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VIP

The Fluoride-Free Transmetalation of Organosilanes to Gold

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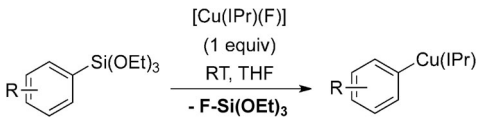
During the last decade, homogenous gold catalysis has been one of the most active research areas with new reactivities and methodologies being developed continuously. As a soft π-acid, gold has been shown to be very efficient in the activation of multiple bonds toward nucleophilic attack, thus creating new C–C bonds.[1] In these reactions, a key step is the formation of an organogold intermediate, which is followed by its trapping with either an electrophile or a proton to afford the desired product and regenerate the catalyst. Very recently, the development of facile and straightforward stoichiometric routes to access and isolate these intermediates has attracted significant interest in order to support mechanistic proposals.[2] Very recently, they have been shown to be very efficient in dual metal catalysis to transmetalate to palladium,[3] rhodium,[4] nickel[5] or ruthenium and iron centres.[6] Noteworthily, these isolated "intermediate" complexes display not only good stability toward air, light and moisture, but also very interesting photoluminescent properties for possible uses in cancer therapy and imaging.[7] Earlier syntheses of aryl gold(I) complexes have often relied on organolithium or Grignard reagents, which preclude the use of sensitive functional groups.[8]

Consequently, recent investigations have focused on the use of stable arylboronic acids, in the presence of a base and a gold species. The procedures allow the preparation of a wide variety of arylgold compounds in good to high yields. Moreover, this methodology has proven successful with complexes bearing phosphines or *N*-heterocyclic carbenes.[9] We have investigated very recently the role of the base in this transmetalation of organoboron reagents using well-defined basic complex [Au(IPr)(OH)] (**1**) [IPr = 1,3-bis(diisopropyl)phenyl-imidazol-2-ylidene; $pK_{aDMSO} = 30.5$].[10,11] In the initial report, mechanistic studies revealed that **1** was a very active species in the transmetalation reaction and that the transfer of the aryl moiety to gold readily occurred within 10 min! Still intrigued by the efficiency of this gold hydroxide complex as an organic moiety transfer promoter, other organometallic partners, typically used in cross-coupling reactions, were considered as potential transmetalation partners. Unlike Grignard reagents, organozinc reagents are more tolerant to functional groups but their sensitivity to air, moisture and acidic hydrogen atoms[12] does not make them a particularly attractive partner for the study we envisaged.[13] Although organostannanes are milder, more stable and readily prepared reagents, the toxicity of the tin reagents and their by-products make them unattractive.[14] In contrast, organosilanes are mild and stable and their price make them very attractive. Additionally, a wide variety of Hiyama-type couplings have recently been developed and have led to a resurgence in the use of these reagents as coupling partners.[15] A major disadvantage of the method is the need for a fluoride source to act as an activator, forming a hypervalent silicon species that facilitates the transfer of the organic group onto the metal. Most organic-soluble fluoride sources are very expensive, corrosive and incompatible with silicon protecting groups.[16] Consequently, a number of fluoride-free Hiyama-type couplings using base have recently been developed.[17] Ball and co-workers recently reported a facile and straightforward route to access arylcopper complexes using arylsiloxanes with a copper fluoride species at room temperature in THF (Scheme 1).[18] This method proved to be very efficient but required the prior synthesis of [Cu(IPr)(F)].



Scheme 1. Synthesis of functionalised arylcopper by transmetalation of arylsilanes.

The latter complex was prepared by a two-step synthesis, starting from the copper chloride via the formation and isolation of unstable and air-sensitive [Cu(NHC)(O*t*Bu)].[19] With these precedents in mind and taking advantage of the recent and very promising reactivity of the Brønsted base **1** in transmetalation reactions, we examined whether the synthesis of organogold complexes under fluoride-free conditions could be achieved (Scheme 2).

