Gold(I)-Mediated Silicon–Silicon Bond Metathesis at Room Temperature

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Dedicated to Professor Gerd Becker on the occasion of his 70th birthday

Whereas silyl complexes of copper have been known for many decades and have been employed as valuable reagents for organic syntheses,^[1] only very few homologous derivatives of the heavier coinage metals had been synthesized and almost nothing is known about their reactivity. In particular for gold complexes, unique properties may be expected that are related to the existence of the two competing oxidation states +I and +III. The majority of the few gold complexes that had been synthesized to date have the composition $R'_{3}P$ -AuSiR₃. Most of these were reported by Schubert et al. to be obtained in low yields (about 20-30%) by metathesis reactions of triorganylphosphane complexes of gold halides with the appropriate lithium silanides.^[2] The parent homoleptic neutral derivatives AuSiR₃ are however still unknown. Herein we present a route to anionic hypersilyl complexes of gold and present some very unexpected reactions arising from attempts to use them in the synthesis of the neutral compound hypersilylgold, $[AuSi(SiMe_3)_3]$ (1).

We are currently investigating a novel route to phosphane-free silvl complexes of the coinage metals; that is, the metathesis of coinage-metal halides MX (M = Cu, Ag, Au; X = Cl, Br, I) and potassium silanides in liquid ammonia. As both reactants generally show good solubility in ammonia, such reactions can be performed under homogenous conditions and usually deliver the products in high yields.^[3] If freshly prepared gold(I) iodide^[4] is thus reacted with potassium hypersilanide KHyp $(Hyp = Si(SiMe_3)_3)$ in liquid ammonia at -40 °C in a stoichiometric ratio 1:2, the homoleptic aurate KAuHyp₂ 2 is the only product detected by NMR spectroscopy, and it may be isolated as colorless crystalline toluene solvate in excellent yields. The molecular structure of 2 greatly resembles the structure of its known copper analogue KCuHyp₂ (3).^[5,6] Complex 2 consists of an aurate anion with an almost linear AuSi2 dumbell and is intimately coordinated by the potassium countercation. As expected from the difference in atomic radii, the observed Au-Si bond lengths (average 2.388 Å) are significantly longer than the Cu-Si bonds in 3 (2.297 Å), and even longer than the Au-Si

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bonds in the few neutral phosphane-stabilized silyl gold complexes (2.290–2.363 Å) characterized to date.^[2]

In contrast to the copper salts, a change in the initial ratio of the reactants from 1:2 to 1:1.5 or 1:1 does not lead to multinuclear anionic or neutral products.^[7] We expected, however, that neutral and putatively oligonuclear gold complexes should be accessible through desilylation of the aurate **2** with chlorotrimethylsilane, because treatment of the homologous cuprate **3** with that reagent furnishes the neutral complex CuHyp in high yields (Scheme 1).^[5,8,9]

 $\begin{array}{r} \text{KCuHyp}_2 + \text{Me}_3\text{SiCl} \xrightarrow[-20^\circ\text{C}]{} \xrightarrow{\text{toluene}} \text{CuHyp} + \text{Me}_3\text{SiHyp} + \text{KCl} \\ 3 \end{array}$

Scheme 1. Desilylation of KCuHyp₂ with Me₃SiCl.

Therefore we attempted to desilvlate complex 2 by treatment with an excess of Me₃SiCl in diethyl ether at -20°C to yield the parent neutral hypersilylgold compound AuHyp (1). Indeed, after a few hours the formation of Si(SiMe₃)₄ and of one new gold complex is detected by NMR spectroscopy, and after one day at -20 °C the aurate 2 had been totally consumed. The workup furnishes colorless crystals that contain the dinuclear aurate [(toluene)K]-[Au₂Hyp₃] (4), the product of an incomplete desilvlation of 2. The potassium cation is coordinated by a toluene molecule and located on top of the Au₂Si₃ scaffold of the anion (Figure 1).^[6] The structure of the [Au₂Hyp₃] anion resembles that of the homologous dicuprate anion in the salt [Li₇-(OtBu)₆][Cu₂Hyp₃], with relatively short terminal and long internal Au-Si bonds.^[10] All the NMR spectra obtained for [D₆]benzene solutions of **2** reveal a fast exchange of terminal and bridging Hyp ligands on the NMR timescale (¹H NMR, 400 MHz, 298 K).

