### Mechanism of the Dehydrogenative Silylation of Alcohols Catalyzed by Cationic Gold Complexes: An Experimental and Theoretical Study

### Stéphanie Labouille, Aurélie Escalle-Lewis, Yves Jean,\* Nicolas Mézailles,\* and Pascal Le Floch<sup>†[a]</sup>

**Abstract:** The catalytic activity both of cationic [(XDPP)Au][X]  $(XDPP=bis-2,5-diphenylphosphole xantphos X = BF<sub>4</sub>) and of the isolated gold hydride complex <math>[(XDPP)_2Au_2H][OTf]$  in the dehydrogenative silylation process is presented. A parallel theoretical study using density functional theory revealed a mechanism involving the

counter anion as a co-catalyst, which was experimentally confirmed by testing various counterions (X = OTf,

**Keywords:** dehydrogenative silylation • density functional calculations • gold • gold catalysis • phosphane ligands NTf<sub>2</sub>, PF<sub>6</sub>). Finally, a "Au<sub>2</sub>H<sup>+</sup>" species was determined as the intermediate during the catalytic cycle, which correlates well with the experimental findings on the first example of catalytic activity of an isolated "Au–H" complex.

#### Introduction

Catalytic processes involving gold-gold(0) on supports for heterogeneous processes, and gold(I) or gold(III) complexes for homogeneous processes-have been studied in great detail over the past decades.<sup>[1,2]</sup> The seminal discoveries of the very high efficiency of the hydrogenation of olefins by Au<sup>0</sup> in the early 1970s,<sup>[3]</sup> and of the addition of a C nucleophile to a carbonyl moiety catalyzed by a Au<sup>I</sup> complex in 1986,<sup>[4]</sup> truly launched these two parallel research domains. Since then, focusing only on homogeneous processes, very efficient and selective processes have been devised, including hydrogenation,<sup>[5]</sup> hydrosilylation,<sup>[6]</sup> or nucleophilic additions to  $\pi$ -systems.<sup>[1,4,7]</sup> Recently, the dehydrogenative silylation of alcohols using Au<sup>I</sup> chloride complexes was reported by Ito et al.<sup>[8]</sup> In the above-mentioned processes involving "H-Y" (Y=H, BR<sub>2</sub>, SiR<sub>3</sub>) reagents, Au-H intermediates have been postulated<sup>[5c-e,6a,8]</sup> in direct analogy with the same processes using other transition metals for which such M-H bonds have been observed and fully characterized. However, no such species had been isolated for gold<sup>[9]</sup> until 2008, when Sadighi et al. reported the first stable Au-H complex, A (Scheme 1), featuring an NHC ligand.<sup>[10]</sup> This complex is

[a] S. Labouille, A. Escalle-Lewis, Prof. Y. Jean, Dr. N. Mézailles, Prof. P. Le Floch Laboratoire "Hétéroéléments et Coordination" UMR CNRS 7653 (DCPH), Département de Chimie Ecole Polytechnique 91128 Palaiseau Cedex (France) Fax: (+33)169-33-44-40 E-mail: nicolas.mezailles@polytechnique.edu yves.jean@polytechnique.edu
[†] Deceased, March 17, 2010.
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rather unreactive, and so far its use as a catalyst has not been reported.

Following previous work on the stabilization of unsaturated, low-valent transition-metal fragments using the widebite-angle, electron-accepting ligand XDPP (bis-2,5-diphenylphosphole xantphos 1),<sup>[11,18]</sup> in 2009 we isolated the first Au-H complex featuring a phosphine ligand in the form of the Au<sub>2</sub>H<sup>+</sup> species, 2-OTf (Scheme 1).<sup>[12]</sup> The stability of this species is undoubtedly linked to our peculiar ligand, as it is known in the literature that the reaction of [(R<sub>3</sub>P)AuCl] complexes with stoichiometric amounts of hydride sources leads to the formation of Au clusters without observation of Au-H bonds,<sup>[13,14]</sup> and that an excess of hydride sources can lead to the formation of phosphine-stabilized Au nanoparticles.<sup>[15]</sup> As far as catalysis is concerned, Ito showed that only Au<sup>I</sup> chloride complexes, **B** (Scheme 1), featuring wide-biteangle ligands of the xantphos (xantphos=4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) type, were efficient precatalysts for dehydrogenative silvlation. In 2009, the same group reported an interesting experimental, mechanistic study,<sup>[16]</sup> in which they presented convincing evidence for an

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intermediate binuclear " $Au_2H$ " species, the structure of which, however, could not be fully ascertained.

