# **ORGANOMETALLICS**

# Gold-Mediated Insertion of Oxygen into Silicon–Silicon Bond: An Original Au(I)/Au(III) Redox Sequence

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**Supporting Information** 

**ABSTRACT:** The diphosphine-disilane  $iPr_2(o-C_6H_4)$ -SiMe<sub>2</sub>SiMe<sub>2</sub>( $o-C_6H_4$ )P $iPr_2$  reacts with AuCl(SMe<sub>2</sub>) via coordination of the two phosphines and oxidative addition of the  $\sigma$ -Si-Si bond. The ensuing bis(silyl) gold(III) complex has been unequivocally authenticated by NMR spectroscopy at -60 °C.



Upon heating, it evolves cleanly to give a disiloxane gold(I) complex that has been fully characterized, including by X-ray diffraction analysis. Oxidation of the disilane proceeds via an original Au(I)/Au(III) redox sequence. According to <sup>18</sup>O labeling experiments, both water and dioxygen are competent oxygen sources. Oxidative addition of the  $\sigma$ -Si–Si bond to form a bis(silyl) gold(III) complex seems to be a prerequisite for the disilane  $\rightarrow$  disiloxane conversion to occur.

O ver the past decade, homogeneous catalysis with gold complexes has attracted considerable interest and it has been applied to a wide range of organic transformations with very high, often unprecedented efficiency and selectivity.<sup>1</sup> The vast majority of these reactions are based on the unique carbophilic Lewis acidity of gold complexes that is typically used to activate alkynes, alkenes, allenes, etc. toward nucleophilic attack. Recently, the scope and versatility of homogeneous gold catalysis has been further extended, in particular toward oxidative coupling and addition reactions (in the presence of external oxidants)<sup>2</sup> as well as C–C bond forming reactions using dual Au–Pd catalysis.<sup>3</sup>

In parallel with these very rapid and important synthetic achievements, increasing efforts have been made over the past few years to shed light into the underlying mechanistic issues. The recent characterization of some putative intermediates involved in gold activation of  $\pi$  systems<sup>4</sup> (side-on complexes,<sup>5</sup> vinyl gold complexes,<sup>6</sup> geminal digold complexes<sup>7</sup>) has provided valuable information and contributed to refine mechanistic proposals. Comparatively, the precise factors involved in controlling two-electron redox and dual catalysis with gold complexes remain less understood, but some insight has started to be gained into key transformations (oxidative addition/reductive elimination, transmetalation, etc.)<sup>8,9</sup>

In that general context, we have recently shown, thanks to phosphine chelating assistance, that gold can undergo unexpectedly facile oxidative addition of  $\sigma$ -Si–Si bonds, affording original bis(silyl) gold(III) complexes.<sup>10,11</sup> Upon varying the substituents at the phosphorus anchors, we have incidentally found that the disilane moiety can be converted into a disiloxane moiety (oxygen insertion) via a Au(I)/Au(III) sequence. These results are reported herein. Labeling experiments have been performed to identify the possible source of the oxygen atom, and the role of gold in the disilane  $\rightarrow$  disiloxane conversion has been probed.

As previously reported, <sup>10</sup> the diphosphine-disilane ligand 1areadily reacts with [AuCl(SMe<sub>2</sub>)] in dichloromethane at -78 °C via coordination of the two phosphines and oxidative addition of the  $\sigma$ -Si–Si bond at gold (Scheme 1). The ensuing bis(silyl) gold(III) complex 2a can be detected and characterized by NMR at low temperature, but it rapidly decomposes above -60 °C, giving a mixture of unidentified products. Addition of GaCl<sub>3</sub> to complex 2a significantly improves the stability and allows for the structural characterization of the cationic bis(silyl) gold(III) complex with GaCl<sub>4</sub>as the counteranion.<sup>10</sup> At this point, we were intrigued about the role of the phosphorus substituents in the oxidative addition process and the stability of the resulting complex. We thus replaced the Ph groups by more electron donating iPr substituents. The corresponding diphosphine-disilane ligand  $1b^{12}$  was reacted with  $[AuCl(SMe_2)]$  at low temperature in an NMR tube. Similarly to 1a, spontaneous formation of the bis(silyl) gold(III) complex 2b was unequivocally established by <sup>31</sup>P and <sup>29</sup>Si NMR spectroscopy ( $\delta$ (<sup>31</sup>P) s, 86.7 ppm;  $\delta$ (<sup>29</sup>Si) dd, 36.9 ppm,  $J_{SiP}$  = 112.8 and 8.4 Hz). Disappointingly, complex 2b is stable only below -60 °C, but in marked contrast with 2a, it evolves cleanly upon warming to give the new complex 3b. A single <sup>31</sup>P NMR resonance signal is observed at 60 ppm for 3b, indicating that the two phosphorus atoms remain symmetrically coordinated to gold. Upon transformation of 2b into 3b, the <sup>29</sup>Si NMR signal shifts to

