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Gold Complexes

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Direct Evidence for Intermolecular Oxidative Addition of σ(Si–Si) Bonds to Gold**

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Abstract: *Oxidative addition plays a major role in transition-metal catalysis, but this elementary step remains very elusive in gold chemistry. It is now revealed that in the presence of $GaCl_3$, phosphine gold chlorides promote the oxidative addition of disilanes at low temperature. The ensuing bis(silyl) gold(III) complexes were characterized by quantitative ^{31}P and ^{29}Si NMR spectroscopy. Their structures (distorted Y shape) and the reaction profile of σ(Si–Si) bond activation were analyzed by DFT calculations. These results provide evidence for the intermolecular oxidative addition of σ(Si–Si) bonds to gold and open promising perspectives for the development of new gold-catalyzed redox transformations.*

Recently, the scope of gold-catalyzed transformations was spectacularly expanded,[1–3] and our knowledge of gold reactivity has significantly increased.[4] Fundamental studies have shown that gold complexes display versatile reactivity, and examples of all common mechanistic elementary steps have progressively been documented.

The ability of gold to undergo transmetalation has been illustrated with various main group elements[5] and transition metals.[5h,6] The feasibility of *syn* insertion was recently corroborated for the reaction of alkynes and allenes with silyl gold(I) complexes.[7] Reductive elimination from gold(III) complexes to form C–C[8,9] and C–X[10–12] (X = N, I, F) bonds has also been confirmed. Furthermore, reductive elimination from tetrathiolate gold(III) complexes to form S–S bonds was disclosed by Bachmann and co-workers; this reaction was found to be reversible.[13]

For oxidative addition reactions, however, comparatively little and generally only indirect information has been gained.[14,15] Aside from the work of Bachmann et al. on σ(S–S) bond activation, direct spectroscopic and crystallographic evidence for the intramolecular oxidative addition of σ(Si–Si) bonds was reported by our group.[16] In this project, we took advantage of chelating assistance with a phosphine to pre-orientate the σ(Si–Si) bond and to stabilize the ensuing oxidative addition product. The results obtained substantiated our interest in and the potential of the chelating strategy for the study of unusual bonding situations and reactivity.[17] However, at the same time, the role and the importance of the anchoring sites that are used to promote disilane activation remain unclear. We therefore asked ourselves to which extent intramolecular reactions with such an assistance were representative of the intrinsic reactivity of gold complexes, and whether similar transformations could also proceed intermolecularly. Therefore, we explored the reactions of simple phosphine gold complexes with disilanes; herein, we report unambiguous evidence for the intermolecular oxidative addition of σ(Si–Si) bonds. The ensuing bis(silyl) gold(III) complexes were characterized by quantitative ^{31}P and ^{29}Si NMR spectroscopy at low temperature, and the reaction profile of σ(Si–Si) bond activation was thoroughly analyzed by DFT calculations.

In a first control experiment, one equivalent of the disilane $(PhMe_2Si)_2$ was added to the phosphine gold complex $[(Ph_3P)AuCl]$ in toluene. No reaction occurred at room temperature over several days, and progressive heating up to 100 °C only led to decomposition of the gold precursor. Neutral [(L)AuCl] complexes are commonly activated with chloride abstractors, and we thus sought to generate a more electrophilic gold species using $GaCl_3$.[18] Upon addition of $(PhMe_2Si)_2$ to a 1:1 mixture of $[(Ph_3P)AuCl]$ and $GaCl_3$ in CD_2Cl_2 at −90 °C (Scheme 1), the solution immediately turned light yellow. Analysis of the reaction mixture by ^{31}P NMR spectroscopy at −80 °C indicated the formation of a new species **1a**. The ^{31}P resonance signal was significantly shifted downfield (δ 60.9 ppm) and appeared in the same region as those of the bis(silyl) phosphine gold(III) complexes that we had recently generated from chelating phosphine disilanes.[16] Compound **1a** was the major phosphorus-con-

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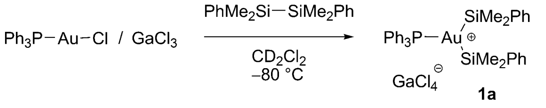


Scheme 1. Formation of the bis(silyl) gold(III) complex **1a** upon oxidative addition of a disilane.

taining species (ca. 66 %). Another resonance in the ^{31}P NMR spectrum is observed at δ 43.7 ppm, which suggests the formation of the cationic complex $[(Ph_3P)_2Au]^+$ as a side product.