Initial reactivity studies were performed by stirring phenyltrimethoxysilane **2** with **1** in [D_6]benzene at room temperature for 30 min. Monitoring the reaction by ^{1}H NMR spectroscopy revealed that complete conversion had been reached at this time. To our surprise, a different complex than the expected NHC-gold-phenyl species was observed

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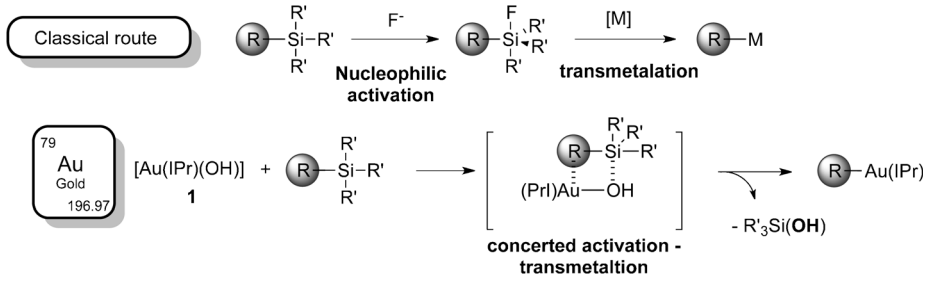
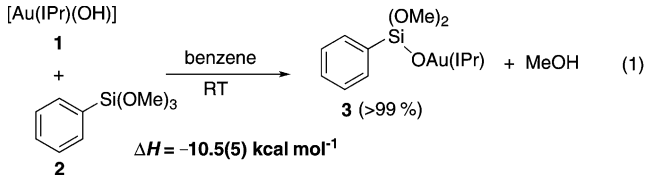


Scheme 2. Proposed classical transmetalation-reaction pathway and the fluoride-free route envisaged involving **1**.

by ^{1}H NMR spectroscopy. A singlet at δ=3.07 ppm led us to propose the formation of the gold silanolate species **3** that would result of the extrusion of a molecule of methanol according to Equation (1). This new species was very stable



and could be isolated in excellent yield. Our hypothesis was confirmed by the presence of a peak at δ=−54.3 ppm in the ^{29}Si NMR spectrum. To unequivocally confirm atom connectivity in **3**, single crystals were grown by slow diffusion of pentane into a saturated solution of **3** in dichloromethane at room temperature (Figure 1).[20]

Optimising the reaction time revealed the reaction to be nearly instantaneous, being complete within the time required to analyse an NMR sample after mixing. Solution calorimetric studies revealed the reaction to be exothermic by −10.5 (0.5) kcal mol^{-1} [Eq. (1)]. Reports of phosphine–gold(I) silanolate complexes could be found in the literature. These complexes were obtained by reaction of a phosphine gold(I) complex with either a sodium silanolate[21] or a silanol species.[22] To our knowledge, this is the first report of an isolated and fully characterised *N*-heterocyclic carbene gold(I) silanolate complex.

The reactivity of phenyl silanes with either [Au(IPr)(OH)] (**1**) or [Au(IPr)Cl] (**4**) was then explored (Table 1). No reaction occurred when using **4** with phenyltrimethoxysilane **2** (Table 1, entry 3). This suggests a crucial role for the −OH moiety on gold, either acting as a base or a nucleophile. Similar reactivity was encountered when using triethoxyphenylsilane and loss of a molecule of ethanol was observed by ^{1}H NMR spectroscopy. However, in this case, the process was rather slow and required 4 h to reach complete conversion (Table 1, entry 2). In general, no reactivity was observed with any silanes or siloxanes when using **4** (Table 1, entries 3, 5 and 6). Likewise, **1** did not react with trimethylphenylsilane, suggesting that the hydroxide moiety is not nucleophilic enough to activate this substrate (Table 1, entry 4). Of note, when using **4** in the presence of 2.5 equiv KOH with **2**, the reaction did not proceed at all.

With this new reactivity in hand, the generality and functional group tolerance of the reaction was explored (Table 2). Much to our satisfaction, this methodology was