When we began this study, our goals were manifold. First, we wished to conduct a combined experimental/theoretical study using our XDPP-Au<sup>+</sup> $X^-$  complex 3-X (Scheme 1), in order to elucidate the mechanism of the dehydrogenative silylation of alcohols. Secondly, we hoped that our isolated "Au<sub>2</sub>H<sup>+</sup>" complex 2-X would be the first "Au-H"-containing complex to be catalytically efficient. The results, presented herein, exceeded our expectations. Indeed, complex 3-X proved to be a very efficient catalyst for the transformation, a result validated through DFT calculations. A mechanism was postulated and calculated, and the results are in full accord with experimental observations. A few DFT studies pertaining to catalytic processes involving cationic metal complexes explicitly incorporate the counterion,<sup>[17]</sup> and in two cases, the assistance of the counterion in proton transfer was observed.<sup>[17e,f]</sup> Our DFT calculations then prompted us to test various counterions, and the results supported our mechanism. Finally, a Au<sub>2</sub>H<sup>+</sup> intermediate was determined as a minimum in the cycle, which corroborated the fact that complex 2-X is the first isolated gold hydride species to act as an efficient catalyst.

#### **Results and Discussion**

**Experimental catalytic study**: Ito et al. recently reported the dehydrogenative silylation of alcohols catalyzed by a gold(I) complex **B**, [AuCl(xantphos)].<sup>[8,16]</sup> Interestingly, in their first report, they showed that only wide-bite-angle ligands promoted the reaction. As mentioned above, in a subsequent study, the same authors observed a complex featuring a  $\{(xantphos)_2Au_2H\}$  fragment, but the data did not allow them to fully elucidate the structure of this species. In the past, we have demonstrated the superior activity of the XDPP ligand **1** compared to xantphos, in the allylation of amines catalyzed by Pd or Pt complexes;<sup>[18]</sup> this prompted us to study the XDPP–Au<sup>I</sup> couple as a potential catalyst in the dehydrogenative silylation process [Eq. (1)].

Ph 
$$OH + HSiEt_3 \xrightarrow{3-BF_4 (1mol \%)}_{Cl Cl 50°C, 2h} Ph OSiEt_3 + H_2$$
 (1)  
1 equiv 1 equiv

In 2009, we showed that ligand **1** reacted with one equivalent of [AuCl(tht)] (tht=tetrahydrothiophene) to form a mixture of two complexes.<sup>[12]</sup> Using this mixture of gold chloride complexes was not a suitable way to test the catalytic reaction. On the other hand, a single cationic complex, **3**-BF<sub>4</sub>, was obtained from the mixture upon chloride abstraction by the silver salt AgBF<sub>4</sub> [Eq. (2)], which was then tested. Typically, the catalyst, the alcohol, the silane, and the solvent (dichloroethane) were mixed in a schlenk flask under an inert atmosphere, and the resulting mixture was heated at 50 °C. The reaction was followed by taking <sup>1</sup>H NMR spectra at regular intervals. Aliquots were taken; the solvent and the silane evaporated, and the signals of the remaining alcohol versus signals of the silyl ether were integrated. Using stoichiometric amounts of alcohol and silane, the conversion was 25% within 2 h with 1% of complex **3**-BF<sub>4</sub> as the catalyst, and was complete within 24 h. As a control, the analogous reaction was performed without a catalyst, and resulted in a small yet significant 4% yield within 2 h. This result shows that the reaction is favorable without a catalyst, but that is shows slow kinetics. The complex **3**-BF<sub>4</sub> therefore acts as a true catalyst for this transformation.