According to variable-temperature NMR measurements, compound **1a** is thermally unstable. Decomposition occurred rapidly above −60 °C,[19] and further spectroscopic characterization was thus performed at −80 °C. The ^{29}Si NMR spectrum of the reaction mixture displays three resonance signals that correspond to the starting disilane (δ −21.0 ppm), the chlorosilane PhMe$_2$SiCl (δ 21.0 ppm) and complex **1a** (δ 40.7 ppm). The signal for **1a** appears as a doublet ($J_{Si,P}$ = 39.8 Hz) and correlates with the ^{31}P NMR signal at δ 60.9 ppm, as established by 2D HMBC(^{31}P–^{29}Si) and ^{29}Si{selective ^{31}P} NMR experiments.[20] The magnitude of the $J_{Si,P}$ coupling constant that was observed for **1a** is not consistent with a phosphine gold(I) silyl structure ($J_{Si,P}$ (*trans*) = 165–210 Hz),[7,21] and may rather be attributed to the formation of a phosphine bis(silyl) gold(III) complex with a symmetric Y shape structure. However, at this stage, it was not possible to unambiguously establish the presence of two silyl groups per gold center. We thus envisioned to count the silicon atoms per PPh$_3$ moiety, and hence recorded a ^{31}P NMR spectrum with a long acquisition time.[20] Apart from the main signal, three sets of satellites, which correspond to the ^{29}Si and ^{13}C isotopomers of **1a**, could be distinguished (Figure 1). After deconvolution of the overlapping signals, the area of each satellite was precisely determined, and taking into account the natural abundance of the ^{13}C (1.11 %) and ^{29}Si (4.70 %) isotopes, we found two silyl groups per PPh$_3$ moiety.

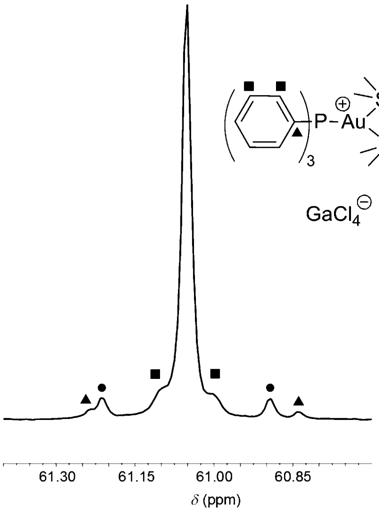
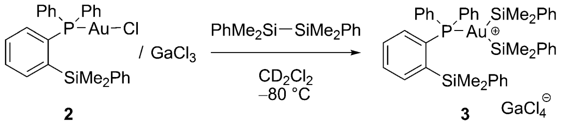


Figure 1. Long-acquisition ^{31}P{^{1}H} spectrum of complex **1a** that shows the ^{13}C (▲ and ■) and ^{29}Si (●) satellites.

These results are consistent with the phosphine bis(silyl) gold formulation of **1a**; for this compound, the presence of a single signal in the ^{29}Si NMR spectrum and the value of $J_{Si,P}$ suggest a Y shape structure. Compounds such as **1a** are unprecedented, but Marko and co-workers have recently disclosed an isoelectronic N-heterocyclic carbene (NHC) platinum bis(silyl) complex.[22]

To obtain further evidence on the formation of phosphine gold(III) bis(silyl) species upon oxidative addition of σ(Si–Si) bonds, we prepared complex **2** in which one of the phenyl substituents at the phosphorus atom bears a SiPhMe$_2$ group in the *ortho* position (Scheme 2). This spectator silyl group may be used as an internal standard for ^{29}Si NMR spectroscopy to enable the direct counting of the silyl groups at the gold center. For complex **2**, the corresponding ^{29}Si NMR signal appears as a doublet ($^3J_{Si,P}$ = 8.0 Hz) at δ −5.5 ppm. Addition of the disilane (PhMe$_2$Si)$_2$ to a 1:1 mixture of complex **2** and GaCl$_3$ at −80 °C resulted in the instantaneous formation of complex **3** (ca. 60 % yield according to ^{31}P NMR spectroscopy), along with some side products.