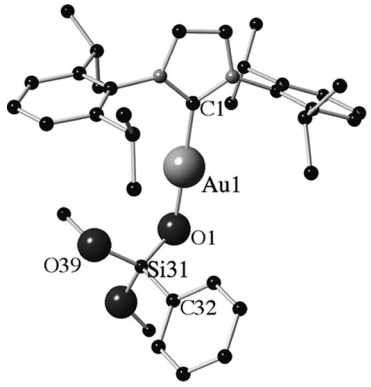
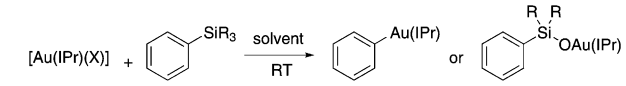
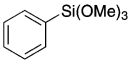
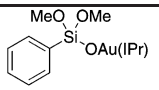
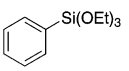
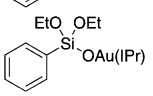
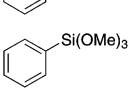
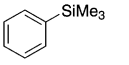
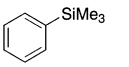
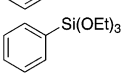


Figure 1. Molecular representation of [Au(IPr)(OSi(OMe)$_2$(C$_6$H$_5$)] (**3**). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: Au1−C1 1.972 (9), Au1−O1 2.023(7), C1−Au1−O1 178.9(3), O1−Si31 1.616(9), Si31−O39 1.629(8), Si31−C32 1.852(11).

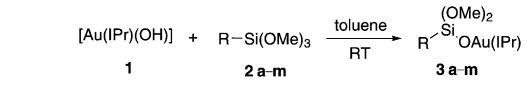
Table 1. Reactivity of [Au(IPr)X] species with various organosilanes.[a]

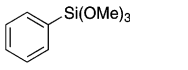
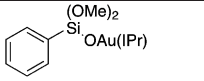
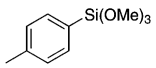
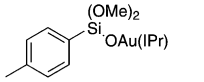
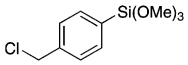
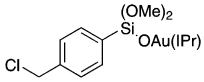
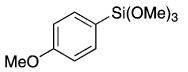
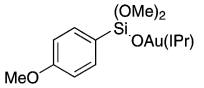
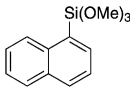
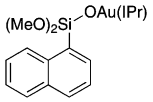
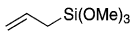
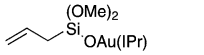
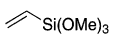
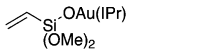
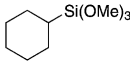
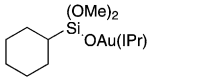
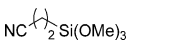
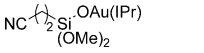
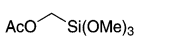
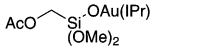
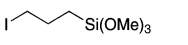
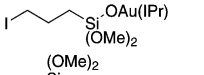
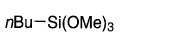
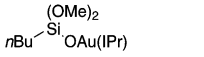
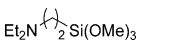
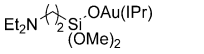
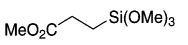
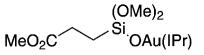


Entry	Gold complex	Silane	*t* [h]	Product	Yield [%][a]
1	**1**		0.1		100 (97 %)
2	**1**		4		100 (88 %)
3	[Au(IPr)Cl]		15	–	0
4	**1**		15	–	0
5	[Au(IPr)Cl]		15	–	0
6	[Au(IPr)Cl]		15	–	0

[a] Reaction conditions: **1** (0.07 mmol), silane (2 equiv), solvent (0.5 mL). [b] Determined by ^{1}H NMR spectroscopy with hexamethylbenzene as external standard (isolated yield in brackets).

Table 2. Preparation of gold silanolate species.[a]



Entry	Siloxane		t [h]	Product		Yield [%][b]
1		**2**	0.1		**3**	>99
2		**2a**	1		**3a**	>99
3		**2b**	1		**3b**	92
4		**2c**	1		**3c**	90
5		**2e**	1		**3e**	94
6		**2f**	1		**3f**	91
7		**2g**	2		**3g**	97
8		**2h**	2		**3h**	87
9		**2i**	1		**3i**	92
10		**2j**	1		**3j**	88
11		**2k**	0.5		**3k**	74
12		**2l**	1		**3l**	81
13		**2m**	1		**3m**	78
14		**2n**	1		**3n**	80

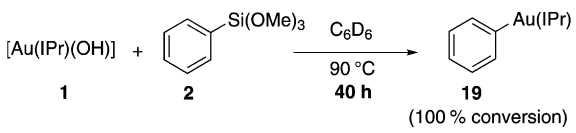
[a] Reaction conditions: **1** (0.07 mmol), siloxane (1 equiv), toluene (0.4 mL). [b] Isolated yields.

