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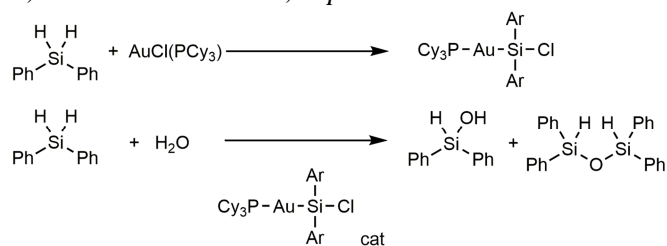
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Gold(I) complexes with chloro(diaryl)silyl ligand. Stoichiometric reactions and catalysis for *O*-functionalization of organosilane

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ABSTRACT

An Au(I) complex with a chloro(diphenyl)silyl ligand [Au(SiPh₂Cl)(PCy₃)] (**1a**) is obtained from the reaction of Ph₂SiH₂ with [AuCl(PCy₃)]. (4-FC₆H₄)₂SiH₂, (4-MeC₆H₄)₂SiH₂, and Ph₂GeH₂ react with [AuCl(PCy₃)] to form complexes with the chlorodiarylsilyl ligand, [Au(SiAr₂Cl)(PCy₃)] (**1b**: Ar = C₆H₄F-4, **1c**: Ar = C₆H₄Me-4) and with the chloro(diphenyl)germyl ligand, [Au(GePh₂Cl)(PCy₃)] (**2a**), respectively. Complex **1a** reacts with H₂O to form Ph₂SiH(OH) and (Ph₂SiH)₂O, whereas the reaction of EtOH with **1a** yields Ph₂SiH(OEt) exclusively. Complex **1a** catalyzes the hydrolysis of Ph₂SiH₂ ([Au]:[H₂SiPh₂]:[H₂O] = 0.05:1.0:10.0) at 60 °C to yield Ph₂SiH(OH) and (Ph₂SiH)₂O. The reaction of Ph₂SiH₂ with HOEt in the presence of a catalytic amount of **1a** affords Ph₂SiH(OEt). Both stoichiometric and catalytic reactions using **1a** lead to the recovery of [AuCl(PCy₃)] from the reaction mixture.

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1. Introduction

Late transition metal complexes with Si-ligands have been studied extensively [1]. Major interests on this field are related to the mechanisms of synthetic organic reactions catalyzed by the transition metal complexes to convert organosilicon compounds to their derivatives [2]. Coordination of various Si-ligands and their chemical properties were investigated for the complexes of Fe, Ru, Co, Rh, Pd, and Pt. Gold complexes with Si-ligands, however, are much less common, although synthetic organic reactions catalyzed by Au complexes have become more significant over the past few decades.

Shubert reported the metathesis reaction of LiSiPh_3 with $[\text{AuCl}(\text{PPh}_3)]$ to produce the corresponding silylgold(I) complex, $[\text{Au}(\text{SiPh}_3)(\text{PPh}_3)]$ [3]. Klinkhammer reacted $\text{K}(\text{Si}(\text{SiMe}_3)_3)$ with AuI to form a homoleptic aurate having silyl ligands, $\text{K}[\text{Au}\{\text{Si}(\text{SiMe}_3)_3\}_2]$ [4]. The product is further derivatized to multinuclear Au complexes having Si-ligands. Bourissou and Amgoune synthesized Au(III) complexes with Si-ligands via oxidative addition of disilane to a Au(I) complex, Au(I)-Si complexes with an NHC ligand, and a Au(I) complex with a tetrapodal ligand having a Si-coordination site [5]. They investigated in detail the mechanism of insertion of alkyne and allene into the Au(I)-Si bond [6], which is one of the few studies of the chemical properties of the Au complexes having Si-ligands. In this paper, we report preparation and structure of Au(I) complexes with a chloro(diphenyl)silyl ligand, their stoichiometric reactions with OH-containing compounds, and the hydrolysis of organosilanes catalyzed by the complexes.

2. Results and Discussion

2.1 Synthesis and Structure of Silylgold Complexes

The chlorogold(I) complex $[\text{AuCl}(\text{PCy}_3)]$ formed via the ligand exchange of $[\text{AuCl}(\text{tht})]$ (tht: tetrahydrothiophene) with PCy_3 reacts with Ph_2SiH_2 to afford $[\text{Au}(\text{SiPh}_2\text{Cl})(\text{PCy}_3)]$ (**1a**) as colorless crystals. The reaction of the diarylsilanes, (4- FC_6H_4) $_2\text{SiH}_2$ and (4- MeC_6H_4) $_2\text{SiH}_2$, with $[\text{AuCl}(\text{PCy}_3)]$ forms the corresponding silylgold(I) complexes $[\text{Au}(\text{SiAr}_2\text{Cl})(\text{PCy}_3)]$ (**1b**: $\text{Ar} = \text{C}_6\text{H}_4$ -4-F, **1c**: $\text{Ar} = \text{C}_6\text{H}_4$ -4-Me). The Au(I) complex with a Ge-ligand, $[\text{Au}(\text{GePh}_2\text{Cl})(\text{PCy}_3)]$ (**2a**), is obtained similarly from Ph_2GeH_2 and $[\text{AuCl}(\text{PCy}_3)]$. $\text{Et}_2\text{N}(\text{SiPh}_2)(\text{Bpin})$ (pin = $\text{O}_2\text{C}_2\text{Me}_4$) is known as a precursor of the diphenylsilylene group in synthetic organic reactions catalyzed by Pd complexes [7] and in preparation of organo-palladium and -platinum complexes with Si-ligands [8]. The direct reaction of $\text{Et}_2\text{N}(\text{SiPh}_2)(\text{Bpin})$ with $[\text{AuCl}(\text{PCy}_3)]$ forms **1a**, at a lower rate than the reaction of H_2SiPh_2 . The reactions for the preparation of the complexes are summarized in Scheme 1. The use of PPh_3 and an NHC ligand instead of PCy_3 did not yield a silylgold complex.

