Gold Complexes

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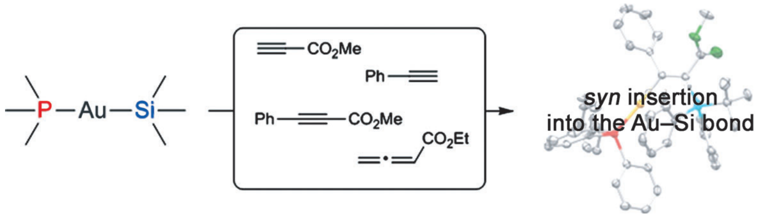
Direct *syn* Insertion of Alkynes and Allenes into Au–Si Bonds



Complete control: Alkynes and allenes are shown to insert into Au–Si bonds with complete stereocontrol and in most cases complete regiocontrol. The ensuing β-silyl vinylgold complexes have been characterized by spectroscopic and crystallographic means. These results provide unequivocal evidence for *syn* insertion reactions at gold.

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Direct *syn* Insertion of Alkynes and Allenes into Au–Si Bonds**

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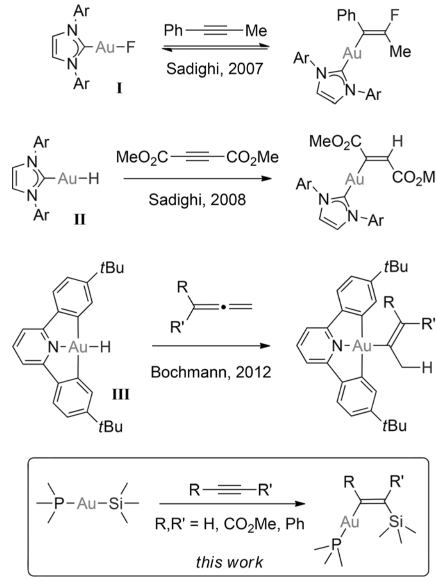
Over the past decade, gold catalysis has emerged as a very active field in homogeneous catalysis. Nowadays gold complexes are no longer considered as chemically inert species, but appear as powerful and versatile catalysts for a broad range of transformations for the formation of C–C and C–X bonds.[1] All these synthetic developments have stimulated interest in the formation, stability, and reactivity of organogold complexes. In particular, several key intermediates of π-activation processes have been detected in situ or even isolated in the last few years, thereby providing valuable mechanistic insights.[2–5] Recent studies have also shown that the reactivity of gold complexes extends well beyond the coordination/activation of π bonds, and compelling evidence has been reported for *gem*-diauration of alkynes and arenes,[6,7] two-electron redox transformations,[8] as well as transmetallation reactions.[9]

The reactivity of gold complexes seems more versatile than anticipated, but compared with the other transition metals, our knowledge of gold chemistry is still in its infancy and much remains to be explored. This is particularly true for insertion reactions that are ubiquitous in transition metal chemistry but very elusive with gold.[10–13] Among the relevant literature, the few recent contributions depicted in Scheme 1 are particularly noteworthy. Reversible addition of the N-heterocyclic carbene (NHC) gold fluoride **I** across several alkynes was reported by Sadighi and co-workers.[14] The vinylgold complex isolated from the reaction of **I** with 1-phenyl-1-propyne displays *trans* arrangement of the gold and fluoride atoms, and the reaction was thus proposed to proceed through displacement of the fluoride, followed by nucleophilic *anti* addition to the π-coordinated alkyne. The isolation of gold hydride complexes **II** and **III** by Tsui, Sadighi, and Bochmann[15] has also stimulated studies on insertion reactions. Upon reaction with dimethyl acetylenedicarboxylate, the NHC gold(I) hydride **II** readily afforded the *trans* addition product. In contrast, the pincer gold(III) hydride **III** was unreactive towards dimethyl acetylenedicarboxylate; but with allenes, vinylgold complexes were obtained smoothly and regiospecifically. Last but not least, Hashmi, Köppel, and co-workers investigated experimentally and computationally the reaction of complex **II** with ethene,[16] and came to the conclusion that insertion of olefins into the Au–H bond is not a favorable process.[17] Thus, no definite proof for a true insertion reaction at gold has been reported to date, and the ability of gold complexes to undergo *syn* insertion can be legitimately questioned.



Scheme 1. Reactions of gold fluoride, gold hydride, and gold silyl complexes with alkynes and allenes.

Our recent work on the activation of σ-SiSi bonds at gold[8e,f] prompted us to investigate the feasibility of such insertion reactions into Au–Si bonds.[18] Here we report that phosphine gold(I) silyl complexes indeed undergo *syn* insertion of alkynes and allenes. The stereo- and regioselectivity of the process has been studied, as well as the reactivity of the ensuing β-silyl vinylgold(I) complexes.

