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Gold nanoparticles-catalyzed activation of 1,2-disilanes: hydrolysis, silyl protection of alcohols and reduction of *tert*-benzylic alcohols[†]

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Gold nanoparticles supported on TiO_2 catalyze under mild conditions the activation of a series of 1,2-disilanes towards hydrolysis and alcoholysis, with concomitant evolution of H_2 gas. For the case of *tert*-benzyl alcohols, the main or only pathway is reduction to the corresponding alkanes.

Despite the significant body of gold-catalyzed reactions in which Au(I) is acting as a soft π Lewis acid,¹ little progress has been achieved regarding the participation of gold in reactions proceeding through oxidative insertion of the metal into a σ bond. Such reactions are long known to occur readily in the presence of Pd, Pt and other late transition metals. As Au(I) has the same electronic configuration to Pd(0), Au(1) substances should formally expected to be catalytically active in typical cross coupling reactions catalyzed by palladium. The few reports so far deal with the homo-coupling of aryl boronates,² Suzuki³ or Sonogashira⁴ cross coupling reactions. Interestingly, the majority of those cases involve catalysis by supported gold nanoparticles. The ability of Au(I) to participate in Sonogashira cross coupling reactions has been disputed, and ascribed to traces of Pd impurities present in commercially available gold catalysts.5 However, an indirect proof for the catalytic efficiency of palladium-free gold was shown immediately after.⁶ Recently, evidence was provided that Au(1) can spontaneously undergo oxidative insertion into σ Si–Si bonds forming bis(silyl)gold(III) complexes,⁷ typical behavior of other late transition metals.⁸ It was actually questioned^{7a} whether gold-catalyzed bis-silylation reactions are achievable.

Our continuous interest on catalysis by supported gold nanoparticles supported on titania (Au/TiO₂),⁹ and especially the fact that we have observed the facile dehydrogenative bissilylation of alkynes by tetramethyldisiloxane,¹⁰ a reaction most likely proceeding *via* oxidative insertion of gold into the Si–H bond, urged us to examine whether Au/TiO₂ can activate σ 1,2-disilanes towards addition from nucleophiles. We found that upon adding Au/TiO₂ (1 mol%) to a mixture of a symmetrical 1,2-disilane and 1.2 equiv. of H₂O, quantitative

oxidative hydrolysis occurs (Table 1) yielding the corresponding 1,3-disiloxane, accompanied by evolution of H_2 gas. The reaction is feasible in a variety of solvents, including DCM, hexane or toluene, yet, it proceeds significantly faster in ethyl acetate. The overall reaction stoichiometry is such that the oxygen atom of H₂O is formally inserted into the Si-Si bond of the 1,2-disilane, with formation of one equivalent of H₂. For the case of hexaphenyldisilane (Table 1, entry 5) the corresponding silanol, was exclusively formed. Au/Al₂O₃ and Au/ZnO11 also catalyze the hydrolyses, less efficiently, however (see ES1[†]). The reactions are heterogeneous in nature, as after heating a slurry of Au/TiO2 in ethyl acetate for two hours, the gold content in the supernatant solution was below ppb level (ICP analysis).^{9b} Notably, among homogeneous Au(I) catalysts, Ph₃PAuNTf₂ catalyses the hydrolytic oxidation of PhMe₂SiSi-Me₂Ph (see ESI[†]), however, at more than two orders of magnitude slower rate, while [(2-biphenyl)di-tert-butylphosphine]AuSbF₆ provides traces of products.

A closer analogy to the above presented Au-catalyzed hydrolytic oxidation of 1,2-disilanes, is the alcoholysis of hexamethyldisilane in the presence of PdCl(n^3 -C₃H₅)₂·(Ph₃P)₂ reported by Hayashi.¹² Thus, we examined the effectiveness of Au/TiO₂ to catalyze the silylative protection of alcohols with Me₃SiSiMe₃. The TMS-silylation of alcohols is traditionally carried out either by reaction with TMSCl in the presence of a stoichiometric base, or with hexamethyldisilazane under catalysis conditions.¹³ Trimethylsilylation of alcohols is also feasible with hexamethyldisilane promoted by TBAF.¹⁴ We found that a series of