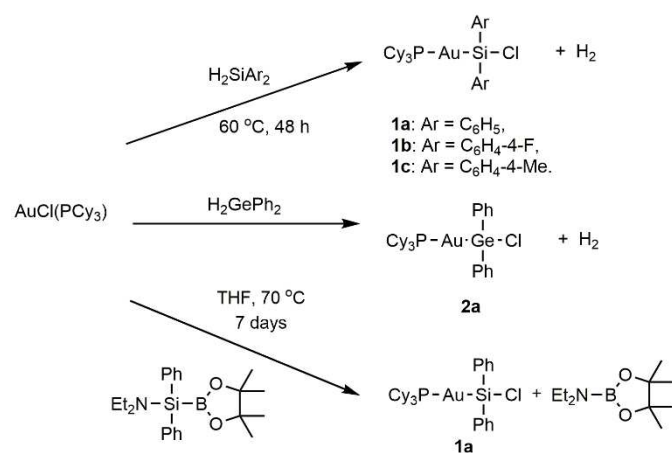


Figure 1 shows the molecular structures of **1a** and **2a** determined by X-ray crystallography. Complex **1a** has a Au-Si (2.343(4) Å) bond, whose length is slightly shorter than that of $[\text{Au}(\text{SiPh}_2\text{tBu})(\text{PPh}_3)]$ (Au-Si 2.3586(6) Å) [6a]. The Au-P bonds of **1a** (2.358(4) Å) and $[\text{Au}(\text{SiPh}_2\text{tBu})(\text{PPh}_3)]$ (2.3552(5) Å) are longer than that of $[\text{AuCl}(\text{PCy}_3)]$ (2.242(4) Å) [9] owing to the larger trans influence of the silyl ligand than of the Cl ligand. Complex **2a** has a similar structure to **1a**, and the Au-Ge bond length of **2a** (2.4084(4) Å) is similar to that of $[\text{Au}(\text{GeCl}_3)(\text{PCy}_3)]$ (2.406(1) Å) [10].

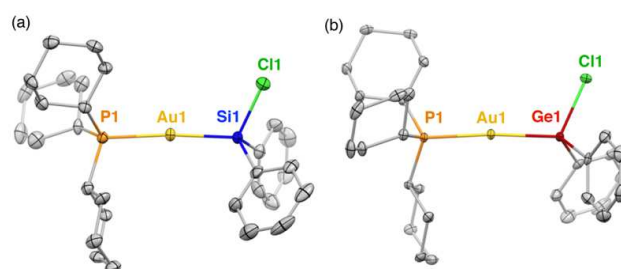


Figure 1. Molecular structures by X-ray crystallography. (a) Complex **1a**. Bond parameters: Au-Si 2.343(4) Å, Au-P 2.358(4) Å, Si-Cl 2.117(6) Å, Si-Au-P 174.2(1)°. (b) Complex **2a**. Bond parameters: Au-Ge 2.4084(4) Å, Au-P 2.3321(9) Å, Ge-Cl 2.227(1) Å, Ge-Au-P 173.99(3)°.

The NMR spectra of **1a** and **2a** are consistent with their crystallographic structures, and are similar to those of **1b** and **1c**. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1a** ($\text{THF}-d_8$) contains a doublet at 57.3 ppm ($^2J_{\text{SiP}} = 198.3$ Hz), which is at a lower magnetic field than that of $[\text{Au}(\text{SiPh}_2\text{tBu})(\text{PPh}_3)]$ (35.4 ppm, $^2J_{\text{SiP}} = 164.8$ Hz (relative to SiMe_4 in CD_2Cl_2) [6a].

Equimolar reactions of Ar_2SiH_2 with $[\text{AuCl}(\text{PCy}_3)]$ were followed by ^1H NMR spectroscopy at 60 °C in C_6D_6 . The decrease in the amount of H_2SiAr_2 obeys apparent second-order kinetics with respect to $[\text{Ar}_2\text{SiH}_2]$, which suggests first-order kinetics with respect to the concentrations of both Ar_2SiH_2 and $[\text{AuCl}(\text{PCy}_3)]$. The rate constants were estimated from the second-order plots of the reactions (Figure 2) to be $6.56 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for Ph_2SiH_2 , $7.65 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for (4- FC_6H_4) $_2\text{SiH}_2$, and $2.30 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for (4- MeC_6H_4) $_2\text{SiH}_2$.

The reaction is retarded by electron-donating substituents at the *para* position of the phenyl group. The rate constant of the reaction using Ph_2SiD_2 ($1.11 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is significantly smaller than that using Ph_2SiH_2 with a kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} = 6.36$. The addition of PCy_3 to the reaction of Ph_2SiH_2 ($[\text{Au}]:[\text{PCy}_3] = 1:2$) decreases the rate constant to $3.06 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The cationic complex formed by the addition of PCy_3 , $[\text{Au}(\text{PCy}_3)_2]^+\text{Cl}^-$, undergoes the reaction more slowly than $[\text{AuCl}(\text{PCy}_3)]$.

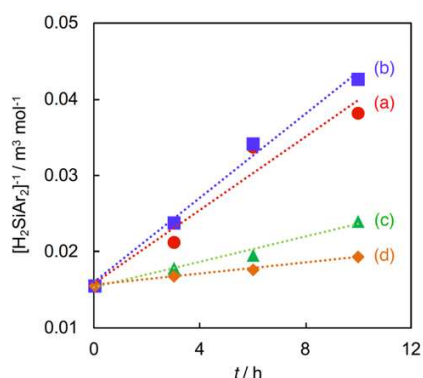


Figure 2. Second-order plots of the reaction of Ar_2SiH_2 with $\text{AuCl}(\text{PCy}_3)$. $[\text{AuCl}(\text{PCy}_3)]_0 = [\text{Ar}_2\text{SiH}_2]_0 = 0.064 \text{ mol L}^{-1}$ in C_6D_6 . At 60°C . Internal standard: dibenzyl. (a) Ph_2SiH_2 , (b) (4- FC_6H_4) $_2\text{SiH}_2$, (c) (4- MeC_6H_4) $_2\text{SiH}_2$, (d) Ph_2SiD_2 .