Most importantly, the course of the catalytic reaction was also followed by <sup>31</sup>P NMR spectroscopy, which showed the presence of a single signal, corresponding to complex **2**-BF<sub>4</sub>, by analogy to the  $[(1)_2Au_2H]^+[OTf]^-$  (**2**-OTf), which we reported previously. In terms of mechanistic considerations, the observation of such a species points to **2**-BF<sub>4</sub> being either a true intermediate in the catalytic cycle, or being a resting state. The mechanism for this transformation was therefore studied, with the constraints of rationalizing all the experimental facts.

**Theoretical study of the catalytic cycle**: To investigate the mechanism of this reaction, DFT calculations<sup>[19]</sup> were performed using the B3PW91 functional.<sup>[20]</sup> The solvent was considered implicitly by performing polarized continuum model (PCM) single-point calculations on gas-phase optimized geometries.<sup>[21,22]</sup> Complex **III**-BF<sub>4</sub> was used as a model for the experimental complex **3**-BF<sub>4</sub>. To save computing time, phenyl substituents on the phosphole ring and methyl groups on the xanthene backbone were replaced by H atoms. A view of the optimized geometry is given in Figure 1, and the main geometrical parameters are reported in Table 1.



Figure 1. DFT-optimized structure of III-BF<sub>4</sub>, model for 3-BF<sub>4</sub> (the counterion BF<sub>4</sub> has been omitted for clarity).

1.814(4)

P1-C6

Tay structure of 5-D1 <sub>4</sub> .						
Bonds	<b>3-</b> BF <sub>4</sub> [Å]	III-BF <sub>4</sub> [Å]	Angles	3-BF <sub>4</sub> [°]	III- $BF_4$ [°]	
Au-P1	2.299(1)	2.322	P2-Au-P1	147.45(4)	147.7	
Au-P2	2.298(1)	2.322	Au-P1-C1	109.62(1)	108.2	
P1C1	1.816(4)	1.834	Au-P2-C4	107.0(1)	108.3	
P2-C4	1.832(4)	1.834	P1-C1-C2	123.9(3)	123.2	
P1-C5	1.814(4)	1 803	$C1_{-}C2_{-}O$	1177(3)	118.0	

Table 1. Comparison of the DFT-optimized geometry III-BF<sub>4</sub> with the X-ray structure of  $\mathbf{3}$ -BF<sub>4</sub>.<sup>[a]</sup>

[a] Experimental structural data are from reference [12].

1.805

The agreement between the theoretical and experimental values for bond lengths and bond angles is excellent, which validates our choice of combination functional/base. In particular, differences of less than 0.02 Å are observed for the most pertinent bond lengths, and the calculated P1-Au-P2 bond angle is overestimated by only 0.2°.

Our proposed mechanism, involving the cationic gold complex III-BF<sub>4</sub> with the explicit counter anion BF<sub>4</sub>, is described in Scheme 2. The first step involves a hydride trans-



Scheme 2. Computed mechanism for dehydrogenative silulation catalyzed by  $3-BF_4$ .

fer from the silane to the gold center, assisted by the counter anion, to generate  $Me_3SiBF_4$  and an intermediate IV. In a second step, intermediate IV reacts with III-BF<sub>4</sub> to form the dinuclear gold hydride complex II-BF<sub>4</sub>. In a parallel reaction,  $Me_3SiBF_4$  reacts with the alcohol to yield the desired silyl ether together with the strong acid HBF<sub>4</sub>. In the third step, regeneration of the starting complex III-BF<sub>4</sub> is achieved by reaction of II-BF<sub>4</sub> with HF•BF<sub>3</sub>, with the concomitant liberation of H<sub>2</sub>.

The energy profile associated with the first step (hydride transfer from the silane to the cationic complex) is reported in Scheme 3. Note that at the beginning the cationic complex is interacting with its counterion.