Received: July 23, 2012 Published: August 14, 2012 Scheme 1. Coordination of the Diphosphine–Disilane Ligands 1 to Gold: Formation and Evolution of the Bis(silyl) Gold(III) Complexes 2



high field ( $\Delta \delta = 34.2 \text{ ppm}$ ) to appear in the typical range of organic siloxane derivatives ( $\delta 2.7 \text{ ppm}$  for 3b, compared with  $\delta$  –2.2 ppm for PhMe<sub>2</sub>SiOSiPhMe<sub>2</sub>).<sup>13</sup> The coupling pattern of the <sup>29</sup>Si NMR signal also changes drastically. The large  $J_{\text{SiP}}$  coupling constant characteristic of bis(silyl) gold(III) complexes 2 (112.8 Hz for 2b) is no longer present for 3b. Instead, we observe a second-order AA'XX' system (A, A' = <sup>29</sup>Si, X, X' = <sup>31</sup>P) with a small value of  $N = \frac{1}{2}(J_{\text{AX}} + J_{\text{A'X}}) = 3.6$  Hz. High-resolution mass spectrometry measurements (HR ESI-MS) also provide valuable information. The signal observed at m/z 715 amu for 3b and associated isotopic distribution correspond to the mass of the starting material 2b plus one oxygen atom. It is most likely that this mass increment results from disilane  $\rightarrow$  disiloxane conversion, in accordance with the <sup>29</sup>Si NMR data.

To shed light on the precise structure of complex 3b, colorless crystals suitable for X-ray diffraction analysis were grown from a dichloromethane/pentane solution at -30 °C (Figure 1).<sup>12</sup> Accordingly, 3b was unambiguously identified as a



**Figure 1.** X-ray crystal structure of complex **3b**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms, lattice solvent molecules, and the chloride counteranion are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–Au, 2.313(1); P2–Au, 2.310(1); Si1–O, 1.646(2); Si2–O, 1.640(2); P1–Au–P2, 171.13(2); Si1–O–Si2, 147.81(12).

cationic diphosphine gold(I) complex featuring a pendant disiloxane moiety. Its ionic nature is apparent from the long distance between the metal center and chloride counteranion (shortest Au…Cl distance 6.434(1) Å). The gold(I) center adopts a classical dicoordinate arrangement<sup>14</sup> with the two phosphorus atoms coordinated in a quasi-linear fashion (P–Au = 2.313(1) and 2.310(1) Å, P–Au–P =  $171.13(2)^{\circ}$ ). The two silicon atoms are no longer bound to gold and remain far away from the metal center (Au…Si distances 3.556(6) and 3.436(7) Å). The oxygen atom inserted between the two silicon atoms also stands far away from the gold center, the Au…O distance

(2.854(2) Å) exceeding the sum of covalent radii  $(2.02 \text{ Å})^{15}$  by more than 41%.

Thus, the bis(silyl) gold(III) complex **2b** spontaneously evolves into the diphosphine gold(I) complex **3b** with insertion of an oxygen atom between the two silicon atoms. The overall reaction scheme involves oxidation of the disilane fragment of **1b** and proceeds via a Au(I)/Au(III) redox sequence.

We tried to gain some insight into the source of oxygen atom and the role of gold in the formation of 3b. Apparently, the reaction conditions strongly influence the transformation of 2b into 3b, and if extreme precautions are taken to exclude any traces of air and moisture, the process can be significantly slowed down. In contrast, the addition of small amounts of water to a dichloromethane solution of complex 2b considerably increases the rate of formation of 3b. Typically, while only 20% of the gold(III) complex 2b is converted into gold(I) complex 3b within 30 h under standard conditions, complete conversion is observed within 20 h upon addition of 1-3 equiv of water. Similarly, the transformation of 2b into 3b is speeded up when a dioxygen atmosphere (1 bar) is applied to complex 2b under anhydrous conditions. To ascertain the origin of the oxygen atom incorporated in the disiloxane moiety, <sup>18</sup>O labeling experiments were performed. In a first set of experiments, a few equivalents of  $H_2^{-18}O$  were added to a dichloromethane solution of 2b under dioxygen-free conditions. Another experiment was carried out with <sup>18</sup>O<sub>2</sub> gas (0.7 bar) and a dichloromethane solution of 2b under anhydrous conditions. In both cases, <sup>31</sup>P NMR spectroscopy indicated the complete transformation of 2b into 3b, and ESI-MS spectrometry revealed up to 80% of <sup>18</sup>O enrichment within the disiloxane fragment.<sup>12</sup> Both water and dioxygen are thus competent oxygen sources for the formation of 3b. The partial <sup>18</sup>O enrichment of **3b** (50-80%) suggests that traces of unlabeled water and/or dioxygen also contribute to the formation of 3b. The exact stoichiometry of these reactions can hardly be determined and the fate of the oxidant remains unclear at this stage. A priori, dihydrogen or water can be envisioned as byproducts. Overall, these observations are consistent with the known ability of gold to promote oxidation reactions with water or dioxygen as oxidants.<sup>16</sup>