The ^1H NMR spectrum of the reaction mixture of Ph_2SiH_2 with $[\text{AuCl}(\text{PCy}_3)]$ provided information on the species formed and the pathway of the reaction, as shown in Figure 3. The ^1H NMR spectrum of the reaction mixture contains the signals assigned to the gold silyl complex **1a**, and signals of HSiPh_2Cl (δ_{H} 5.80) and H_2 (δ_{H} 4.46). Other signals, which appeared at δ_{H} 0.49 (br), 5.90 (s, $J_{\text{Si-H}} = 217 \text{ Hz}$), and 7.62 (dd, $J_{\text{Si-H}} = 7.6$ and 1.7 Hz) can be assigned to the Au-H, Si-H, and aryl hydrogens of the Au(III) intermediate $[\text{AuCl}(\text{H})(\text{SiHPh}_2)(\text{PCy}_3)]$ (**A**), respectively. Position of the high magnetic field signal (δ_{H} 0.49) is close to the calculated position (DFT) of the Au-H hydrogen signal of **A** (δ_{H} 0.40).

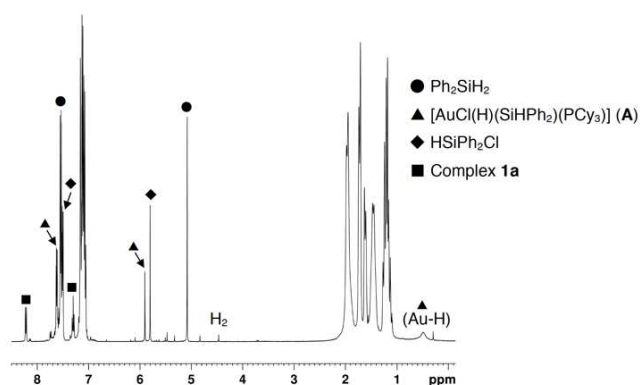
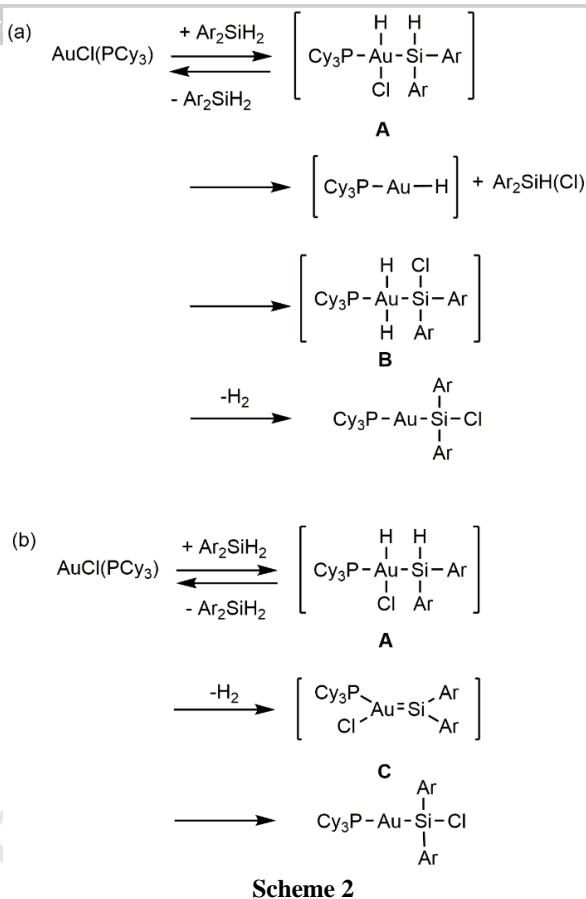


Figure 3 ^1H NMR spectrum of the reaction mixture of Ph_2SiH_2 (0.020 mmol) with $[\text{AuCl}(\text{PCy}_3)]$ (0.020 mol) in C_6D_6 (0.5 mL) after 22 h at 70°C .

Scheme 2 summarizes the possible pathways for the formation of **1a-1c** by the reaction of Ar_2SiH_2 with $[\text{AuCl}(\text{PCy}_3)]$. The oxidative addition of Ar_2SiH_2 to the Au(I) complex forms a Au(III) intermediate with hydride and diarylsilyl ligands (**A**). The reductive elimination of $\text{Ar}_2\text{SiH}(\text{Cl})$ from **A** and the reoxidative addition [11] of the liberated molecule to $[\text{AuH}(\text{PCy}_3)]$ afford a new Au(III) complex having a bond between the chloro(diaryl)silyl ligand and the Au(III) center (**B**) (Scheme 2(a)). The reductive elimination of chlorosilanes from the transition metal complexes having chloro and silyl ligands is known in Rh, Ru, and Ir [12]. *mer*- $[\text{RhCl}(\text{H})(\text{SiHPh}_2)(\text{PMe}_3)_3]$ was reported to undergo thermal isomerization to *fac*- $[\text{RhH}_2(\text{SiClPh}_2)(\text{PMe}_3)_3]$ via a pathway similar to that from **A** to **B** in Scheme 2(a) [12a].



Scheme 2

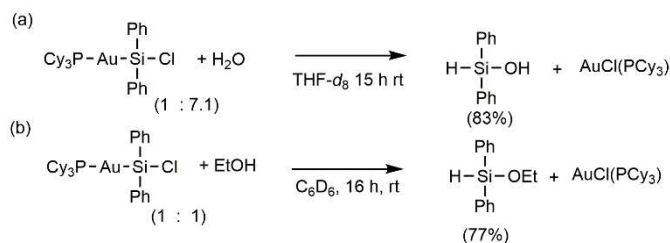
Another reaction pathway involves the α -hydrogen elimination of the SiHPh_2 ligand of an intermediate (**A**) to generate a silylene-coordinated intermediate (**C**) (Scheme 2(b)). Tilley and Tobita independently reported the α -hydrogen elimination of Mo and W complexes with a silyl ligand to afford a product with hydride and silylene ligands [13,14]. We conducted the reaction of AgNTf_2 with **1a** in the presence of 4-dimethylaminopyridine (DMAP) with expectation of isolation or characterization of the base-stabilized silylene-coordinated complex [15]. The reaction, however, forms a trinuclear Au complex $[\text{Au}_3(\mu\text{-Cl})(\text{PCy}_3)_3](\text{NTf}_2)$. Complex $[\text{Au}_3(\eta^3\text{-Cl})(\text{PCy}_3)_3]\text{BARF}$ was similarly obtained by using AgBARF instead of AgNTf_2 , and its structure was determined by X-ray crystallography. Thus, we do not have the experimental results which can be used for discussion of the plausibility of the pathway in Scheme 2(b). Dichlorogermene reacts with $[\text{AuCl}(\text{PPh}_3)]$ to form $[\text{Au}(\text{GeCl}_2)(\text{PPh}_3)]$ via the insertion of an unsaturated species into the Au-Cl bond [10]. The reaction of $\text{Et}_2\text{N}(\text{SiPh}_2)(\text{Bpin})$ with $[\text{AuCl}(\text{PCy}_3)]$ probably involves a similar insertion of a diphenylsilylene species into the Au-Cl bond, forming complex **1a**. These previous papers are related to the process from **B** to **C** and from **C** to **1a-1c** in Scheme 2(b), and support the latter pathway. The reaction of Ph_2SiH_2 with $[\text{AuCl}(\text{PCy}_3)]$ is faster than that of $\text{Et}_2\text{N}(\text{SiPh}_2)(\text{Bpin})$, which suggests that the Scheme 2(a) accounts for the formation of **1a-3a** from Ar_2SiH_2 and $[\text{AuCl}(\text{PCy}_3)]$.

