl group is directly bound to silicon. Since their first report by Brook in 1957,[1] their unique electronic properties—arising from hyperconjugative stabilization and σ^*–π^* interactions involving the silicon atom—have enabled reactivity patterns distinct from those of conventional carbonyl compounds.[2–4] Owing to these characteristics, acylsilanes have found wide utility in organic synthesis, particularly in nucleophile-triggered rearrangements, acyl anion equivalent chemistry, and photochemical transformations.[3,5–9] Beyond these well-established ionic and photochemical modes, the activation of acylsilanes by transition metals remains a comparatively underexplored yet promising strategy for developing novel transformations.[10]

Transition metal-mediated cleavage of the C—Si bond in acylsilanes can proceed through two distinct mechanistic pathways (Scheme 1a).[11] In the more common transmetallation pathway, the silyl group departs as a leaving group to generate an acylmetal species without altering the oxidation state of the metal. This mode has been extensively exploited in cross-coupling reactions in which acylsilanes act as acyl donors.[12–14] In contrast, oxidative addition of a C—Si bond—leading to the formation of an (acyl)(silyl)metal species with a two-electron increase in the oxidation state of the metal—is far less common. Despite its rarity, oxidative addition of C—Si bonds in acylsilanes is mechanistically intriguing and synthetically valuable, as it opens the door to transformations that incorporate both the acyl and silyl units into the product or enable bond constructions via decarbonylation.

In recent years, oxidative addition of acylsilane C—Si bonds has been demonstrated with nickel,[15–17] palladium,[18–23] and rhodium[24] catalysts, enabling decarbonylations, insertions and related bond-forming processes. However, the repertoire of metals capable of effecting such oxidative additions remains narrow. Broadening the range of transition metals that can mediate this key elementary step is important not only for expanding the synthetic scope of acylsilane chemistry but also for discovering reactivity modes that may be inaccessible to the established catalytic systems. In this context, catalytic decarbonylation of acylsilanes[15–18,22,24] represents an attractive testing ground for new catalyst systems: the reaction directly probes the ability of a metal to engage in oxidative addition of a C—Si bond, while also posing the challenges of CO extrusion and catalyst turnover, given the potentially inhibitory effect of CO arising from its strong binding to catalytically active metal species.

In this study, we report the first example of a cobalt-catalyzed decarbonylation of acylsilanes via oxidative addition of the C—Si bond (Scheme 1b). This transformation expands the scope of metal catalysts known to activate acylsilanes through oxidative addition, complementing the established nickel-, palladium-,

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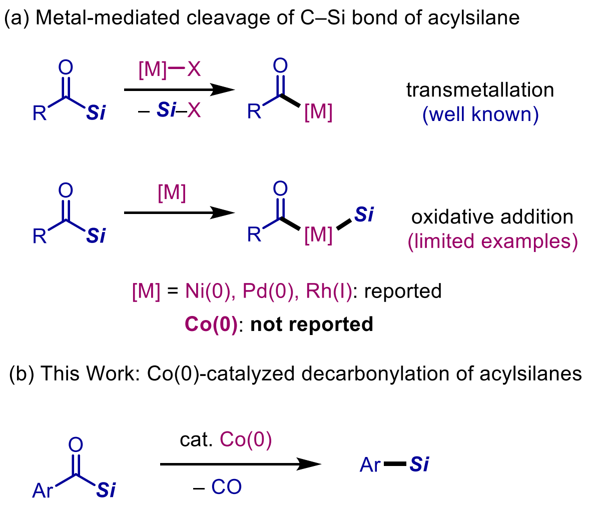
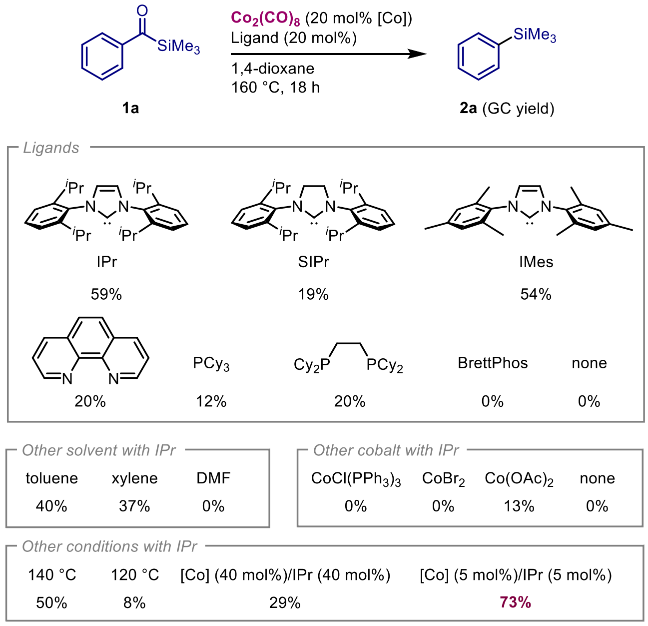