To accomplish further desilylation, we carried out the reaction with Me₃SiCl in Et₂O at room temperature. At first, the dinuclear complex **4** is again detected, but on prolonged stirring for three days, the total consumption of **4**, a color change to dark green, and precipitation of KCl was observed. NMR spectroscopy experiments on the reaction mixture revealed that Si(SiMe₃)₄ is the main component in solution, although ¹H and ²⁹Si NMR spectra indicate that appreciable amounts of hexamethyldisilane are also present in the reaction mixture. As neither HypH nor Hyp₂ nor elemental gold are detected in significant amounts, and the solutions are EPR-silent down to 120 K, we preclude single-electron transfer processes as the main source for the hexamethyldi-

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Figure 1. Molecular structure of diaurate **4** with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–Si1 2.390(2), Au1–Si3 2.579(2), Au2–Si2 2.384(2), Au2–Si3 2.557(2), Au1…Au2 2.7524(4); Au1-Si3-Au2 64.82(4), Si1-Au1-Si3 158.29(6), Si2-Au2-Si3 157.99(7).

silane. Instead, we believe that it mostly stems from partial fragmentation of the hypersilyl substituents by Si–Si bond metathesis with neutral hypersilylgold (1) acting as a possible intermediate. This hypothesis is corroborated by the constitution of the gold complexes that we could finally isolate and structurally characterize (see below).^[6,11]

After evaporating the reaction mixture to dryness, a dark green oily residue was obtained; after dissolving it in a few milliliters of *n*-pentane and storing at -60 °C for four weeks, a significant amount of solid material precipitates, which consists of at least four different crystalline compounds. Apart from a large amount of colorless crystals, a significant amount of burgundy red crystals, fewer yellow specimens, and only two dark blue crystals could be isolated from a typical run. The colorless crystals were identified by NMR spectroscopy and X-ray diffraction to be Si(SiMe₃)₄, whereas the colored specimens proved to be some very unexpected anionic gold complexes that are obviously products from redox and/or Si-Si bond metathesis processes (Scheme 2). The burgundy red crystals consist of the subvalent gold cluster compound $[K(toluene)]_2[Au_4Hyp_4]$ (5). The tetrahedral Au₄ scaffold bears axial hypersilyl groups and two potassium countercations, which cap two of the four faces of the tetrahedron (Figure 2). However, in C₆D₆ solution, all of the hypersilyl groups in 5 are magnetic equivalent at room temperature (¹H NMR, 400 MHz, 298 K). The potassium cations are either mobile on the cluster surface or solventseparated ion pairs may have formed in solution. All Au-Au bonds have similar lengths (ca. 2.76 Å) and are a few picometers longer than in closely related subvalent cationic phosphane-stabilized gold clusters.[12,13]

The two other crystalline compounds and the volatile hexamethyldisilane appear to result from Si–Si bond metathesis processes. The yellow crystals contain the novel molecular tetraaurate(I) complex $K_2[Au_4Hyp_2Dis_2]$ 6 (Figure 3), comprising two different kinds of silyl ligands: two monoanionic hypersilyl (Hyp) and two dianionic bis-(trimethylsilyl)silanediyl (Dis) groups. The $[Au_4Hyp_2Dis_2]$ dianion has an almost planar Au_4Si_4 skeleton; within the rectangular arrangement of gold atoms, two short and two



Scheme 2. Reaction of dihypersilylaurate 2 with Me₃SiCl.