2.2 Stoichiometric and Catalytic Reactions of Au Complexes

Organosilanes are conventionally converted into silanols and siloxanes using various oxidants in the presence or absence of molecular transition metal catalysts [16]. The hydrolysis of organosilanes forms oxygen-functionalized Si-compounds. Schubert reported the hydrolysis of tertiary silanes catalyzed by $[\text{CuH}(\text{PPh}_3)]_6$ to obtain the corresponding silanol

and disiloxane [17]. Chang employed Ru and Ir catalysts and succeeded in the synthesis of silanols from tertiary silanes under H₂O-O₂ conditions [18]. More recently, many reports have appeared in the literature on studies of the oxygen-functionalization of organosilanes by using catalysts containing transition metals, Co [19], Re [20], Fe [21], Ru [22], Rh [23], Ir [24], and Cu [25]. Zargarian reported stoichiometric reactions of Ni complexes having OR ligands with organosilane to form new Si-O bonds [26]. Ito and Sawamura employed dinuclear Au(I) complex with a chelating diphosphine ligand as catalysts and achieved selective alcoholysis of organosilanes [27]. We conducted stoichiometric reactions of complex **1a** with OH compounds and Au-catalyzed functionalization of diphenylsilane with OH-compounds.

Complex **1a** reacts with an excess amount of H₂O in THF at room temperature to form Ph₂SiH(OH) in 83% yield determined by NMR spectroscopy after 15 h at room temperature (Scheme 3(a)). Running the reaction on a larger scale and removal of the solvent and organic products gave a colorless solid, which was identified as [AuCl(PCy₃)₃] on the basis of ¹H and ³¹P{¹H} NMR spectra.



Scheme 3

The reaction of EtOH with **1a** in C₆D₆ produced Ph₂SiH(OEt) in 77% yield. The ³¹P{¹H} NMR spectrum after the reaction contains a major peak corresponding to [AuCl(PCy₃)₃] (53.4 ppm) and an unidentified signal at 71.9 ppm with a peak area ratio of 1.00:0.09.

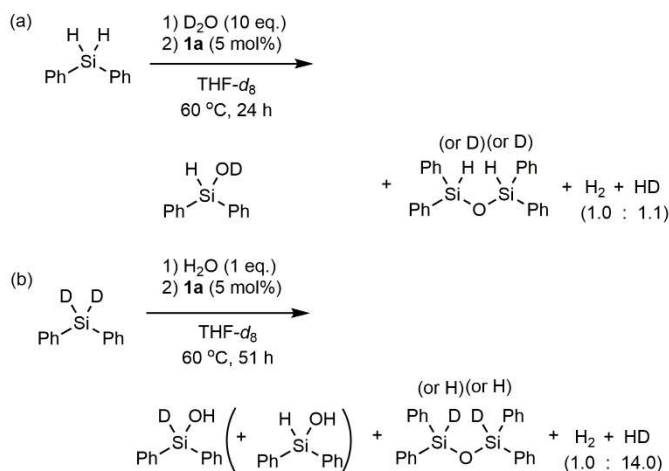
The catalytic reaction of H₂O with Ph₂SiH₂ in a 2.5:1.0 ratio was conducted in the presence of **1a** ([**1a**]/[Ph₂SiH₂] = 1:20) at 60 °C in THF. The ¹H NMR spectrum obtained after the reaction for 18 h revealed the formation of Ph₂SiH(OH) (δ_{H} 5.86 and 5.45 ppm). Further reaction for 100 h resulted in the disappearance of the signals of Ph₂SiH₂ and Ph₂SiH(OH), and the formation of (Ph₂SiH)₂O (δ_{H} 5.67 ppm). Table 1 summarizes results of the reactions for 24 h. The reaction of H₂O with Ph₂SiH₂ (10:1 ratio) catalyzed by **1a** in THF-*d*₈ forms Ph₂SiH(OH) and (Ph₂SiH)₂O in 40% and 47% yields, respectively (run 1). The reaction catalyzed by [Au(PCy₃)₂]PF₆ forms only Ph₂SiH(OH) in a much lower yield (8%) (run 2). The reaction without the catalyst yields two products in 14% and 2%, and uncharacterized by-products signals (δ_{H} 5.82, 5.71, and 5.59). Complex **1a** catalyzes the condensation of EtOH with Ph₂SiH₂ to produce Ph₂SiH(OEt) in 70% yield after 24 h (run 4). ¹H NMR spectrum of the reaction mixture after further reaction for another 27 h contains the signals of Ph₂SiH(OEt) (δ_{H} 7.68, 5.67, 3.70 and 1.11) and of dihydrogen (δ_{H} 4.46) only. The reaction without **1a** gives Ph₂SiH(OEt) in 35% yield after 24 h (run 5).

Table 1. Reaction of H₂O and EtOH with Ph₂SiH₂ catalyzed by Au complex^{a)}

run	catalyst	HOR ^{b)}	solvent	time/h	Conv. (%) ^{c)}	Product(%) ^{c)}	
						Ph ₂ SiH(OR)	(Ph ₂ SiH) ₂ O
1	1a	H ₂ O (1:10)	THF- <i>d</i> ₈	24	100	40	47
2	[Au(PCy ₃) ₂]PF ₆	H ₂ O (1:10)	THF- <i>d</i> ₈	24	14	8	0
3	none	H ₂ O (1:10)	THF- <i>d</i> ₈	23	51	14	2
4	1a	EtOH (1:1)	C ₆ D ₆	24	88	70	-
5	none	EtOH (1:1)	C ₆ D ₆	24	36	35	-

a) At 60 °C. [Catalyst]/[Ph₂SiH₂] = 0.05. b) Molar ratio of Ph₂SiH₂ to HOR is in parenthesis. c) Yield by NMR.