Scheme 1. Metal-mediated activation of a C—Si bond in acylsilanes: background and this work.

and rhodium-based systems. The use of cobalt not only provides a new entry into C—Si bond activation chemistry but also highlights the potential of earth-abundant first-row transition metals in the development of cost-effective and mechanistically diverse catalytic platforms for acylsilane functionalization.

2. Results and Discussion

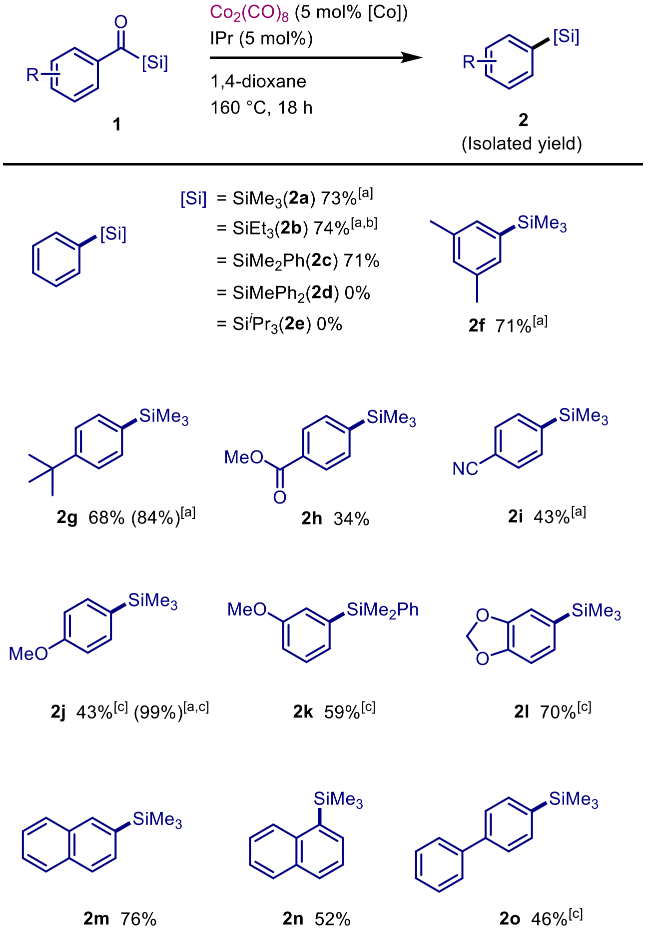
In 2018, Dong and co-workers reported that $Co_2(CO)_8$ can catalyze the insertion of tethered alkynes into cyclobutanones, a transformation that presumably proceeds through the oxidative addition of strained C—C bonds to cobalt complexes.[25] More recently, Wei demonstrated that $Co_2(CO)_8$ is also competent for the decarbonylation of diaryl ketones bearing N-heteroarene-based directing groups.[26] Both of these studies highlight that $Co_2(CO)_8$ can mediate the oxidative addition of otherwise inert C—C bonds when aided by the formation of a stable metallacycle with a suitably placed directing group. Inspired by these precedents, we became interested in exploring $Co_2(CO)_8$ as a catalyst for the decarbonylation of acylsilanes. In contrast to the challenging activation of C—C bonds, we reasoned that C—Si bonds, being weaker and more polarized, might undergo oxidative addition without the assistance of a directing group. We therefore initiated our investigation using acylsilane **1a** as a model substrate under cobalt catalysis. When **1a** was heated in the presence of $Co_2(CO)_8$ (20 mol% [Co]) at 160 °C in 1,4-dioxane in a sealed pressure-resistant vessel, no decarbonylation was observed in the absence of additional ligands. (Scheme 2). However, ligand tuning proved crucial to unlocking catalytic activity. In particular, bulky *N*-heterocyclic carbene (NHC) ligands such as IPr [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and IMes (1,3-dimesitylimidazol-2-ylidene) significantly enhanced the reaction, affording the decarbonylation product **2** in 59% and 54% yield, respectively. Interestingly, the saturated analogue SIPr gave a much lower yield (19%), underscoring the importance of the steric and electronic environment around the NHC ligand.