successfully applied to a wide range of siloxanes including those bearing aryl, vinyl, allyl and alkyl functionalities. One equivalent of the organosilane was sufficient for the reactions to proceed smoothly. Moreover, all siloxanes reacted cleanly within 2 h to afford the corresponding gold silanolate compounds. The latter were obtained in good yields although yields with alkylsiloxanes were slightly lower. No general trend in reactivity could be detected when using electronically different substrates (Table 2, entries 1–5 and 9–14). Vinyl- and cyclohexylsiloxanes required longer reaction times to reach completion. Finally, this methodology tolerates a broad range of functional groups, such as nitrile, halide, substituted amine, methoxy and acetoxy groups. To our delight, the final gold silanolates were all stable and easily isolated; those derived from arylsiloxanes were completely resistant to dimerisation to the corresponding disiloxane unlike their silanol homologues, which is consistent with literature reports dealing with arylsilanolate salts.[23] Unfortunately, the alkylsilanolate-derived complexes decomposed readily in air.

Silanols have recently been considered as an alternative to silanes in fluoride-free palladium-catalysed cross-couplings. A first report by Hiyama et al. described the use of silver(I) oxide as a stoichiometric promoter in conjunction with $Pd(PPh_3)_4$ to prepare biaryls from silanol precursors.[24] Although good yields were obtained, large amounts of a silver activator and long reactions times are needed. Denmark reported the use of Cs_2CO_3 as a promoter in the cross-coupling of (4-methoxyphenyl)dimethylsilanol with a variety of aryl iodides and bromides.[25] Unfortunately, the scope of the reaction could not be expanded to other arylsilanols. The same group disclosed that replacing the Cs_2CO_3 with CsOH allowed for faster transmetalation and hampered the competitive dimerisation side reaction of these silanols.[26] More recent work from Denmark et al. has described the efficient cross-coupling of arylsilanolate salts with a broad range of aryl bromides to afford in good to high yields biaryl moieties.[27]

Mechanistic studies showed that arylsilanols could be used as activators to form, in the presence of base, an arylsilanolate salt that would displace the halide on palladium, in Ar−Pd−X species, to form palladium silanolate complexes. A second molecule of silanolate is then proposed to function as a nucleophilic activator, generating a pentacoordinate siliconate, which is then capable of transmetalation.[28] We have previously encountered similar reactivities of gold to palladium in the synthesis of organogold complexes.[10] We hypothesised that once again a similar reactivity could be observed with optimised conditions.

To our delight, the formation of gold-phenyl species **19** could be observed by ^{1}H NMR spectroscopy when reacting **1** with **2** in [D_6]benzene at 90 °C, but the reaction was particularly slow and completion was reached after a lengthy 40 h [Eq. (2)]. Moreover, under



(2)

these conditions, the reaction medium turned pink after 5 h, which is typically a sign of gold decomposition. With this first encouraging result, we next optimised the reaction conditions by screening solvents, temperatures and times (Table 3). The choice of solvent had a considerable effect on the reaction progress. Indeed, the use of more polar solvents, such as 1,4-dioxane or DMF, greatly reduced the reaction time. Likewise, the use of dry solvents allowed for shorter reaction times reaching completion after only 5 h in

Table 3. Optimisation of the transmetalation reaction of $PhSi(OMe)_3$ with [Au(IPr)(OH)].[a]

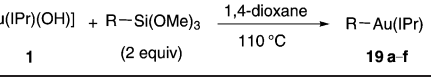
Entry	Solvent	T [°C]	t [h]	Yield [%][b]
1	benzene	90	40	>99
2	toluene	110	12	>99 (65)
3	anhydrous toluene	110	5	>99 (72)
4	anhydrous dioxane	110	5	>99 (97)
5	DMF	110	5	>99 (84)
6	1,2-DCE	90	10	traces
7	**anhydrous dioxane**	**110**	**1.5**	**>99 (99)**