Isotope-labeled compounds were employed for the reaction to obtain insights to the details of the reaction. The reaction of D₂O with Ph₂SiH₂ (10:1) catalyzed by **1a** produced Ph₂SiH(OD) (33%) and (Ph₂SiH)₂O (50%) (Scheme 4(a)). The ¹H NMR spectrum of the mixture showed the formation of H₂ and HD in 1.0:1.1 ratio. This result suggests the partial scrambling of hydrogen. ESI-TOF-mass spectrometry measurement of the reaction on a larger scale indicated the formation of an isotopomer mixture of (Ph₂SiH)₂O (*m/z* = 405.1107, Na adduct), (Ph₂SiD)OSiPh₂H (*m/z* = 406.1147), and (Ph₂SiD)₂O (*m/z* = 407.1166).



The reaction of H₂O with Ph₂SiD₂ in the presence of catalyst **1a** forms Ph₂SiD(OH) and (Ph₂SiD)₂O (Scheme 4(b)). The dihydrogen in the mixture consists of H₂ and HD in 1.0:14.0 ratio. The products contain not only Ph₂SiD(OH) and (Ph₂SiD)₂O but also compounds containing Si-H bonds.

Complex **1a** catalyzes the hydrolysis of the Si-H bond of Ph₂SiH₂ to form Ph₂SiH(OH), and further conversion into (Ph₂SiH)₂O under the reaction conditions. The latter reaction has two possible pathways. One involves dehydrogenative condensation of Ph₂SiH₂ and Ph₂SiH(OH) promoted by the Au catalyst, and the other involves dehydrative condensation of Ph₂SiH(OH) molecules to also form the siloxane as the product. The reaction involves scrambling of hydrogen among Si-H groups and OH groups of the substrates and products, which suggests the occurrence of side reactions that are not included in the described reaction sequence. Consequently, the entire reaction is more complicated than expected from the chemical equation. Complex **1a** is regenerated after the reactions despite the occurrence of multiple reactions during catalysis. The chlorine atom is suggested to play an important role in the reactions because [Au(PCy₃)₂]PF₆ catalyzes the process at a much lower rate than that catalyzed by **1a**.

3. Conclusion.

Complex **1a** is formed easily from Ph₂SiH₂ and [AuCl(PCy₃)], and reacts with H₂O and EtOH to produce Ph₂SiH(OR) (R = H, Et) accompanied by regeneration of [AuCl(PCy₃)]. As expected from the sequence of the reactions, **1a** catalyzes hydrolysis and alcoholysis of Ph₂SiH₂ to afford Ph₂SiH(OH), (Ph₂SiH)₂O, and Ph₂SiH(OEt). The catalysis also produces [AuCl(PCy₃)] after the completion of reactions. The chloro ligand is involved in the bond-forming and -cleaving reactions because the Cl-free complex shows a much lower activity.

4. Experimental Section.

4-1. General Procedures.

All manipulations were carried out using standard Schlenk line techniques under an atmosphere of argon or nitrogen or in nitrogen-filled glovebox (Miwa MFG). ¹H, ¹³C{¹H}, ¹⁹F{¹H}, ²⁹Si{¹H}, and ³¹P{¹H} NMR spectra were recorded on Bruker Biospin Avance III 400 MHz, and Avance III HD 500 MHz NMR spectrometers. The chemical shifts in the ¹H and ¹³C{¹H} NMR spectra were referenced to the residual peaks of the solvents used. The peak positions of the ¹⁹F{¹H}, ²⁹Si{¹H}, and ³¹P{¹H} NMR spectra were referenced to external CFCl₃ (δ 0), SiMe₄ (δ 0), and 85% H₃PO₄ (δ 0) in deuterated solvents. Mass spectroscopic data were obtained on a Bruker Daltonics micrOTOF II (ESI and APCI) spectrometer. The chemical reagents, H₂SiPh₂ (TCI), HSiPh₂Cl (TCI), HAuCl₄ · 4H₂O (Tanaka or WAKO), NaBARF (Alfa Aesar), AgNTf₂ (TCI) were used as received. (4-FC₆H₄)₂SiH₂, (4-MeC₆H₄)₂SiH₂, and Ph₂GeH₂ were prepared by LiAlH₄ reduction of Ar₂SiCl₂ and Ph₂GeCl₂. Et₂N(SiPh₂)(Bpin), [AuCl(PCy₃)], [AuCl(PPh₃)], [AuCl(tht)], [AuCl(IPr)], [Au(PCy₃)₂]PF₆ were prepared according to the literatures [7, 9b, 28].

4-2. Preparation of Gold Complexes.

4.2.1 Preparation of **1a** using H₂SiPh₂.

In a glovebox, to a THF solution (10 mL) of [AuCl(tht)] (201 mg, 0.62 mmol) was added PCy₃ (351 mg, 1.25 mmol) forming [AuCl(PCy₃)] *in situ*. H₂SiPh₂ (115 mg, 123 μL, 0.62 mmol) was injected to the reaction mixture *via* micro syringe. The reaction mixture was stirred at 60 °C for 24 h. After the

solvent was removed under reduced pressure, the resulting material was washed by hexane (2 mL×2), CH₃CN (0.5 mL×2) and dried *in vacuo* to give [Au(SiPh₂Cl)(PCy₃)] (**1a**) as a white solid (204 mg, 47%). Recrystallization by slow diffusion of CH₂Cl₂/hexane (1:10) in a glovebox afforded colorless crystals of **1a** suitable for X-Ray crystallography (CCDC No. 1957767). Anal. Calcd for C₃₀H₄₃AuClPSi: C, 51.83; H, 6.23. Found; C, 51.71; H, 6.42. ¹H NMR (400 MHz, C₆D₆, rt): δ 8.22 (d, J_{HH} = 7.52 Hz, 4H), 7.30 (t, J_{HH} = 0.44 Hz, 4H), 1.87 (br, 9H), 1.63 (br, 6H), 1.39 (br, 6H), 1.07 (br, 9H). ³¹P{¹H} NMR (202 MHz, toluene-*d*₈, rt): δ 69.8 (s, PCy₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, rt): δ 146.2 (s, *ipso*-C), 137.4 (s, *ortho*-C), 135.8 (s, *meta*-C), 128.9 (s, *para*-C), 33.6 (d, J_{PC} = 18.3 Hz, PCH(CH₂CH₂)CH₂), 30.8 (s, PCH(CH₂CH₂)CH₂), 27.3 (d, J_{PC} = 11.8 Hz, PCH(CH₂CH₂)CH₂), 26.1 (s, PCH(CH₂CH₂)CH₂). ²⁹Si{¹H} NMR (99 Hz, THF-*d*₈, 253 K): δ 57.3 (d, ²J_{SiP} = 198.3 Hz, SiPh₂).