The hydride-transfer reaction was found to require a significant activation energy ( $\Delta E_{PCM}^{+}=29.9 \text{ kcal mol}^{-1}$  from the reactants), and turned out to be the rate-determining



Scheme 3. Energy profile in solution (dichloroethane) for the transformation of III-BF<sub>4</sub> into IV (kcalmol<sup>-1</sup>). Gibbs free energies (kcalmol<sup>-1</sup>) in the gas phase are in parentheses.

step of the catalytic cycle. As can be seen from the transition-state structure  $\mathbf{TS}_{III-BF4-IV}$  given in Figure 2, the hydride transfer is assisted by the approach of a fluorine atom from



Figure 2. View of the transition state  $TS_{III-BF4.IV}$  Hydrogen atoms (except the hydride) have been omitted for clarity. Selected bond lengths [Å) and angles [°]: Au–P1 2.381, Au–P2 2.440, Au–H 1.732, Si–H 1.774, Si–F1 1.947, B–F1 1.562, B–F2 1.378; P1-Au-P2 113.2, Au-H-Si 166.7, H-Si-F1 73.7.

the counterion, that is, BF<sub>4</sub>, on the silyl group. Thus, the reaction proceeds through a concerted mechanism involving the complex, the silane, and the counterion. The involvement of the counterion in this process is one of the major findings in this study. As a consequence, the counterion had to be taken into account in our calculations in order to describe the overall mechanism. The formation of the complex **IV**, a hydride gold(I) complex with only one phosphole unit coordinated to the metal center, appears to be endothermic ( $\Delta E_{\text{PCM}} = 13.0 \text{ kcal mol}^{-1}$ ).

The second step of the reaction is the addition of the cationic complex III-BF<sub>4</sub> to the hydride complex IV to form

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Scheme 4. Energy profile in solution (dichloroethane) for the transformation of **IV** into **II**-BF<sub>4</sub> (kcalmol<sup>-1</sup>). Gibbs free energies (kcalmol<sup>-1</sup>) in the gas phase are in parentheses.

the dinuclear gold hydride complex **II**-BF<sub>4</sub> (Scheme 4). This step is found to be thermodynamically favored ( $\Delta\Delta E_{PCM} =$ -17.0 kcal mol<sup>-1</sup>), and despite an extensive search, no transition state was located for this addition reaction. We note here that given the exergonicity of this reaction, no equilibrium can possibly be considered between the dinuclear species **II**-BF<sub>4</sub> and the two monomeric complexes **IV** and **III**-BF<sub>4</sub>.

At this point the alcohol silylation (Me<sub>3</sub>Si-F···BF<sub>3</sub>+ MeOH $\rightarrow$ Me<sub>3</sub>SiOMe+H–F···BF<sub>3</sub>) had to be considered. This reaction was found to be moderately endothermic ( $\Delta E_{PCM}$ =+8.6 kcalmol<sup>-1</sup>), but no attempts were made to study its mechanism in detail. As a matter of fact, such alcohol silylation reactions are known to occur rather easily, without the need for the participation of the gold complex, but require a proton-trapping molecule (typically a base).<sup>[23]</sup> In our case, the proton trap is the binuclear gold hydride complex **II**-BF<sub>4</sub> (vide infra).

Let us now focus on the last step of the catalytic cycle, which starts with the approach of HF BF<sub>3</sub> toward **II**-BF<sub>4</sub>, and leads to the formation of dihydrogen and the regeneration of the catalytic species **III**-BF<sub>4</sub> (Scheme 5).<sup>[24]</sup>

Several approaches of the acid HF BF<sub>3</sub> to **II**-BF<sub>4</sub> were calculated, and it appeared to be feasible only on the hydride side of the dinuclear gold complex. In the resulting complex V-BF<sub>4</sub> a weak interaction between the acid proton and the Au-H-Au unit is found. The elimination of H<sub>2</sub> goes through the  $TS_{V-BF4-VI-BF4}$  transition state (Figure 3), and has an activation barrier of nearly zero at the PCM level. It is worth noting that, as was found for  $TS_{\mbox{\scriptsize III-BF4-IV}}$ , the process is concerted, with simultaneous formation of the hydrogen-hydrogen and fluorine-boron bonds. This again underlines the importance of taking into account the counterion in the overall mechanism. Finally, although the dinuclear complex VI-BF<sub>4</sub> was characterized as a minimum when solvent effects were considered, the difference in energy compared to the two separate mononuclear complexes III-BF<sub>4</sub> is small enough to allow these structures to be in dynamic equilibrium. There-



Scheme 5. Energy profile in solution (dichloroethane) for the transformation of II-BF<sub>4</sub> into III-BF<sub>4</sub> (kcalmol<sup>-1</sup>). Gibbs free energies (kcalmol<sup>-1</sup>) in the gas phase are in parentheses.