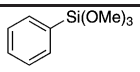
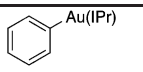
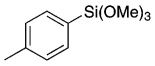
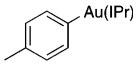
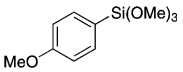
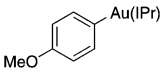
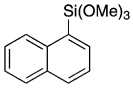
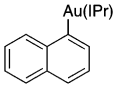
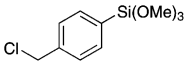
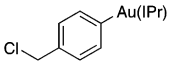
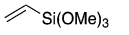
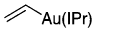
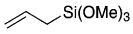
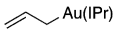
[a] Reaction conditions: **1** (0.07 mmol), siloxane (2 equiv), anhydrous 1,4-dioxane (0.5 mL). [b] Determined by ^{1}H NMR spectroscopy with hexamethylbenzene as external standard (isolated yield in brackets).

dry toluene whereas the same yield required 12 h in wet toluene. Optimal conditions required 1,4-dioxane at 110°C, which avoided the decomposition issues that occurred in non-polar solvents, such as toluene and benzene.

Once these optimal conditions were identified, they were applied to previously used siloxanes (Table 4). Most arylsiloxanes were successfully converted to the arylgold species. The transmetalation of arylsilanes was clean and all reactions reached complete conversion within 2 h. The arylgolds were obtained in good to excellent yields. Pleasingly, efficient transmetalation also occurred with vinyl- and allylsilanes affording the vinyl- and allylgold complexes, albeit in lower yields. Unexpectedly, the reaction conversion of (4-chloromethyl)phenyltrimethoxysilane could not exceed 75% conversion and traces of **4** could be observed by ^{1}H NMR spectroscopy. Reaction of the alkylsiloxanes using this protocol only led to decomposition.

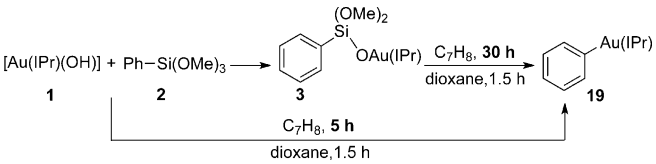
Table 4. Synthesis of functionalised organogold compounds.



Entry	Silane	t [h]	Product		Yield [%][a]
1		1.5		**19**	>99
2		0.8		**19a**	94
3		1.5		**19b**	>99
4		1.5		**19c**	88
5		3		**19d**	75[b]
6		0.8		**19e**	92
7		3		**19f**	68

[a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopy with hexamethylbenzene as external standard.

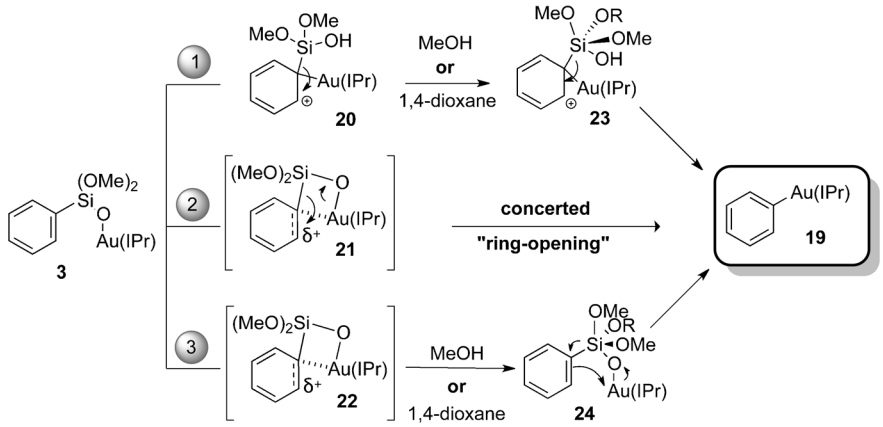
Monitoring the reaction by ^{1}H NMR spectroscopy confirmed our first hypothesis that **3** was a key intermediate in the transmetalation of the organic moiety to gold. The formation of several other gold species was also observed but none of them could be isolated. Notably, completely different reactivity in solvents of varied polarity was observed when starting from intermediate **3** to form **19**. Indeed, in dry toluene, transfer of the phenyl group starting from **3** required 30 h, but only needed 5 h to reach completion starting from **1** and **2**. However, this difference in reactivity was not observed in 1,4-dioxane and both reactions were complete after 1.5 h (Scheme 3).