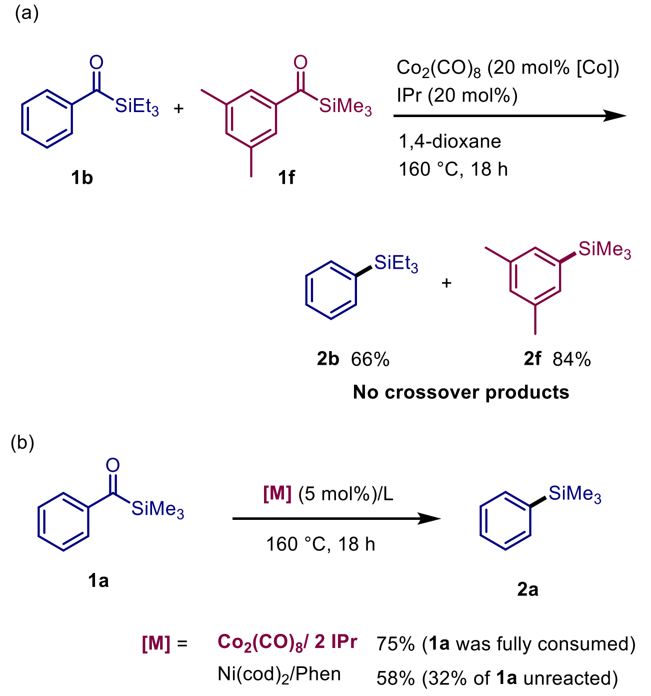
Scheme 2. Optimization for cobalt-catalyzed decarbonylation of **1a**.

Other classes of ligands were also evaluated. 1,10-Phenanthroline, which has previously proven highly effective in nickel-catalyzed decarbonylation,[16] delivered only modest activity under cobalt catalysis (20%). Commonly employed phosphine ligands such as PCy_3 and dcype, which are often used in decarbonylation reactions,[27,28] were also markedly less effective, providing yields of only 12% and 20%, respectively. Furthermore, Buchwald's BrettPhos ligand, which is optimal in the rhodium-catalyzed decarbonylation of acylsilanes,[24] was completely ineffective under cobalt catalysis. Encouraged by the relatively high performance of IPr, we next optimized other reaction parameters using this ligand. Solvent screening revealed that, in addition to 1,4-dioxane, non-polar solvents such as toluene and xylene were also suitable, whereas polar solvents such as DMF completely inhibited catalysis. Variation of the cobalt source showed that $CoCl(PPh_3)_3$ and $CoBr_2$ were inactive, while $Co(OAc)_2$ exhibited weak activity, providing product **2** in 13% yield. Reaction temperature was also found to be critical: while 160 °C proved optimal, lowering the temperature led to decreased efficiency (50% yield at 140 °C; 8% yield at 120 °C). Finally, the effect of catalyst loading was examined. Remarkably, reducing the loading of $Co_2(CO)_8$ from 20 mol% [Co] to 5 mol% significantly improved the reaction outcome, affording **2** in 73% yield.