Figure 3. View of the transition state  $\mathbf{TS}_{V-BF4-VI-BF4}$ . Hydrogen atoms (except the proton and the hydride) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–P1 2.512, Au1–P2 2.376, Au–Au 2.864, Au2–P3 2.392, Au2–P4 2.366, Au1–H1 1.748, Au2–H1 2.172, H1–H2 1.033, H2–F1 1.185, F1–B 1.580; P1-Au1-P2 109.5, P3-Au2-P4 126.5.

by, this last step regenerates the catalytic complex III-BF<sub>4</sub> and closes the catalytic cycle.

The entire energy profile for this catalytic cycle involving the counter anion is given in Scheme 6. The rate-determining step is the first step, corresponding to the hydride transfer from the silane to the cationic complex III-BF<sub>4</sub>. This mechanism is consistent with the fact that only the dinuclear gold complex II-BF<sub>4</sub> was observed in <sup>31</sup>P NMR spectroscopy

#### E<sub>PCM</sub> (kcal mol<sup>-1</sup>)



Scheme 6. Energy profile in solution (dichloroethane) for the complete catalytic cycle (kcal mol<sup>-1</sup>) involving the counter anion  $BF_4^-$ . Gibbs free energies (kcal mol<sup>-1</sup>) in the gas phase are in parentheses.

during all the catalysis experiments, as this was found to be the structure of lowest energy ( $\Delta E_{PCM} = -4.0 \text{ kcal mol}^{-1}$ ) within the catalytic cycle. Note that the two structures on the right-hand side of the energy profile are lower in energy than **II**-BF<sub>4</sub>, a result which illustrates the fact that the overall reaction process is exergonic.

**Influence of the counter anion on the catalysis: experimental and theoretical study**: The key finding of the involvement of the counterion in the calculated process prompted us to investigate this involvement experimentally.<sup>[25]</sup> Indeed, one could envision that a different counterion would modify the energies of some intermediates, and therefore alter the kinetics of the reaction. Therefore, new gold complexes with different counterions were synthesized in the same way as complex **3**-BF<sub>4</sub> using the appropriate silver salts [Eq. (3)].



Moreover, a dinuclear hydride complex (II-BF<sub>4</sub>) was calculated to be a plausible intermediate, and was observed during the process. We recently reported the synthesis of such a complex, **2**-OTf, which prompted us to test its efficiency in the catalytic process. These complexes were then engaged in the same reaction [Eq. (1)]. For the sake of comparison, the reaction was stopped after two hours (at 50 °C). The results are presented in Table 2. We were very pleased to observe a tremendous influence of the counterion on the kinetics of the reaction, corroborating the DFT calculations. Indeed, the yield of the catalysis with the complex **3**-OTf

Table 2. Catalytic results with different complexes for the reaction given in Equation (1).

Entry	Complex	NMR yield [%]
1	no complex	4
2	3-OTf	100
3 <sup>[a]</sup>	3-OTf	13
4	$3-PF_6$	49
5	3-NTf <sub>2</sub>	34
6	$3-BF_4$	25
7	<b>2</b> -OTf	100

[a] Room temperature.

(Table 2, entry 2) was quantitative, whereas only 25 % yield was obtained with complex **3**-BF<sub>4</sub> (entry 6). Being very efficient, the same reaction was then performed at room temperature with complex **3**-OTf, but the yield was only 13 % (entry 3). Mild heating was therefore very beneficial. Intermediate results were obtained with complexes **3**-PF<sub>6</sub> and **3**-NTf<sub>2</sub>, with yields of 49 and 34 %, respectively. Finally, the dinuclear gold hydride complex **2**-OTf (featuring the most favorable counterion effect) appeared as efficient as complex **3**-OTf (entry 7). Note that all of these reactions were followed using <sup>31</sup>P NMR spectroscopy, and, whichever complex was used, only the dinuclear gold hydride complex **2**-X was observed (singlet at 23.6 ppm).

A novel question arose from these experimental results: can they be rationalized by the proposed mechanism? The energy profile of the first step, that is, the rate-determining step of the catalytic cycle involving the hydride transfer, was recalculated with the most efficient system: trifluoromethanesulfonate as the counter anion (TfO<sup>-</sup>). The computed energy profile for this reaction is shown in Scheme 7.