Scheme 2. Synthesis of the bis(silyl) gold(III) complex **3**, which features a silicon-labeled phosphine.

Complex **3** is thermally unstable and decomposes within hours at −80 °C. As expected, its ^{29}Si NMR spectrum displays two resonance signals (Figure 2). One signal (δ −7.6 ppm, d, $^3J_{Si,P}$ = 4.6 Hz, 1 Si) appears in the region where the resonances of ArSiPhMe$_2$ derivatives are usually found and is analogous to that of the starting complex **2**. The second signal (δ 40.2 ppm, d, $^2J_{SiP}$ = 38.3 Hz, 2 Si) appears in the region of gold silyl species and is similar to those of complex **1a**. The relative integration of these two signals unequivocally confirmed the formulation of **3** as a phosphine gold(III) bis(silyl) complex.

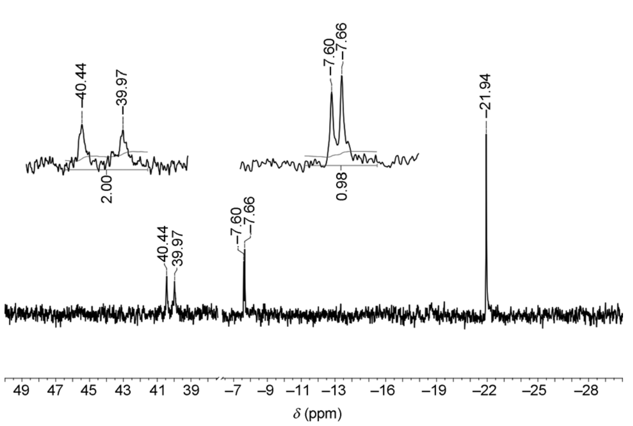


Figure 2. Quantitative ^{29}Si{^{1}H} NMR spectrum after addition of the disilane (PhMe$_2$Si)$_2$ to a 1:1 mixture of complex **2** and GaCl$_3$.

The oxidative addition process was then explored with other disilanes. The reaction proceeded similarly with the disilane $(Ph_2MeSi)_2$, and the ensuing complex **1b** (obtained in ca. 40 % yield according to ^{31}P NMR spectroscopy) displayed a very similar ^{29}Si NMR pattern (δ 34.5 ppm, d, $^2J_{Si,P} = 39.8$ Hz). Interestingly, the non-symmetric disilane $Ph_2MeSi{-}SiMe_2Ph$ was also activated by gold. The resulting complex **1c** is highly unstable even at low temperatures (ca. 12 % yield according to ^{31}P NMR spectroscopy), but its structure could be established by ^{29}Si NMR spectroscopy at −80 °C. As expected from the dissymmetric nature of the disilane, complex **1c** displayed two distinctive ^{29}Si NMR resonance signals in the region typical for gold–silyl species that correspond to $SiMe_2Ph$ (δ 42.8 ppm, d, $^2J_{Si,P} = 27.5$ Hz) and $SiMePh_2$ (δ 33.1 ppm, d, $^2J_{Si,P} = 49.6$ Hz).

To evaluate the role of PPh_3 in the oxidative addition process, other phosphines were tested. The substitution pattern at phosphorus was found to strongly influence the stability and reactivity of the $[(R_3P)AuCl]/GaCl_3$ ion pairs. With phosphites, such as $P(OPh)_3$ and $P(OMe)_3$, addition of $(PhMe_2Si)_2$ induced fast degradation and led to a mixture of unidentified products. Under the same conditions, no reaction occurred with $P(t\mathrm{Bu})_3$, whereas the use of the sterically less demanding phosphine PCy_3 readily afforded the corresponding bis(silyl) gold(III) complex **4**.[20] Interestingly, the PCy_3 ligand was found to impart a somewhat higher stability to the bis(silyl) gold(III) species. Indeed, complex **4** is stable up to about −40 °C, but all our attempts to crystallize this species at low temperatures have unfortunately remained unsuccessful thus far.