The role of gold in the disilane  $\rightarrow$  disiloxane conversion was then investigated. First, the coordination of the diphosphine– disilane ligand to gold was found to be a prerequisite for the oxidation of the disilane moiety. In contrast with the bis(silyl) gold(III) complex **2b**, no evolution of the disilane fragment is detected when a solution of **1b** is left without precaution under air, indicating that the diphosphine–disilane ligand is much more stable toward hydrolysis and oxidation. Then, we wondered whether oxidative addition of the  $\sigma$ -Si–Si bond at gold is necessary or not for the oxidation of the disilane moiety. To address this question, the diphosphine–disilane ligand **4** was prepared and coordinated to gold.<sup>12</sup> The short methylene bridge between the P and Si atoms was envisioned to maintain the disilane moiety in a position remote from gold and thereby prevent geometrically the oxidative addition of the  $\sigma$ -Si–Si bond. Upon reaction of 4 with [AuCl(SMe<sub>2</sub>)] in dichloromethane at -78 °C, complex 5 was isolated as a white powder in 87% yield (Scheme 2).

## Scheme 2. Synthesis and Behavior of the Diphosphine– Disilane Gold(I) Complex 5



 $^{31}$ P and  $^{29}$ Si NMR spectroscopy indicate both the symmetric coordination of the two phosphines and the retention of the disilane moiety. Colorless crystals of **5** were obtained from a dichloromethane/pentane solution at -30 °C, and its molecular structure was analyzed by X-ray diffraction (Figure 2). The gold center is surrounded by the two phosphorus



**Figure 2.** X-ray crystal structure of complex **5**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–Au, 2.311(2); P2–Au, 2.315(2); Si1–Au, 3.673(2); Si2–Au, 3.726(2); Si1–Si2, 2.347(2); P1–Au–P2, 143.53(6).

atoms and the chlorine atom, organized in a trigonal-planar arrangement (P–Au–P = 143.53(6)°). The two Si atoms remain far away from the metal center (Au…Si distances 3.726(2) and 3.673(2) Å), and the  $\sigma$ -Si–Si bond is not elongated (2.347(2) Å),<sup>17</sup> indicating that the disilane fragment stays pendant. DFT calculations further corroborate the preference for this coordination mode. Oxidative addition of the  $\sigma$ -Si–Si bond is thermodynamically disfavored, the bis(silyl) gold(III) isomer being found 16 kcal/mol higher in energy than the gold(I) isomer.<sup>12</sup>

In contrast with complexes 2, the gold(I) complex 5 was found to be very stable. No reaction occurs within days in the presence of water or dioxygen. Thus, oxidative addition of the  $\sigma$ -Si–Si bond to form a bis(silyl) gold(III) complex seems to be a prerequisite for the disilane  $\rightarrow$  disiloxane conversion.

In conclusion, an original redox sequence has been evidenced at gold. It involves first oxidative addition of a disilane to give a bis(silyl) gold(III) complex and then insertion of an oxygen atom between the two silicon atoms to form a gold(I) complex with a pendant disiloxane moiety. These results lend further credence to the ability of gold to undergo two-electron redox transformations. The group 10 metals, in particular Pd and Pt, have been shown to efficiently promote the activation and functionalization of  $\sigma$ -Si–Si,  $\sigma$ -Sn–Sn,  $\sigma$ -Si–Sn, ... bonds,<sup>18–21</sup> while to the best of our knowledge, such transformations remain unprecedented with the coinage metals. Future work will seek to further generalize the ability of gold and the other coinage metals to participate in redox sequences combining oxidative addition of  $\sigma$ -bonds and subsequent functionalization.

# ASSOCIATED CONTENT

#### **Supporting Information**

Text, figures, tables, and CIF files giving detailed experimental conditions and procedures, analytical data for new compounds **1b**, **2b**, and **3**–**5**, theoretical details for **5**, and crystal data for **3b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### **Author Contributions**

All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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