Having established the optimized reaction conditions, we next investigated the substrate scope of this cobalt-catalyzed decarbonylation of acylsilanes (Scheme 3). Variation of the silicon substituent revealed that, in addition to the trimethylsilyl group (**1a**), bulkier silyl groups such as triethylsilyl (**1b**) and dimethylphenylsilyl (**1c**) were also compatible, thus enabling the introduction of structurally diverse silyl groups into the products. In sharp contrast, sterically demanding diphenylmethylsilyl (**1d**) and triisopropylsilyl (**1e**) substituents completely suppressed the reaction, most likely due to steric congestion around the cobalt center that hampers oxidative addition of the C—Si bond. The



Scheme 3. Reaction scope. a) Yield of **2** was determined by GC using dodecane as an internal standard due to the volatility of the product. b) $Co_2(CO)_8$ (20 mol% [Co])/IPr (20 mol%). c) $Co_2(CO)_8$ (10 mol% [Co])/IPr (10 mol%).



Scheme 4. Crossover and comparative experiments.

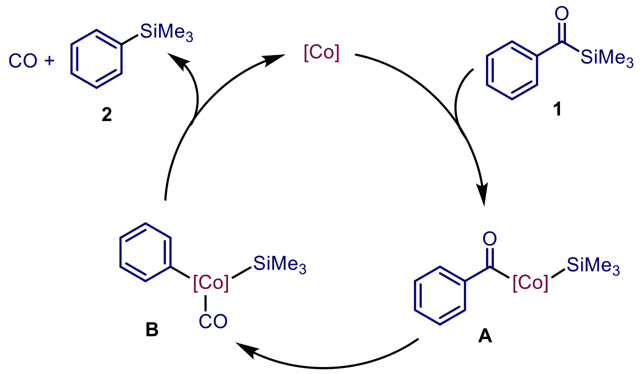
electronic and steric properties of the aryl group were also well tolerated. For example, benzoylsilanes bearing alkyl substituents at the 3,5-positions (**1f**) or a bulky *tert*-butyl group at the para-position (**1g**) underwent smooth decarbonylation, delivering the corresponding arylsilanes in good yield. Furthermore, the reaction displayed a high degree of functional-group compatibility: esters (**1h**), nitriles (**1i**), ethers (**1j** and **1k**), and even acid-sensitive acetals (**1l**) were all tolerated under the standard catalytic conditions. The method was applicable to acylsilanes containing π-extended aromatic frameworks. Substrates bearing naphthyl (**1m** and **1n**) and biphenyl (**1o**) groups also participated successfully in the decarbonylation reaction, providing the corresponding arylsilanes. These results underscore the robustness of the cobalt catalyst system and its ability to accommodate both sterically and electronically diverse aryl substituents.

As described in the Introduction, both Ni(0)[15,16] and Rh(I)[24] complexes are known to catalyze the decarbonylation of aromatic acylsilanes, yet these systems proceed through notably different pathways. The distinction becomes particularly evident in crossover experiments. With Ni(0), only the direct decarbonylation products are observed, indicating a strictly intramolecular process. In contrast, Rh(I) gives rise to crossover products in which the aryl and silyl fragments are exchanged, pointing to the involvement of an intermolecular pathway. This mechanistic divergence highlights the sensitivity of acylsilane decarbonylation to the nature of the transition-metal center, and raises the intriguing question of how cobalt would behave in comparison.

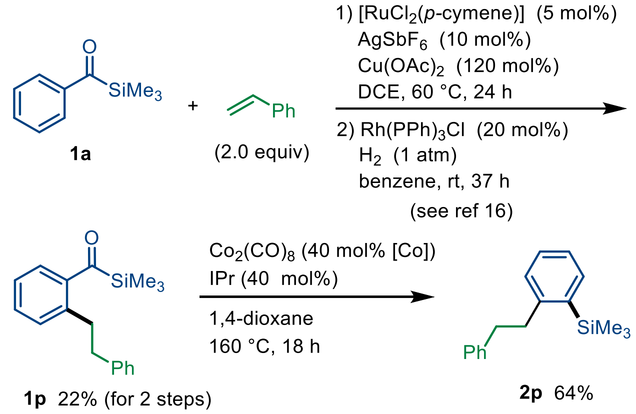
Our crossover study with cobalt provided a clear answer: when acylsilanes **1b** and **1f** were subjected to cobalt catalysis, only the simple decarbonylation products **2b** and **2f** were obtained, with no evidence of crossover (Scheme 4a). This outcome strongly suggests that, unlike Rh(I), cobalt does not promote intermolecular fragment exchange, but instead follows a mechanistic pathway more closely resembling that of nickel. Thus, cobalt appears to combine mechanistic features of Ni(0) catalysis with distinct reactivity advantages.