DFT calculations (B3PW91) were carried out to gain more insight into the mechanism and reaction profile of the oxidative addition of σ(Si−Si) bonds. The reaction of the neutral complex $[(Ph_3P)AuCl]$ (**I**) was examined first. Activation of the disilane was found to be endothermic ($\Delta H = 16.0$ kcal mol^{-1}) and to have a rather high activation barrier ($\Delta H^{\neq} = 27.8$ kcal mol^{-1}; Supporting Information, Figure S29).[20] This is consistent with the fact that no reaction had occurred in the absence of the chloride abstractor. The presence of $GaCl_3$ was thus taken into account computationally (Figure 3).

From complex **I**, the formation of a close adduct **II** is thermodynamically favored by 17.6 kcal mol^{-1} in ΔH (6.4 kcal mol^{-1} in ΔG).[23] The chlorine atom that is directly attached to the gold center interacts tightly with the gallium center (Cl–Ga distance: 2.39 Å), and the Au−Cl bond is noticeably elongated (from 2.30 Å in **I** to 2.38 Å in **II**). Dissociation of $GaCl_4^-$ from the ion pair **II** is predicted to be endothermic by 19.6 kcal mol^{-1}, which makes the formation of the bare cationic gold complex $[(Ph_3P)Au]^+$ highly unlikely.[24] Upon reaction of **II** with the disilane $(PhMe_2Si)_2$, the system reaches the transition state of the oxidative addition, $\mathbf{TS_{II\text{-}III}}$. The corresponding activation barrier is relatively low (11.7 kcal mol^{-1} from **II**), which is in line with a kinetically facile reaction. The σ(Si−Si) bond is located in the plane that is defined by the phosphorus, gold, and chlorine atoms, and it is substantially elongated (from 2.38 Å in the free disilane to 2.50 Å in $\mathbf{TS_{II\text{-}III}}$). Following the intrinsic reaction coordinate, $\mathbf{TS_{II\text{-}III}}$ leads to the oxidative addition product **III** in which the σ(Si−Si) bond is fully broken (3.3 Å).[20] Taking into account the residual contact with the $GaCl_4^-$ counteranion (Cl⋯Au: 3.09 Å), the gold center is tetracoordinated and adopts a distorted square planar geometry. Dissociation of $GaCl_4^-$ from **III** to give the ion pair complex **IV** is exothermic by 3.1 kcal mol^{-1}, which makes the whole oxidative addition process from $[(Ph_3P)AuCl]$ and $GaCl_3$ slightly thermodynamically favorable.[25] The phosphine gold bis(silyl) complex **IV** adopts a distorted Y shape geometry (P–Au–Si bond angles of 129.6° and 145.9° on average). The situation differs somewhat from that encountered for the isoelectronic NHC Pt bis(silyl) complex.[22,26] Careful examination of the potential energy surface (PES) of **IV** revealed the presence of several rotamers of similar structure and energy (Figure S28).[20] In all of them, the two silyl groups are found in different environments. Conversely, a single ^{29}Si NMR signal was observed experimentally. The most likely interpretation for the apparent magnetic equivalence of the two silyl groups is a fast isomerization of complex **IV** on the NMR time scale. Indeed, a low-energy pathway was identified computationally ($\Delta H^{\neq} = 2.0$ kcal mol^{-1}; Figure S30).[20] Finally, the key NMR data of complex **IV** was evaluated (gauge-including atomic orbital (GIAO) calculations using both the relativistic effective core potential (RECPs) and all-electron basis sets). The computed values for the chemical shifts of ^{29}Si (56.2 ppm) and ^{31}P (66.6 ppm), as well as for the $^2J_{Si,P}$ coupling constant (34.5 Hz), were in good agreement with the experimental results.