Table 1 Oxidative hydrolysis of 1,2-disilanes catalyzed by Au/TiO₂

$R_1 = R_1$	Au/TiO ₂ (1%) H ₂ O	R ₁ R	1 Roth Ho
R_3 R_3	EtOAc	R ₃ R ₃	3

Entry	Substituents	Time/Temperature	Yield ^a (%)
1	$R_1 = R_2 = R_3 = Me$	1.5 h/25 °C	> 99 ^b
2	$R_1 = R_2 = R_3 = Et$	3 h/55 °C	96
3	$R_1 = R_2 = Me, R_3 = Ph$	30 min/25 °C	98
4	$R_1 = R_2 = Ph, R_3 = Me$	1 h/25 °C	98 ^c
5	$\mathbf{R}_1 = \mathbf{R}_2 = \mathbf{R}_3 = \mathbf{P}\mathbf{h}$	5 h/55 °C	92^{d}

^{*a*} Isolated yields. ^{*b*} Calculated by G. C. using an internal standard. ^{*c*} The overall yield represents the total amount of 1,3-disiloxane + silanol in a relative ratio 80/20. ^{*d*} Ph₃SiOH was exclusively formed (2 equiv. of H₂O).

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Table 2Protection of primary and secondary alcohols as silyl ethersby symmetrical 1,2-disilanes^a catalyzed by Au/TiO_2

R₃SiSiR₃

	$R-OH \xrightarrow{Au/TiO_2(1\%)} R-OSiR_3$	
Alcohol	Silylated product	Yield ^b /Time
1	OTMS 1a	97%/1.5 h
1	OSiMe ₂ Ph	92%/1 h
2	Me Me OTMS	96%/2 h
3	PhOTMS 3a	96%/1 h
4	Ph 4a	97%/3 h
5	MeOSiMePh ₂ 5a	93%/1.5 h
6	6a OSiEt ₃	87%/16 h
7	OTMS 7a	96%/3 h
8	Ph_OTMS Me ^{8a}	93%/3 h
8	Ph OSiEt ₃ Me 8b	85%/24 h
8	Ph_OSiMePh ₂ Me 8c	88%/4 h
9	OTMS Ph OTMS 9a°	98%/4 h
10	Br-OTMS 10a	97%/4 h
11	MeO-OTMS	98%/3 h

^{*a*} 1–2 mmol of disilane per 1 mmol of alcohol were used in the case of open air conditions. If dry solvent and inert atmosphere conditions are applied, 0.6 mmol of disilane per 1 mmol of alcohol can be used. ^{*b*} Isolated yield. ^{*c*} Molar ratio Me₃SiSiMe₃/diol = 3/1 (under open air conditions).

primary and secondary alcohols or phenols are readily and quantitatively protected as TMS-ethers (Table 2)¹⁵ with hexamethyldisilane under milder conditions to those in the analogous Pd-catalyzed transformation,¹² and more importantly by using significantly lower loading of catalyst. Ethyl acetate is the most suitable solvent, whereas under strictly dry conditions, 50-60% molar ratio of Me₃SiSiMe₃ is necessary to drive the reaction to completion, indicative that both trimethylsilvl groups of the disilane participate in the reaction. In case that non-dried EtOAc is utilized (open air conditions), roughly a 1-2 fold molar excess of Me₃SiSiMe₃ may be used to compensate its hydrolytic tendency by the moisture present in the reaction vessel. As the hydrolysis products of hexamethyldisilane are volatile, even though the silylating agent is in excess, the isolated TMS-protected alcohols are very pure. Silvlation of alcohols is also feasible with bulkier 1,2-disilanes, such as Et₃SiSiEt₃, PhMe₂SiSiMe₂Ph and Ph₂MeSiSiMePh₂ (Table 2).

Table 3 Reaction of hexamethyldisilane with tertiary alcohols catalyzed by Au/TiO_2

R₁ R₂ → OH R₃	$\frac{\text{Me}_3\text{SiSiMe}_3^a}{\text{Au/TiO}_2 (1 \%)}$ EtOAc, 55 °C	$\begin{array}{c} R_1 \\ R_2 \xrightarrow{R_1} H + R_2 \xrightarrow{R_1} OS \\ R_3 a \\ R_3 b \end{array}$	iMe ₃
Alcohol	Alkane (a)	TMS-alcohol (b)	Yield ^b /Time
Me PhOH Me 12	12a (75%)	12b (25%)	82%/1.5 h
p-Tolyl Me OH Me 13	13a (73%)	13b (27%)	81%/1.5 h
Me Ph → OH Ph 14	14a (60%)	14b (40%)	94%/2 h
Ph Ph / OH Ph 15	15a ^c	_	95%/24 h
Me OH 16	16a (73%)	16b (27%)	96%/1 h
Ph Me OH 17 Me	_	17b ^d	67%/3 h
	_	18b ^d	62%/3 h