Gold silyl complexes have been synthesized and structurally characterized early on by Schubert and co-workers and Schmidbaur and co-workers,[19] but very little is known about their reactivity.[20,21] Sterically demanding substituents are usually necessary to impart reasonable stability, and we thus worked on $(Ph_3P)Au\text{-}SitBuPh_2$ (**1**). By following the reported methodology,[19] that is coupling the corresponding phosphine gold chloride with lithiosilane, complex **1** was obtained in 91% yield.[22] Its ability to undergo insertion reactions was

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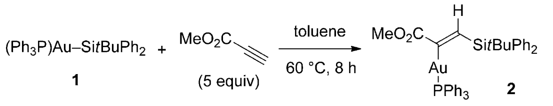
first evaluated with methyl propiolate (5 equiv) in toluene at 60 °C (Scheme 2). $^{31}\text{P}\{^{1}\text{H}\}$ NMR-spectroscopic monitoring indicated the gradual and clean transformation of **1** ($\delta =$ 56.5 ppm) into a single species **2** displaying a resonance signal at $\delta = 41.5$ ppm, in the region typical for (triphenylphosphine) vinylgold complexes.[23] The reaction reached full conversion within 8 h. After work-up, complex **2** was isolated as an air-stable white solid (95 % yield) and fully characterized.



Scheme 2. *syn* Insertion of methyl propiolate in the Au–Si bond of the gold silyl complex **1**.

Several NMR signals are diagnostic of a β-silyl vinylgold complex.[22] The vinylic proton appears in the ^{1}H NMR spectrum at $\delta = 8.47$ ppm (d, $^{4}J_{\text{HP}} = 17.8$ Hz). The ^{29}Si NMR resonance signal is shifted to higher field ($\delta = 35.4$ ppm for **1**, versus -12.5 ppm for **2**) and the associated J_{SiP} coupling constant decreases drastically (from 164.8 Hz in **1** to 3.9 Hz in **2**). To unambiguously assess the structure of **2**, crystals were grown (from a pentane/toluene solution) and an X-ray diffraction study was performed (Figure 1). Despite severe steric crowding, the central C=C double bond adopts a perfectly planar geometry, with *cis* arrangement of the gold and silicon atoms, and *trans* arrangement of the silyl and CO$_2$Me moieties.

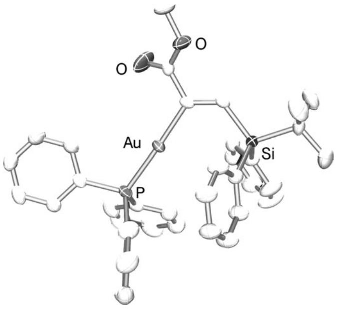
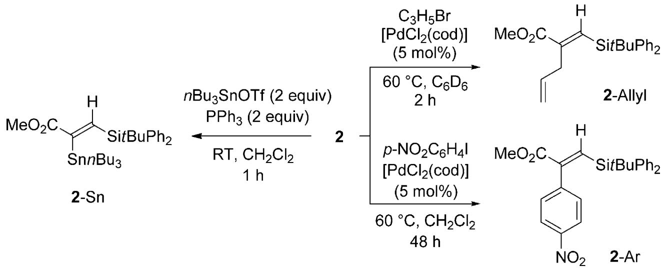


Figure 1. Molecular view of complex **2** in the solid state (thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity).[25]

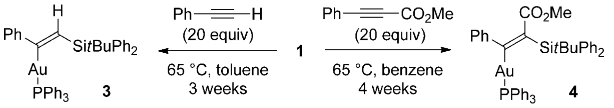
Complex **2** is formed in a selective manner. The observed regioselectivity is consistent with the polarity of the alkyne and the nucleophilic character of the silyl group at gold. The stereoselectivity indicates that the reaction takes place by *syn* insertion of the alkyne into the Au–Si bond. This pathway markedly contrasts with the outer-sphere mechanism normally observed upon functionalization of alkynes at gold. Typically, coordination of the alkyne first gives a π complex that subsequently undergoes *anti* nucleophilic attack, resulting in the formation of *trans*-vinyl complexes.[5,14]

To capitalize on the direct access to the β-silyl vinylgold complex **2**, we then explored its reactivity towards intermolecular functionalization reactions (Scheme 3).[11] First, Au/Sn transmetalation was readily achieved upon reaction with nBu$_3$SnOTf at room temperature, affording the α-stannyl-β-silylacrylate **2**-Sn in 81 % yield. Complex **2** was also engaged in Pd-catalyzed C–C cross-coupling reactions in the presence of [PdCl$_2$(cod)] (5 mol %) at 60 °C, using allyl bromide and p-nitroiodobenzene as electrophiles. The resulting allyl- and aryl-functionalized products **2**-Allyl and **2**-Ar were thereby obtained in good yields (73 and 84 %, respectively). Complex **2** is highly functional and sterically hindered, yet it reacts smoothly and cleanly, affording access to trisubstituted olefins with complete regio- and stereocontrol.