In conclusion, phosphine gold chlorides have been shown to readily react with disilanes at low temperature in the presence of $GaCl_3$. This joint experimental and computational

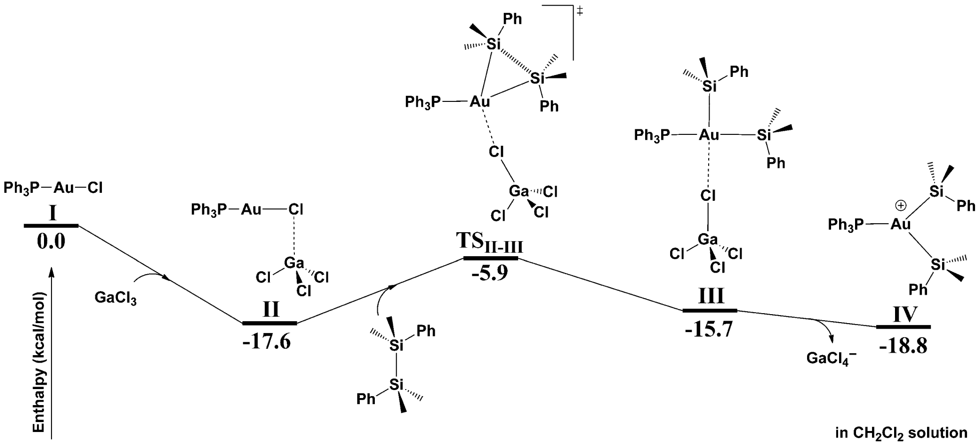


Figure 3. Computed reaction profile for the oxidative addition of the disilane $(PhMe_2Si)_2$ upon reaction with $(Ph_3P)AuCl/GaCl_3$.

study provides evidence for a very elusive elementary step at gold, namely oxidative addition. The feasibility of such reactions at the intermolecular level was demonstrated, which gave access to unusual cationic Y-shaped bis(silyl) gold(III) complexes. These thermally unstable complexes are closely related to the intermediate species that were proposed by the groups of Klinkhammer and Stratakis to account for disilane activation in gold-mediated processes.[27] Chelating assistance is a common strategy in organometallic chemistry, but it is always questionable as to which extent the anchoring sites enforce the observed reactivity. The intermolecular reactions described herein substantiate that oxidative addition can readily proceed at gold centers. These results provide important insights into the intrinsic reactivity of gold complexes and open promising perspectives for the development of new gold-catalyzed redox transformations. Future work in our group will seek to study the ability of gold to activate other σ bonds and to gain an improved knowledge of the factors that govern the reactivity of gold complexes towards oxidative addition.

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[18] Upon addition of $GaCl_3$ (1 equiv), the ^{31}P NMR resonance signal of $[(Ph_3P)AuCl]$ shifted from $\delta = 33$ to 31 ppm. The resulting

adduct is stable for hours at −80°C, but rapidly decomposes at higher temperatures.

[19] According to ^{29}Si NMR spectroscopy, the main decomposition products are the chlorosilane $PhMe_2SiCl$ and the disiloxane $PhMe_2SiOSiMe_2Ph$.

[20] See the Supporting Information for details.

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[23] As the reaction is accompanied by a decrease in molecularity (three molecules giving a single ion pair), the computed entropy is not correct, and therefore, the ΔG value will not be discussed further in this manuscript.

[24] For comparison, the reaction profile for the bare complex, denoted as **VI**, is given in the Supporting Information, Figure S32.

[25] Calculations also suggested reductive elimination to form a Si−Cl bond as a possible decomposition pathway for the gold bis(silyl) complexes; an activation barrier of 26.1 kcal mol^{-1} was predicted for the formation of the chlorosilane and the silyl gold(I) complex (Figure S29).[20]

[26] N. Takagi, S. Sakaki, *J. Am. Chem. Soc.* **2012**, *134*, 11749–11759.

[27] a) M. Wilfling, K. Klinkhammer, *Angew. Chem.* **2010**, *122*, 3287–3291; *Angew. Chem. Int. Ed.* **2010**, *49*, 3219–3223; b) C. Gryparis, M. Stratakis, *Chem. Commun.* **2012**, *48*, 10751–10753.