The activation energy associated with the hydride transfer is still rather high ( $\Delta E_{PCM} = 24.7 \text{ kcal mol}^{-1}$ ), but significantly lower (by 5.2 kcal mol<sup>-1</sup>) than that required with BF<sub>4</sub><sup>-</sup> as the counterion (29.9 kcal mol<sup>-1</sup>, see Scheme 3). This result is fully consistent with the experimental kinetic effect of the counterion, and thus provides a new argument in favor of the proposed mechanism. The structure of the transition state **TS**<sub>III-OTf-IV</sub> is given in Figure 4. It is, in fact, quite similar to the one found for  $BF_4^-$ : the hydride transfer is concerted with the approach of the OTf toward the silane. It should also be noted that the addition of IV to III-OTf leads to the formation of **II**-OTf, with a smaller gain in energy compared to the formation of II-BF<sub>4</sub> from III-BF<sub>4</sub> ( $\Delta\Delta E_{PCM}$  =  $-14.5 \text{ kcal mol}^{-1} \text{ versus } -17.0 \text{ kcal mol}^{-1}$ ). The last step of the mechanism, that is, the formation of dihydrogen (see Scheme 5), was not calculated with X = OTf, because it was not expected to affect the kinetics of the catalysis.

**Dinuclear gold hydride as catalyst**: The last point of our study deals with the high catalytic activity of the dinuclear gold hydride complex 2-OTf (Table 2, entry 7), and the way in which it could enter the catalytic cycle. Indeed, even though the formation of this complex during catalysis has been rationalized above, its own catalytic activity, without the simultaneous formation of a stoichiometric amount of

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Scheme 7. Energy profile in solution (dichloroethane) for the transformation of **III**-OTf into **II**-OTf (kcal mol<sup>-1</sup>). Gibbs free energies (kcal mol<sup>-1</sup>) in the gas phase are in parentheses.



Figure 4. View of the transition state **TS**<sub>III-OTF-IV</sub> with OTf as counter anion. Hydrogen atoms (except the hydride) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Au–P1 2.467, Au–P2 2.364, Au–H 1.727, Si–H 1.767, Si–O1 1.988, S–O1 1.528; P1-Au-P2 114.0, Au-H-Si 172.0, H-Si-O1 73.9.

acid, remained unclear. In the subsequent part, the potential counterion effect on the catalytic activity of the dinuclear complex was not studied. To be as close as possible to the experimental system, the complex **II**-OTf was used for all the following calculations. Starting from **II**-OTf and the silane, two routes were considered for the formation of the catalytic gold complex **III**-OTf (note that a simple equilibrium between **II**-OTf and the two monomeric species **III**-OTf

and **IV** has already been excluded, see Schemes 4 and 7 and associated discussion).

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1) **II**-OTf could react with the silane to give dihydrogen, gold(0), and Me<sub>3</sub>SiOTf; the latter could then react with alcohol to form the acid HOTf. In turn, the acid would react with a second equivalent of **II**-OTf to form **III**-OTf, similarly to the last step of the catalytic cycle (Scheme 8, pathway 1);



Scheme 8. Two computed pathways for the generation of the catalytic complex **III**-OTf from the dinuclear species **II**-OTf.

2) **II**-OTf could react with the counter anion to give gold(0) and the acid HOTf; the latter would then react with another equivalent of **II**-OTf to yield **III**-OTf (Scheme 8, pathway 2).

Pathway 1 was studied first. A transition state for the approach of the silane to **II**-OTf was located (**TS**<sub>II-OTf-Me3SiH-VII</sub>), which leads to the elimination of H<sub>2</sub> (Scheme 9). However, this transition state was found to lie 55.3 kcalmol<sup>-1</sup> ( $\Delta E_{PCM}$ ) above the reactants. Therefore, this pathway is too disfa-



Scheme 9. Pathway 1: approach of the silane to **II**-OTf.

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vored on energetic grounds to account for the catalytic activity of **II**-OTf.

Next, we investigated the possibility for the dinuclear gold hydride complex to react with its counter anion (pathway 2) under the experimental conditions of the catalysis (Scheme 10).