The difference in catalytic efficiency between cobalt and nickel further underscores this point (Scheme 4b). With identical catalyst loadings (2.5 mol%, assuming $Co_2(CO)_8$ generates two equivalents of active cobalt species) and optimal ligands (IPr for $Co_2(CO)_8$ and 1,10-phenanthroline for $Ni(cod)_2$), the cobalt system completely consumed **1a** to afford **2a** in 75% yield, whereas the nickel catalyst delivered 58% yield, leaving 32% of **1a** unreacted. These results clearly show that cobalt is not only mechanistically analogous to nickel but also exhibits superior catalytic activity. Overall, cobalt emerges as a uniquely effective catalyst for acylsilane decarbonylation, combining a clean intramolecular pathway with higher efficiency than its nickel analogue.

Based on the experimental observation that no crossover products were detected, we propose the mechanism shown in Scheme 5. In this pathway, an NHC-ligated cobalt(0) complex serves as the active species, mediating the oxidative addition of



Scheme 5. Proposed mechanism.



Scheme 6. Synthetic application.

the C—Si bond in acylsilane **1** to generate cobalt(II) intermediate **A**. This acyl–cobalt complex then undergoes CO extrusion to afford aryl–cobalt species **B**, which subsequently delivers the decarbonylation product **2** through reductive elimination.

While our initial motivation for studying this transformation was to identify a new metal catalyst capable of activating the C—Si bond of acylsilanes, we also sought to demonstrate the synthetic utility of this cobalt-catalyzed system. In particular, we were intrigued by the fact that the carbonyl group in benzoylsilane derivatives is known to function as a directing group in metal-catalyzed ortho C—H bond functionalization reactions.[29] We envisioned that our protocol would allow post-modification of such an acylsilane directing group (Scheme 6). Indeed, treatment of **1a** with styrene under ruthenium catalysis,[30] followed by hydrogenation, furnished ortho-alkylated acylsilane **1p** in a site-selective fashion. Subsequent cobalt-catalyzed decarbonylation of **1p** cleanly produced ortho-substituted arylsilane **2p**. As this sequence illustrates, complex ortho-substituted arylsilanes can be accessed through C—H functionalization followed by cobalt-catalyzed decarbonylation, in which the trimethylsilyl group formally acts as a directing group. This dual role of acylsilanes—as both directing groups and precursors to arylsilanes—underscores the versatility of the present strategy.

3. Conclusion

In conclusion, we have demonstrated that cobalt catalysts are capable of promoting the decarbonylation of aromatic acylsilanes through selective activation of the C—Si bond. Mechanistic studies revealed that the cobalt pathway operates in a manner analogous to nickel catalysis and distinct from rhodium systems. Moreover, by combining cobalt-catalyzed decarbonylation with C—H functionalization, we showcased the potential of acylsilanes to serve not only as directing groups but also as versatile precursors to synthetically valuable arylsilanes. Importantly, this study highlights decarbonylation as a representative example of a unimolecular fragment coupling (UFC) process,[31–33] in which the elimination of a small molecule—in this case CO—enables coupling of the remaining fragments. The discovery that cobalt can mediate decarbonylation via C—Si bond activation thus provides a significant mechanistic and synthetic insight that may inspire the development of new classes of UFC transformations. Further investigations along this line are currently ongoing in our laboratory.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Acknowledgments

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Conflict of Interests

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Acylsilane · C—Si bond activation · Cobalt · Decarbonylation · Homogeneous catalysis

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