4.2.2 Preparation of **1a** using Et₂N(SiPh₂)(Bpin).

In a glovebox, to a toluene solution (10 mL) of [AuCl(tht)] (100 mg, 0.24 mmol) was added PCy₃ (68 mg, 0.24 mmol) forming [AuCl(PCy₃)] *in situ*. A toluene solution (5 mL) of Et₂N(SiPh₂)(Bpin) (139 mg, 0.365 mmol) was added to the reaction mixture. The reaction mixture was stirred at 70 °C for 7 days. After the solvent was removed under reduced pressure, the resulting material was washed by hexane (3 mL×3) and dried *in vacuo* to give **1a** as a white solid (19 mg, 11%).

4.2.3 Reaction of [Au(PCy₃)]BARF with Et₂N-SiPh₂-B(pin).

In a glovebox, to a THF solution (10 mL) of [AuCl(PCy₃)] (200 mg, 0.62 mmol) was added NaBARF (350 mg, 0.39 mmol) forming [Au(PCy₃)]BARF *in situ*. The reaction mixture was stirred at 60 °C for 2 h. Et₂N-SiPh₂-B(pin) (157 mg, 0.41 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 5 min, which was gradually colorless suspension to dark brown solution. After the solvent was removed under reduced pressure, the resulting material was washed by hexane (6 mL×2) and dried *in vacuo* to give brown crude containing [Au₃(η³-Cl)(PCy₃)₃]BARF and organosilanes. The crude product was recrystallized by slow diffusion of toluene/hexane (1:10) in a glovebox afforded a brown crystal of [Au₃(η³-Cl)(PCy₃)₃]BARF suitable for X-Ray crystallography (CCDC No. 1966558). ³¹P{¹H} NMR (C₆D₆, 161 MHz, rt) δ 64.7.

4.2.4 Dechlorination reaction of **1a** in the presence of DMAP.

In a glovebox, [Au(SiPh₂Cl)PCy₃] (**1a**) (0.20 g, 0.29 mmol) was dissolved in THF (12 mL). (*N,N'*-dimethylamino)pyridine (DMAP) (0.11 g, 0.29 mmol) and AgNTf₂ (0.11 g, 0.29 mmol) were added to the reaction mixture at -80 °C. The reaction mixture was stirred at -10 °C for 2 h. Colorless suspension was changed to dark brown solution gradually. The solid was removed by filtration, and the filtrate was concentrated and removed under reduced pressure. The resulting material was washed with hexane (6 mL×2) and dried *in vacuo* to give a brown oil containing [Au₃(μ³-Cl)(PCy₃)₃]NTf₂ and organosilanes. ³¹P{¹H} NMR (C₆D₆, 400 MHz, rt): δ 64.4 (s, PCy₃).

4.2.5 Preparation of **1b**.

In a glovebox, to a THF solution (10 mL) of [AuCl(tht)] (200 mg, 0.62 mmol) was added PCy₃ (437 mg, 1.6 mmol) forming [AuCl(PCy₃)] *in situ*. (4-FC₆H₄)₂SiH₂ (138 mg, 130 μL, 0.62 mmol) was injected to the reaction mixture. The reaction mixture was stirred at 60 °C for 24 h. After the solvent was removed under reduced pressure, the resulting material was washed with hexane (2 mL×2), CH₃CN (3 mL×2) and dried in

vacuo to give [Au(SiAr^F₂Cl)PCy₃] (**1b**) as a white solid (29.9 mg, 7%). ¹H NMR (400 MHz, C₆D₆, rt): δ 7.98 (q, *J*_{HH} = 6.36 Hz, *J*_{FH} = 8.28 Hz, 4H), 6.97 (t, *J*_{HH} = 8.88 Hz, 4H), 1.83 (br, 9H), 1.61 (br, 6H), 1.53 (br, 3H), 1.36 (br, 6H), 1.05 (br, 9H). ¹⁹F{¹H} NMR (C₆D₆, 376 MHz, rt): δ -113.5 (s, (4-*F*-C₆H₄)). ³¹P{¹H} NMR (161 MHz, C₆D₆, rt): δ 69.7 (s, PCy₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, rt): δ 141.5 (d, *J*_{CF} = 3.7 Hz, *ipso*-C), 137.6 (d, *J*_{CF} = 7.6 *ortho*-C), 115.2 (d, *J*_{CF} = 18.9 *para*-C), 33.8 (br, PCH(CH₂CH₂)CH₂), 30.9 (s, PCH(CH₂CH₂)CH₂), 27.4 (s, PCH(CH₂CH₂)CH₂), 26.3 (s, PCH(CH₂CH₂)CH₂). The SiAr^F₂ (*meta*) signal was not assigned clearly due to overlapping with solvent signal.

4.2.6 Preparation of **1c**.

In a glovebox, to THF (10 mL) solution of [AuCl(PCy₃)] (200 mg, 0.39 mmol) was added (4-MeC₆H₄)₂SiH₂ (83 mg, 0.39 mmol). The reaction mixture was stirred at 60 °C for 48 h. After the solvent was removed under reduced pressure, the resulting material was washed with hexane (2 mL×2) and dried in *vacuo* to give [Au(Si(C₆H₄Me-4)₂Cl)(PCy₃)] (**1c**) as a gray solid (108 mg). ¹H NMR (400 MHz, C₆D₆, rt): δ 8.17 (d, *J*_{HH} = 7.72 Hz, 4H), 2.12 (s, 3H), 1.97 (br, 9H), 1.67 (br, 6H), 1.52 (br, 3H), 1.26 (br, 6H), 1.14 (br, 9H). The Si(tol)₂ (*meta*) signal was not assigned clearly due to overlapping with solvent signal. ³¹P{¹H} NMR (161 MHz, C₆D₆, rt): δ 69.8 (s, PCy₃).