Scheme 3. Difference of reactivity when using **3** or **1** to access gold-phenyl species.

After these observations, it was clear that the molecule of methanol generated when forming intermediate **3** had a non-innocent role in the subsequent transmetalation reaction. Indeed, adding dry MeOH to both reactions allowed the reduction of the reaction times. Moreover, as mentioned before when starting from **3**, changing the solvent to a more polar one may facilitate the reaction by coordination of the solvent to the silicon atom. This leads us to propose the following mechanism (Scheme 4). With **3** being an intermediate starting from **1** or a starting material, three pathways were envisioned for this reaction. When using **1** to access **19**, a molecule of methanol would be generated when forming intermediate **3**. The latter could evolve via two pathways and form either intermediate **20** or **21** with the β-silyl effect. In the presence of methanol, a pentavalent silicon species could be formed by nucleophilic attack on the silicon atom in carbocation **20** to lead to **23**. Reverting to a more stable Si^{IV}, this intermediate would rearrange to provide the phenylgold compound **19**. Going through the four-membered cyclic intermediate **21**, a similar mechanism with the nucleophilic attack of methanol onto silicon would first lead to **24** that would rearrange to give stable product **19**. Finally, heating **3** in 1,4-dioxane directly could first give rise to either intermediate **20** or **21**. From **20**, the two same possible pathways as in the direct reaction of **1** were envisioned. The coordinating oxygen atoms of dioxane would permit to follow the two pathways previously described. The second alternative would involve concerted ring-opening of **21**, which would furnish **19** in one step. Unfortunately, we have not yet been able to isolate any of the proposed intermediates and silicate side products.

In conclusion, we have developed a new synthetic approach to NHC-aryl-, vinyl- and allylgold systems. To our



Scheme 4. Proposed mechanism for the transmetalation of arylsiloxanes to gold.

knowledge this is the first report of a transmetalation of organosilanes to gold under fluoride-free conditions. The complex [Au(IPr)(OH)] can be employed to obtain silanolate salts in a very efficient process and with high yields. The advantages of these salts include their stability to storage, their resistance to disiloxane formation and their self-activating properties. The facile isolation and characterisation of this new gold silanolate compound allowed the discovery of a new pathway for transmetalation from silanes to gold. Moreover, the functional group compatibility and the extension to allyl- and vinylsiloxanes bode well for the adoption of this method particularly in cases in which boron- or lithium-based reagents are problematic. This methodology has revealed a new and very different pathway in the activation of siloxanes with gold. The present results provide the first key fundamental insight into the mechanism of transfer of the organic fragment from silane to gold and establish that the reactivity of gold is similar to that of palladium in the Hiyama coupling. Furthermore, the fact that gold mimics palladium along this reactivity manifold suggests to us that other late transition metal-hydroxides (or more generally late transition metal-alkoxides)[17] may behave in this manner. The basic understanding of this transmetalation reaction of silanes to gold could also permit further synthetic functionalisation (or to rapidly gain molecular complexity) in one-pot reactions involving diverse electrophiles. Mechanistic studies of this process are currently ongoing.

Experimental Section

General procedure in the synthesis of gold silanolate compounds: A vial was charged with [Au(IPr)(OH)] (**1**) (40 mg, 0.07 mmol), and the corresponding siloxane (0.07 mmol) in toluene (0.6 mL). The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy. Upon completion, the solvent was removed, in vacuo. The crude mixture was triturated with pentane. The resulting white suspension was filtered, and the collected solids were washed with pentane (3×3 mL) to afford the title compound as a microcrystalline solid.

General procedure for the transmetaltion of siloxanes to gold: A vial was charged with [Au(IPr)(OH)] (40 mg, 0.07 mmol) and the corresponding siloxane (0.07 mmol) in anhydrous 1,4-dioxane (0.5 mL). The reaction mixture was stirred at 110 °C. Upon completion, the solvent volume was reduced to 0.1 mL. The reaction mixture was allowed to cool at room temperature for 30 min, allowing the product to precipitate. The white suspension was filtered and washed with pentane to afford the title compound as a microcrystalline solid.

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Keywords: fluoride-free · gold · *N*-heterocyclic carbenes · silanes · transmetalation

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