Scheme 3. Functionalization of the β-silyl vinylgold complex **2** by transmetalation/cross-coupling. cod = cyclooctadiene.

The generality of the insertion process, as observed with methylpropiolate, was then evaluated by treating complex **1** with various substrates. No reaction occurred with ethylene, methyl acrylate, or ethyl 2,3-butadienoate even under forcing conditions (solvent-free, pressures up to 10 bar, temperatures up to 80 °C). But complex **1** was found to react with phenylacetylene and methyl phenylpropiolate (Scheme 4). The reactions require rather drastic conditions (several weeks at 65 °C) but proceed with complete stereo- and regioselectivity.



Scheme 4. *syn* Insertion of terminal and internal alkynes in the Au–Si bond of the gold silyl complex **1**.

The vinylgold complexes **3** and **4** were fully characterized,[22] and their connectivity was unambiguously confirmed by X-ray diffraction studies (Figure 2). In both cases, the gold atom is positioned *cis* to silicon, consistent with *syn* insertion of the alkyne into the Au–Si bond. Both the terminal and internal alkynes insert so as to position the phenyl group geminal to gold. Steric repulsion between this phenyl group and the silyl moiety may explain the selective formation of these regioisomers. But the regioselectivity of the insertion is apparently governed by subtle stereoelectronic effects, as suggested by the different outcomes observed with methyl propiolate and methyl phenylpropiolate (the silyl group is

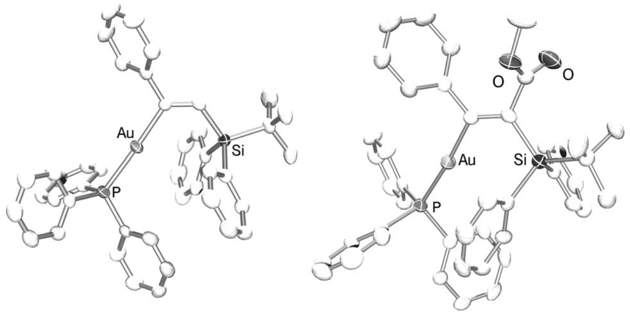
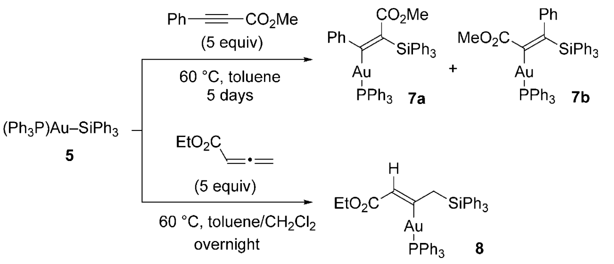


Figure 2. Molecular view of complexes **3** (left) and **4** (right) in the solid state (thermal ellipsoids set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity).[25]

introduced in β- or α-position to the CO_2Me substituent, respectively).

The substitution pattern at Si was then varied and the Si*t*BuPh$_2$ group was replaced by $SiPh_3$. The corresponding gold silyl complex **5**[19b] was found to also react readily with methyl propiolate, yielding selectively the product of *syn* insertion (93% yield after isolation). Interestingly, complex **5** was far more reactive than **1** towards methyl phenylpropiolate (Scheme 5). At 60 °C, the insertion proceeded to completion within five days (instead of four weeks) and gave two vinylgold complexes **7a** and **7b** (ca. 1:1 ratio according to $^{31}P\{^1H\}$ NMR), which were separated by column chromatography. Their respective structures were unequivocally assigned by multinuclear NMR spectroscopy and X-ray diffraction analysis (for **7b**).[22] They both result from *syn* insertion of the internal alkyne into the Au–Si bond of **5** (*cis* arrangement of the Au and Si atoms) and correspond to the two conceivable regioisomers, with the Ph group geminal to Au (**7a**) or geminal to Si (**7b**). Finally, the increase in reactivity observed upon lowering the steric shielding around silicon prompted us to reconsider the insertion of allenes. Gratifyingly, complex **5** was found to react with ethyl 2,3-butadienoate at 65 °C giving complex **8** as the sole product. As shown by crystallography,[22] the insertion involves the terminal C=C bond of the allene, and the silyl group is introduced in γ position to the CO_2Et substituent.



Scheme 5. Alkyne and allene *syn* insertions in the Au–Si bond of the gold silyl complex **5**.

In conclusion, the results reported here provide evidence for a fundamental, yet unprecedented, elementary step at gold, namely *syn* insertion. Terminal and internal alkynes, as well as allenes are shown to insert readily into Au–Si bonds. The reaction is broad in scope and gives access to a variety of stable β-silyl vinylgold compounds in a stereoselective and regioselective manner. Future work from our laboratory will seek to shed light on the mechanism of this reaction,[24] to explore its scope (regarding both the organic substrates and the Au–X bonds) and to determine the factors controlling its regio- and stereoselectivity.

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[25] CCDC-934773 (**2**), 934774 (**3**), and 934775 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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