Figure 2. Molecular structure of the gold cluster **5** with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Au1–Au2 2.7549(3), Au1–Au3 2.7885(3), Au1–Au4 2.7458(3), Au2–Au3 2.7563(3), Au2–Au4 2.7657(3), Au3–Au4 2.7521(3).

long Au-Au contacts are found (2.726-2.736 and 3.663-3.708 Å, respectively). There are also two groups of Au-Si bonds: short (2.372-2.384 Å) to the four-coordinate central silicon atoms of the Dis substituents, and markedly longer (2.542–2.610 Å) to the five-coordinate silicon atoms of the hypersilyl groups, thus indicating higher or lower bond orders, respectively. This assumption is corroborated by NBO analysis of DFT densities derived from calculations using the experimental structural parameters.^[14] The potassium countercations are located above and below the Au₄Si₄ plane; intermolecular agostic K...Me interactions lead to one-dimensional coordination polymers.^[15] Although compound 6 is obtained in only very small amounts, it could be fully characterized by NMR spectroscopy. Whereas the ²⁹Si NMR signal for the central silicon atom of the hypersilyl groups ($\delta =$ -65.9 ppm) lies in the region found for the other hypersilvlgold complexes, the central silicon atom of the dianionic



Figure 3. Molecular structure of the aurate **6** with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Au1–Si1′ 2.378(2), Au1–Si2 2.559(2), Au2–Si1 2.376(2), Au2–Si2 2.579(2), Au1···Au2 2.7518(5), Au1···Au2′ 3.7017(6), K1···Au1 3.353(2), K1···Au2 3.350(2).

Dis group is shifted significantly upfield and has a resonance at $\delta = -134.4$ ppm.

The blue crystals indeed contain the desired neutral hypersilylgold **1**. It is, however, not present as a pure compound, but as adduct to the π system of a much-unexpected dianionic disilene. The planar disilene unit of the potassium salt **7** bears two *cis*-oriented trimethylsilyl substituents and two formally negatively charged hypersilyl-aurato groups (Figure 4).

The length of the formal Si=Si double bond (2.341 Å) is in the typical single-bond range, however, and only slightly shorter than the single bond Si1-Si11 (2.350 Å) to the SiMe₃ group. This elongation may be partially attributed to electrostatic repulsion of the two anionic silylene fragments, but also to a significant weakening of the π bond by coordination to two Lewis acidic neutral hypersilylgold moieties. The NAO-Wiberg bond index (WBI) from DFT calculations clearly indicate appreciable covalent Au-Si bonding (WBI: 0.27) between the disilene fragment and the coordinating AuHyp moieties and also significant weakening of the Si-Si double bond (WBI: 1.20).^[14] The calculated bond indices for Au-Si bonds within the disilene scaffold are about 0.5, similar bond indices are calculated for the Au-Si bonds of similar length (ca. 2.38 Å) within the simple aurate 2. In accordance with calculated bond ndices of about 0.25, the coordinative Au-Si interactions in complex 7 to the neutral AuHyp moieties are about 0.15 Å longer. The potassium countercations are located above and below the gold atoms of the disilene moieties such that similar distances to three gold atoms are accomplished. Apart from intermolecular agostic interactions to methyl groups of the hypersilyl ligands, no additional solvation of the cations is observed. Unfortunately, we have not yet been able to obtain spectroscopic data for 7.

A further very unexpected silylgold complex is obtained when aurate **2** is reacted with Me₃SiCl in acetonitrile instead of toluene. After four days, a green suspension is obtained and again some expected products, such as $Si(SiMe_3)_4$ and hexamethyldisilane, are detected in larger amounts by



Figure 4. Molecular structure of disilene **7** with hydrogen atoms omitted for clarity. The almost planar Au_2Si_6 scaffold is highlighted by open (=) bonds. Selected bond lengths [Å] and angles [°]: Si1–Si1′ 2.337(4), Au1–Si1 2.387(2), Au1–Si3 2.396(2), Au2–Si2 2.401(2), Au2–Si1 2.524(2), Au2–Si1′ 2.527(2), Si11-Si1-Si1′ 129.12(7), Si11-Si1-Au1 116.29(5), Au1-Si1-Si1′ 114.24(9).

¹H NMR spectroscopy. However, after storing the concentrated filtrate for 1 month at -60 °C, small dark green crystals could be isolated.