4.2.7 Preparation of **2a**.

In a glovebox, to a toluene solution (10 mL) of [AuCl(tht)] (200 mg, 0.62 mmol) was added PCy₃ (438 mg, 1.6 mmol), forming [AuCl(PCy₃)] *in situ*. Ph₂GeH₂ (357 mg, 1.56 mmol) was injected to the reaction mixture *via* micro syringe. The reaction mixture was stirred at 110 °C for 5 days. The solvent was removed under reduced pressure. The resulting material was washed with hexane (6 mL×2), acetone (1 mL×2) and dried in *vacuo* to give [Au(GePh₂Cl)(PCy₃)] (**2a**) as a white solid (209 mg, 25%). Recrystallization by slow diffusion of CH₂Cl₂/hexane (1:10) in a glovebox afforded a colorless crystal of [Au(GePh₂Cl)(PCy₃)] suitable for X-Ray crystallography (CCDC No. 1957766). ¹H NMR (400 MHz, C₆D₆, rt): δ 8.21 (d, *J*_{HH} = 6.96 Hz, 4H), 7.30 (t, *J*_{HH} = 7.44 Hz, 4H), 1.80 (br, 9H), 1.60 (br, 6H), 1.31 (br, 6H), 1.05 (br, 9H). ³¹P{¹H} NMR (161 MHz, C₆D₆, rt): δ 64.7 (s, PCy₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, rt): δ 150.6 (s, *ipso*-C), 134.8 (s, *ortho*-C), 128.6 (s, *meta*-C), 128.4 (s, *para*-C), 33.5 (d, *J*_{PC} = 20.7 Hz, PCH(CH₂CH₂)CH₂), 30.7 (s, PCH(CH₂CH₂)CH₂), 27.1 (s, PCH(CH₂CH₂)CH₂), 26.0 (s, PCH(CH₂CH₂)CH₂).

4-3. Kinetics study for formation of **1a**, **1b**, **1c**.

In a J. Young NMR tube, to a C₆D₆ solution (0.5 mL) of [AuCl(tht)] (10 mg, 0.032 mmol) was added PCy₃ (9.0 mg, 0.032 mmol) forming [AuCl(PCy₃)] *in situ*. Dibenzyl (internal standard: 4.2 mg) was added to the reaction mixture. H₂SiAr₂ (0.032 mmol) was injected to the reaction mixture *via* 10 μL micro syringe. The reaction mixture was stirred at 60 °C for 24 h, which was monitored by ¹H NMR, to afford [Au(SiAr₂Cl)(PCy₃)] as the product. By comparing integration of the methylene signal of the internal standard (δ_H 2.74) with the Si-*H* signals of reactant (δ_H 5.07 (**1a**); δ_H 4.88 (**1b**); δ_H 5.16 (**1c**)) and product (δ_H 8.22 (**1a**); δ_H 7.98 (**1b**); δ_H 8.17 (**1c**)), the conversion of the reactant and the NMR yield of the product were determined (**1a**, 26% yield, *k* = 6.56 × 10⁻⁷ m³ mol⁻¹ s⁻¹; **1b**, 38% yield, *k* = 7.65 × 10⁻⁷ m³ mol⁻¹ s⁻¹; **1c**, 6% yield, *k* = 2.30 × 10⁻⁷ m³ mol⁻¹ s⁻¹).

4-4. Deuterium labeling study.

In a J. Young NMR tube, to a C₆D₆ solution (0.5 mL) of [AuCl(tht)] (10 mg, 0.032 mmol) was added PCy₃ (9.0 mg, 0.032 mmol) forming [AuCl(PCy₃)] *in situ*. Dibenzyl (internal

standard: 4.2 mg) was added to the reaction mixture. D₂SiPh₂ (9.0 mg, 0.032 mmol) was injected to the reaction mixture *via* 10 μL micro syringe. The reaction mixture was stirred at 60 °C for 24 h, which was monitored by ¹H NMR, to afford [Au(SiPh₂Cl)(PCy₃)] as the product. By comparing with the signals corresponding to reactant (δ_H 7.50) and product (δ_H 8.22), the conversion of the reactant and the NMR yield of the product were determined (15% yield, *k* = 1.11 × 10⁻⁷ m³ mol⁻¹ s⁻¹, *k*_H/*k*_D = 6.36).

4-5. Synthesis of *O*-functionalized organosilane

4.5.1 Reaction of **1a** with H₂O.

In a J. Young NMR tube under inert gas, to a THF-*d*₈ (0.5 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (10 mg, 0.014 mmol) and dibenzyl (3.7 mg) was added H₂O (1.8 μL, 0.10 mmol). The reaction mixture was stirred at room temperature for 15 h. The conversion of the reactant and the NMR yield of the product were determined by comparing integration of the methylene signal of the internal standard (dibenzyl, δ_H 2.88) with the signals corresponding to reactant (**1a**: δ_H 7.67) and product (HSiPh₂OH: δ_H 7.60). The ¹H and ³¹P{¹H} NMR spectra of the reaction mixture exhibited quantitative conversion to give HSiPh₂OH (83% NMR yield).

4.5.2 Reaction of **1a** with excess H₂O.

In a 25 mL Schlenk tube under inert gas, to a THF (2 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (20 mg, 0.029 mmol) was added H₂O (50 μL, 2.8 mmol). After the reaction mixture was stirred at room temperature for 39 h, the solvent was removed under reduced pressure. The resulting material was washed by hexane (2 mL × 2) and dried in *vacuo* to give [AuCl(PCy₃)] as a white solid. ³¹P{¹H} NMR (161 MHz, C₆D₆, rt): δ 53.1 (s, PCy₃).

4.5.3 Reaction of **1a** with EtOH.

In a J. Young NMR tube under inert gas, to a C₆D₆ (0.5 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (8 mg, 0.012 mmol) and dibenzyl (3.7 mg) was added EtOH (0.7 μL, 0.015 mmol). The reaction mixture was stirred at room temperature for 16 h. The conversion of the reactant and the NMR yield of the product were determined by comparing integration of the methylene signal of the internal standard (dibenzyl, δ_H 2.74) with the signals corresponding to reactant (**1a**: δ_H 8.21) and product (HSiPh₂OEt: δ_H 5.66). The ¹H and ³¹P{¹H} NMR spectra of the reaction mixture exhibited quantitative conversion to give HSiPh₂OEt (77% NMR yield).