Scheme 10. Pathway 2: approach of the counter anion OTf<sup>-</sup> toward the Au-H-Au unit of **II**-OTf.

A transition state corresponding to the formation of HOTf through the approach of TfO<sup>-</sup> on the Au–H–Au unit of **II**-OTf, **TS**<sub>II-OTF-VII</sub> was located 25.5 kcal mol<sup>-1</sup> above complex **II**-OTf. The structure of **TS**<sub>II-OTF-VII</sub> is presented in Figure 5. The mechanism is concerted between the elongation of the two Au–H bonds, the formation of the H–O bond, and the elongation of the S–O bond. A significant elongation of one of the two Au–P bonds is also observed, in agreement with a rearrangement of the coordination sphere around the metal: the geometry changes from almost trigonal planar to linear. This reaction is a formal reduction of the complex into two Au<sup>0</sup> moieties. It is likely that this



Figure 5. View of the transition state  $TS_{II-OTF-VII}$ . Hydrogen atoms (except the hydride) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–P1 2.470, Au1–P2 2.565, Au1–H 1.727, Si–H 1.878, Au2–H 2.472, H–O1 1.241, S–O1 1.538; P1-Au1-P2 102.5.

process would not stop at this "Au<sup>0</sup> dimer" stage, but rather would form the more thermodynamically favored Au bulk.

It is worth noting that these two pathways imply the formation of  $Au^0$  species for the generation of catalytically active **III**-OTf from **II**-OTf.

Experimentally, in the early stages of the catalysis with the dimer 2-OTf, such formation is observed. An experiment to discriminate the two pathways was carried out based on the fact that pathway 1 involves the silane, whereas pathway 2 does not. The thermal stability of complex 2-OTf in the absence of silane was probed, and was shown to evolve quantitatively within two hours at 50 °C in 1,2-dichloroethane [Eq. (4)]. This thermal decomposition formed a mononuclear complex, 8,<sup>[12]</sup> as well as Au<sup>0</sup> particles (see Supporting Information). In parallel, the same complex was synthesized quantitatively by the stoichiometric addition of ligand 1 to 3-OTf (see Supporting Information). The formation of complex 8 is therefore proof that complex 3-OTf formed and reacted with the free ligand 1, itself liberated from the Au<sup>0</sup> species during the formation of nanoparticles. Thus, complex 3-OTf can be generated efficiently from complex 2-**OTf** in the absence of silane.



Finally, from both experimental and theoretical studies, it can be concluded that the catalytically active complex **III**-OTf is formed through pathway 2 (Scheme 8), by a self-decomposition process of **II**-OTf. Overall, the calculated reactivity of the dinuclear gold complex **II**-X (X=BF<sub>4</sub>, OTf), as well as the experimental observations with **2**-OTf, prove that the bridging hydrogen can react either with an acid (hydride behavior) or with a base (proton behavior), as depicted in Scheme 11.

#### Conclusion

In conclusion, we have presented a combined experimental and theoretical study of the dehydrogenative silylation of alcohols, catalyzed by XDPP–Au<sup>+</sup> complexes. The elucidation of the mechanism revealed a counterion effect, which was subsequently proved experimentally. The observation of  $[{(XDPP)Au}_2H]^+X^-$  (2-X) as the only complex observed in the course of the catalytic process was rationalized by DFT calculations. It is obtained by the addition of the [(XDPP)AuH] species, generated in situ, with the starting

#### x⊖ "HYDRIDE' "ACID TS<sub>VI-X-VI</sub> TS<sub>II-OTf-VII</sub> Π Ð Œ - HOTf ΗХ - H<sub>2</sub> VI-X 2-X or II-X VII x⊖ Au nanoparticles + XDPP Æ

3-X or III-X

Scheme 11. The two opposite reactivities of the bridging hydrogen in complex 2-X.

complex 3-X. In parallel, we have shown here for the first time the use of an isolated gold hydride complex as an efficient catalyst. It is proved that this Au<sub>2</sub>-H dimer 2-X reacts with the counterion X<sup>-</sup> itself to generate an equivalent of acid, which then allows 3-X to be formed. Finally, the calculated reactivity of the dinuclear gold complex II-X, as well as the experimental observations with 2-X, prove that the bridging hydrogen can react either with an acid (hydride behavior) or with a base (proton behavior), as depicted in Scheme 11. These two facile decomposition pathways provide a rationale for the extreme rarity of phosphine/gold hydride species. The very peculiar electronic and steric properties of the ligand XDPP is undoubtedly responsible for the stabilization of the hydride in the form of the Au<sub>2</sub>H<sup>+</sup> dimer.