^{*a*} Molar ratio hexamethyldisilane/alcohol = 5/1. ^{*b*} Isolated yield. ^{*c*} Molar ratio hexamethyldisilane/alcohol = 8/1. ^{*d*} The lower yield is due to the partial dehydration of the alcohols.

The participation of Au in the reaction was proven by the fact that neither disilanes undergo alcoholysis in the absence of Au/TiO₂, nor the support (titania) is catalytically active. In addition, homogeneous Au(1) catalysts are practically inactive.

Tertiary alcohols react much more slowly, requiring refluxing conditions to go to completion and excess of hexamethyldisilane (Table 3). Also, occasionally minor byproducts from dehydration of the alcohols were seen in the crude reaction mixture. Surprisingly, in the case of tertiary benzylic alcohols, the anticipated TMS-silylation pathway is a minor one, with the major product being the corresponding alkane. Notably, in the case of triphenylmethanol, the only product was triphenylmethane. To the best of our knowledge, this is the first example of alcohol "deoxygenation" to an alkane, without any external hydride added. For instance, benzylic alcohols can be reduced into alkanes by hydrosilanes in the presence of a Lewis acid.

From the mechanistic point of view, significant information was gained by the fact that during the progress of the alcoholysis or hydrolysis of PhMe₂SiSiMe₂Ph and Ph₂MeSiSiMePh₂, PhMe₂SiH and Ph₂MeSiH, respectively, were seen in varying amounts within the crude reaction mixture. At the end of the reaction however they disappear, as they either silylate the reacting alcohols or hydrolyse through already established dehydrogenative processes under Au catalysis conditions.¹⁶ We propose in Scheme 1, that alcoholysis and hydrolysis proceed *via* oxidative insertion of catalytically active Au species into the σ Si–Si bond to form intermediate I, followed by capture of I by an alcohol or H₂O.¹⁷ This reaction should



form a silyl-protected alcohol or silanol, respectively, and silyl Au hydrides (II). R₃SiAuH¹⁸ may either reversibly form a hydrosilane (seen under our reaction conditions), or protect an additional molecule of alcohol in a dehydrogenative manner. The above presented rationalization has some similarities to the proposed mechanism in the Pd-catalyzed alcoholysis of hexamethyldisilane, where palladium hydrides were invoked.^{12,19} The role of the support, apart from stabilizing the catalytic sites, is not profound. We postulate that the differences in the reaction rates among TiO₂, Al₂O₃ and ZnO might reflect their affinity^{16g} to the substrates. It is likely that disilane activation by Au nanoparticles is driven by ionic gold clusters²⁰ bearing a cationic Au(I) catalytic site. Recently it was shown that although mononuclear gold(I) complexes are unreactive in Sonogashira cross coupling reactions, trinuclear cationic gold clusters are highly active.²¹ The nature of the active species in processes catalyzed by Au nanoparticles is obscure, thus we emphasize that our proposed mechanism is just a reasonable working hypothesis. Also, as we also observed that in the case of tert-benzylic alcohols, their trimethylsilyl ethers are not direct precursors of the alkanes,²² we propose a rational mechanism shown in Scheme 1 (bottom part), in which the proton of the alcohol indirectly becomes a reducing hydride. The participation of intermediate II cannot be excluded.

In conclusion, we presented herein the first general example of a palladium resembling, Au-catalyzed activation of 1,2-disilanes, towards hydrolysis and alcoholysis. The Au/TiO₂-catalyzed alcoholysis of hexamethyldisilane is a simple, atom economical and clean procedure for the synthesis of trimethylsilyl protected alcohols. The method is more effective as compared to a known homogeneous Pd-catalyzed protocol in terms of mildness and catalyst loading. *tert*-Benzylic alcohols are primarily reduced by hexamethyldisilane into the corresponding alkanes, an unprecedented reaction pathway.

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