X-ray diffraction reveals the formation of the novel pentaaurate $KAu_5[Si(SiMe_3)_2]_6$ (8) comprising an almost planar Au_5Si_6 scaffold (Figure 5). Pentaaurate 8 contains no hypersilyl group at all. Again, Si–Si bond metathesis must have taken place. According to NBO analyses and by comparing the structural parameters with other silyl gold complexes, the best interpretation of its constitution^[14] is that the complex is a 2:1 adduct of two neutral dinuclear hexasilanediyldigold moieties $Au_2Si_2(SiMe_3)_4$ to the mono-



Figure 5. Molecular structure of aurate **8** with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–Si1 2.438(2), Au2–Si2 2.399(2), Au2–Si1 2.544(2), Au3–Si1 2.516(2), Au3–Si3 2.388(2), K1···Au1 3.288(3), K1···Au2 4.124(2), K1···Au3 4.044(2), Si11-Si1-Si12 111.19(12), Au1-Si1-Si11 114.64(10), Au1-Si1-Si12 134.16(10).

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nuclear aurate $K[Au{Si(SiMe_3)_2}_2]$. The anionic part is formally composed of a gold(I) cation and two bis(trimethylsilyl)silylene anion radicals.[16] The potassium countercation is located above the center of the Au₅Si₆ scaffold (K1…Au1 3.288(3) A), and gives rise to the formation of one-dimensional coordination polymer along the crystallographic c axis by agostic K···CH₃ interactions to neighboring aurate anions. The Au-Si bonds within the hexasilanediylgold fragment (2.39-2.40 Å) are of similar lengths to those found for aurate 2, whereas the Au-Si bonds within the central aurate fragment is about 0.05 Å longer. The Au-Si distances between the fragments resemble those found for the coordinative interactions between the AuHyp moieties and the disilene unit of 7.

In our attempt to synthesize neutral hypersilylgold 1 by desilylation of the aurate 2 with the

nucleophile Me₃SiCl in the absence of stabilizing soft neutral bases, such as phosphanes, we found that redox reactions and a Si-Si bond metathesis took place at room temperature (Scheme 2). Although 1 is a probable intermediate, there is are no experimental data available that give hints to the mechanism that is involved. The NMR data gained from the reaction mixtures indicate the presence of further gold containing compounds, but none of them could be isolated to date. As we never observed similar reactions for related silvl complexes of copper or silver, neither in the formation of subvalent cluster compounds nor bond metathesis, the unusual reactivity of the aurates must correlate to the peculiar electronic structure of gold, namely the presence of relativistically stabilized s and p orbitals and destabilized d orbitals.^[17] Filled and empty frontier orbitals of similar energies are available for oxidative addition reactions, and gold(III) species seemed to be very probable intermediates for metathesis reactions.

Indeed, DFT calculations on model systems indicated that a neutral monomeric silvl gold complex R₃SiAu may insert into Si-Si bonds of oligosilanes via a low-lying transition state (Scheme 3).^[18] However, the resulting complex ts1 $[R_3SiAu(R^\prime_3Si\mathchar`siR^{\prime\prime}_3)]\ (\mbox{min2})$ does not exhibit the expected T shape for an Au^{III} complex, but instead it adopts a structure very similar to the experimentally and theoretically investigated Y-shaped dihydrogen complex [HAu(H₂)].^[19] The Si-Si bond of the attacked oligosilane is however markedly stretched and the corresponding bond order is diminished. Further calculations showed that a reaction path from min2 to the isomer min3 with a low-lying transition state (ts2) exists. The transition state ts2 has a structure expected for the initially proposed gold(III) species. Dissociation of min3 via transition state ts3 finally leads to the products (min4) of a formal Si-Si bond metathesis. Such reactions seem to be unique among the coinage metals, as inspection of the hypersurfaces of the corresponding copper and silver systems did not reveal analogous local minima or similar reaction paths. Owingb to very low barriers for the isomerization to the stable states min1 and min4, the Y-shaped intermediates min2 and min3 should has very short lifetimes and are not expected to be detectable by conventional spectroscopic methods. We



Scheme 3. Calculated reaction path for Si–Si bond metathesis in silyl complexes of gold. The numbers given are relative electronic energies (including zero-point energy correction) [kJ mol⁻¹] calculated at the B2PLYP level for local minimum and transition-state structures with $R = R' = R'' = Me.^{[20]}$ Further data and computational details are given in the Supporting Information.

hope, however, that by further theoretical and experimental work, and especially by varying the employed electrophile for the desilylation of KAuHyp₂ (2) and analyzing the resulting products, we hope to be able to gain deeper insight into the mechanisms that are operating.

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