#### **Experimental Section**

**Materials and instrumentation**: All reactions were routinely performed under an inert atmosphere of argon or nitrogen using Schlenk, glove-box techniques, and dry deoxygenated solvents. Dry hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P<sub>2</sub>O<sub>5</sub>. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C, and 121.5 MHz for <sup>31</sup>P NMR spectra. Solvent peaks were used as internal references relative to Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm); <sup>31</sup>P chemical shifts were relative to an 85% H<sub>3</sub>PO<sub>4</sub> external reference. XDPP (1),<sup>[18]</sup> 2-OTf,<sup>[12]</sup> and 3-OTf<sup>[12]</sup> were prepared as reported previously. [AuCl(tht)] was prepared according to the established procedure.<sup>[26]</sup> Dichloroethane was obtained from commercial suppliers. Silver salts were obtained from commercial suppliers, and were stored and weighed in a glove-box.

General synthesis of complex 3-X: [Au(XDPP)]X (X = BF<sub>4</sub>, PF<sub>6</sub>, NTf<sub>2</sub>): The ligand XDPP (169.4 mg, 0.25 mmol) was added to a solution of [AuCl(tht)]] (80 mg, 0.25 mmol) in dichloromethane (3 mL) at room temperature. The solution was stirred for 5 min. The appropriate silver salt AgX (0.25 mmol, 1 equiv) was then added to the solution at room temperature. The mixture was stirred for 15 min, and completion of the reaction was checked by <sup>31</sup>P NMR spectroscopy. The mixture was then filtered and dried. The corresponding solid was washed with hexanes. The solvent was removed by filtration, and the yellow solid 3-X was dried under vacuum. For characterization see ref. [12]. Isolated yields were above 95%.

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General procedure for gold(I)-catalyzed dehydrogenative silylation: The gold complex 3-OTf (5 mg, 0.01 equiv) was placed in a Schlenk flask under nitrogen, and dichloroethane (0.6 mL) was added with stirring. The alcohol (58.4  $\mu$ L, 0.48 mmol, 1 equiv) and then the silane (78  $\mu$ L, 0.48 mmol, 1 equiv) were added to the Schlenk at room temperature. The mixture was heated at 50 °C for two hours. The solvent and the silane were evaporated, and the signals of the remaining alcohol versus the signals of the silyl ether were integrated by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>.

**Computational details**: Calculations were performed with the GAUSSI-AN 03 series of programs.<sup>[27]</sup> Density functional theory (DFT)<sup>[19]</sup> was applied with the B3PW91 functional.<sup>[20]</sup> The Def2-QZVP<sup>[28]</sup> pseudo-potential was employed for the gold atom, and the 6-31++G(d,p) basis set was used for atoms in interaction with the metal center (P, all or part of the counterions, and two hydrogen atoms of the alcohol and silane reactants), and the standard 6-31G(d) basis set was used for all other atoms (Scheme 12).<sup>[29]</sup> Geometry optimizations were performed using a model



+ Me<sub>3</sub>SiH + MeOH

Scheme 12. Basis sets combination used for all the calculations.

for the XDPP ligand, in which the two methyl groups of the xantphos backbone and the phenyl groups of the phosphole rings were replaced by hydrogen atoms. As far as the reactants were concerned, methanol and trimethylsilane were used as models. The stationary points (minima, transition states) were characterized by full vibration frequency calculations, and intrinsic reaction coordinates (IRC) calculations<sup>[30]</sup> were performed to ensure which minima were connected by transition states. Finally, the solvation energies were calculated with dichloroethane on the gas-phase optimized structures using the polarizable continuum model (PCM),<sup>[21,22]</sup> as implemented in Gaussian 03 and using the Bondi radii.<sup>[31]</sup> No entropic effect was considered at this point.

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