4.5.4 Reaction of H₂SiPh₂ with H₂O catalyzed by **1a** in NMR scale.

In a J. Young NMR tube under inert gas, to a THF-*d*₈ (0.5 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (5.3 mg, 0.0076 mmol), H₂SiPh₂ (28 mg, 0.15 mmol), and dibenzyl (4.0 mg) was added H₂O (1.1 μL, 0.061 mmol). The reaction mixture was stirred at 60 °C for 118 h. The conversion of the reactant and the NMR yield of the product were determined by comparing integration of the methylene signal of the internal standard (dibenzyl, δ_H 2.88) with the signals corresponding to reactant (H₂SiPh₂: δ_H 4.89) and product ((HSiPh₂)₂O: δ_H 5.60). The ¹H NMR spectra of the reaction mixture exhibited 85% conversion to give and (HSiPh₂)₂O (56% NMR yield).

4.5.5 Reaction of H₂SiPh₂ with H₂O catalyzed by **1a** in large scale.

In a 25 mL Schlenk tube under inert gas, to a THF (2 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (18 mg, 0.025 mmol), H₂SiPh₂ (93 mg, 0.51 mmol) was added H₂O (8.3 μL, 0.46

mmol). After the reaction mixture was stirred at 60 °C for 3 days, the solvent was removed under reduced pressure. The resulting material was extracted by hexane (2 mL × 2), and filtrate was concentrated under reduced pressure to give colorless oil containing (HSiPh₂)₂O. ¹H NMR (400 MHz, C₆D₆, rt): δ 7.62 (d, J_{HH} = 7.08 Hz), 5.91 (s, J_{SiH} = 109.3 Hz, 2H). The SiPh₂ (*meta*) signal was not characterized clearly due to overlapping with solvent signal. HRMS (ESI): calcd. for C₂₄H₂₂NaOSi₂ [M+Na]⁺ 405.1101; found *m/z* = 405.1093.

4.5.6 Reaction of H₂SiPh₂ with D₂O catalyzed by 1a in NMR scale.

In a J. Young NMR tube under inert gas, to a THF-*d*₈ (0.5 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (8.0 mg, 0.012 mmol), H₂SiPh₂ (45 mg, 0.23 mmol), and dibenzyl (5.1 mg) were added D₂O (42 μL, 2.3 mmol). The reaction mixture was stirred at 60 °C for 24 h. The conversion of the reactant and the NMR yield of the product were determined by comparing integration of the methylene signal of the internal standard (dibenzyl, δ_H 2.88) with the signals corresponding to reactant (H₂SiPh₂: δ_H 4.89, s) and product (HSiPh₂OH: δ_H 7.60).

4.5.7 Reaction of H₂SiPh₂ with D₂O catalyzed by 1a in large scale.

In a 25 mL Schlenk tube under inert gas, to a THF (10 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (**1a**) (10 mg, 0.014 mmol), H₂SiPh₂ (57 mg, 0.29 mmol) were added D₂O (26 μL, 1.44 mmol). After the reaction mixture was stirred at 60 °C for 37 h, the solvent was removed under reduced pressure. The resulting material was extracted by acetone (2 mL × 2), and filtrate was concentrated under reduced pressure to give colorless oil containing (DSiPh₂)₂O, DSiPh₂OSiPh₂H, and (HSiPh₂)₂O based on ESI-TOF-MS analysis. Data for (DSiPh₂)₂O: HRMS (ESI): calcd. for C₂₄H₂₀OSi₂D₂ [M+Na]⁺ 407.1166; found *m/z* = 407.1227. Data for DSiPh₂OSiPh₂H: HRMS (ESI): calcd. for C₂₄H₂₁OSi₂D [M+Na]⁺ 406.1147; found *m/z* = 406.1164. Data for (HSiPh₂)₂O: HRMS (ESI): calcd. for C₂₄H₂₂OSi₂ [M+Na]⁺ 405.1011; found *m/z* = 405.1107.

4.5.8 Reaction of D₂SiPh₂ with H₂O catalyzed by 1a.

In a J. Young NMR tube under inert gas, to a THF-*d*₈ (0.5 mL) solution of [Au(SiPh₂Cl)(PCy₃)] (5.0 mg, 0.0072 mmol), D₂SiPh₂ (27 mg, 0.14 mmol), and dibenzyl (11.3 mg) were added H₂O (2.6 μL, 0.14 mmol). The reaction mixture was stirred at 60 °C for 51 h. The conversion of the reactant and the NMR yield of the product were determined by comparing integration of the methylene signal of the internal standard (dibenzyl, δ_H 2.88) with the signals corresponding to reactant (D₂SiPh₂: δ_H 7.58) and product (DSiPh₂OD: δ_H 7.61, (DSiPh₂)₂O: δ_H 7.55).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

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Highlights

- New gold complexes with chlorosilyl and chlorogermyl ligands characterized fully.
- Reaction pathway determined by results of kinetic study and isotope-labeling study.
- Stoichiometric reaction of water and ethanol with the complexes to afford silanol and silyl ether.
- Catalytic S-O bond-forming reactions promoted by the Au complex that keeps Cl atom during the reaction

Statement

This paper presents synthesis of new Au(I) complexes with chlorodiarylsilyl ligand, $\text{Au}(\text{SiAr}_2\text{Cl})(\text{PCy}_3)$, and its stoichiometric reactions of H_2O and EtOH with the Au(I)-Si complex, forming hydroxy- and ethoxy-silanes and $\text{AuCl}(\text{PCy}_3)$. Reports on Au complexes with Si-ligands and their chemical properties have been rare. This paper provides smooth reactions of the Si-ligand bonded to Au center with the OH compounds.

The above results are developed to conversion of Ph_2SiH_2 into $\text{Ph}_2\text{SiH}(\text{OH})$, $(\text{Ph}_2\text{SiH})_2\text{O}$, and $\text{Ph}_2\text{SiH}(\text{OEt})$ catalyzed by the Au-Si complex. Detailed reaction pathways are discussed based on kinetic results and isotope-labelling experiments.