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Homogeneous gold-catalyzed hydrosilylation of aldehydes

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This paper is dedicated to Professor Gyula Pályi on the occasion of his 70th birthday.

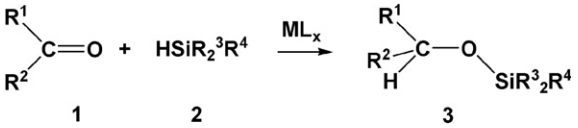
Abstract

The catalytic hydrosilylation of aldehydes in the presence of PBu_3 modified Au(I)-complexes was investigated. In situ IR and NMR experiments have revealed that both, the ligand PBu_3 and the substrate aldehyde play an important role in stabilizing the gold catalyst and/or forming the catalytically active species. In their absence the reducing power of silane destabilizes the gold (I) catalyst giving rise to gold clusters or particles. Several side reactions involving water and oxygen were also investigated. A plausible reaction pathway as an alternative to the well-accepted mechanism for the transition-metal homogeneously catalyzed hydrosilylation of aldehydes has been proposed to accommodate the experimental observations.

Keywords: Hydrosilylation; Homogeneous catalysis; Gold; Reaction mechanisms

1. Introduction

The application of gold compounds as catalysts has been gaining momentum as gold is considered as an environmentally friendly metal and thus can be used in place of toxic heavy metals [1]. In addition, gold and/or its complexes could catalyze a great diversity of catalytic reactions efficiently, some times with unexpectedly high selectivities to products. Since the catalytically active species could be mono- and/or polynuclear gold species and/or nanoparticles in homogeneous catalytic systems, the molecular level understanding of how to control the nuclearity or the particle size is crucial in the design of more stable, efficient and even recoverable catalysts. Thus, molecular architecture depends on the nature of the reaction itself and the additives used. In the case of homogeneous gold catalysis these could be the coordination properties of the substrates, products, and side products as well as the ligands used.



1 2 3 (1)

R^1=H; R^2=Ph, -C_2H_5, -C_9H_{19}; R^3=Me, Et; R^4=Ph, Et

Hydrosilylation of aldehydes and ketones is an important reaction for the preparation of various intermediates in organic synthesis and is generally catalyzed by rhodium, ruthenium, or platinum complexes [2]. On the basis of a PBu_3-modified gold catalyst for the hydrosilylation of aldehydes (Eq. 1) [3] we have recently reported several fluorous gold catalysts to provide facile catalyst recycling [4]. During the development of the fluorous catalysts we have noted several unusual features including the activity and stability of the fluorous gold complexes and nanoparticles, both depending on the ligand and aldehyde concentrations. For example, it is rather surprising that the initial rate of the reaction of PhCHO (**1a**) with $HSiMe_2Ph$ (**2a**) was hardly effected and the yield of $PhCH_2OSiMe_2Ph$ (**3a**)

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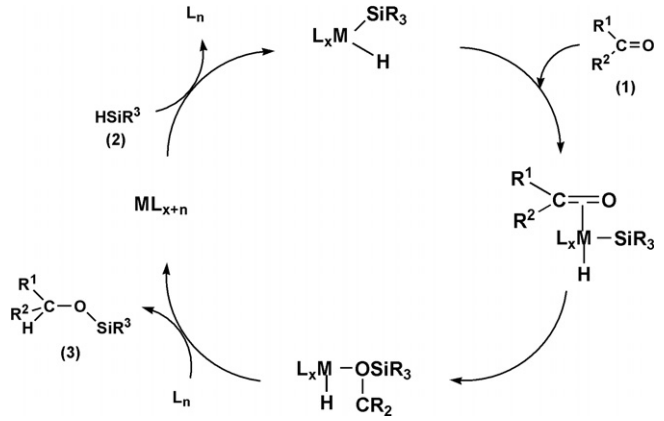


Scheme 1.

was increased from 50% to almost full conversion by increasing the concentration of PBu_3 (**4**) from 10 to 20 mol% with respect to 3 mol% of the gold catalyst [3]. These results are difficult to explain by the well-accepted mechanism of hydrosilylation of aldehydes, which includes the oxidative addition of **2** to the metal center, the coordination and insertion of the carbonyl group of **1** into the metal-silicon bond, and the reductive elimination of **3** (Scheme 1) [2]. We report here our detailed study on the effects of key reaction parameters on rate and selectivity including some of the side reactions.

2. Results and discussion

The gold precursors used in the hydrosilylation of aldehydes were either [AuCl(PPh_3)], as reported [3], or [AuCl(tht)] (tht = tetrahydrotiophene). While these complexes are catalytically inactive even in the presence of excess PPh_3, the addition of PBu_3 results in the formation of the active species of unknown structure(s) [3]. First, we have investigated the reaction of [AuCl(tht)] with various amounts of PBu_3. It has been reported that while the reaction $[Et_4N][AuBr_2]$ with 1 or 2 equiv. of PBu_3 leads to the formation of [$AuBr(PBu_3)$] or $[Au(PBu_3)_2]Br$, respectively, higher PBu_3 concentrations result in a rapidly exchanging $[Au(PBu_3)_3]Br$ species even at −120°C [5]. We have observed a similar behavior at room temperature during the titration of [AuCl(tht)] with various amounts of PBu_3 by ^{31}P NMR (Fig. 1). The formation of [$AuCl(PBu_3)$] and $[Au(PBu_3)_2]Cl$ could be clearly observed by the appearance of the peaks at 23.5 ppm and 33.5 ppm, respectively. Only one peak is observable above P/Au = 2, which is shifted to higher fields and becomes broader at higher ratios indicating the possible formation of $[Au(PBu_3)_n]Cl$ ($n > 2$) and the rapid exchange between these species (Scheme 2).

Next we have investigated the performance of the PBu_3-modified [AuCl(tht)] catalyst in the hydrosilylation of benzaldehyde (**1a**), propanal (**1b**), and nonanal (**1c**) using Me_2PhSiH (**2a**) and Et_3SiH (**2b**) in CH_3CN, CH_2Cl_2 or neat reaction mixture (Table 1). It is important to emphasize that in the absence of [AuCl(tht)] these hydrosilylation reactions do *not* take place. The conversions of the aldehydes with **2a** were higher than that of with **2b**. While the nature of the two solvents employed has little effect, the reaction proceeds somewhat faster in their absence. The products were identified by GC–MS and NMR (Table 2).

The dependence of the reaction rate on key reaction parameters was investigated by in situ NMR measurements at room temperature (see Fig. S1–S4 in Supplementary

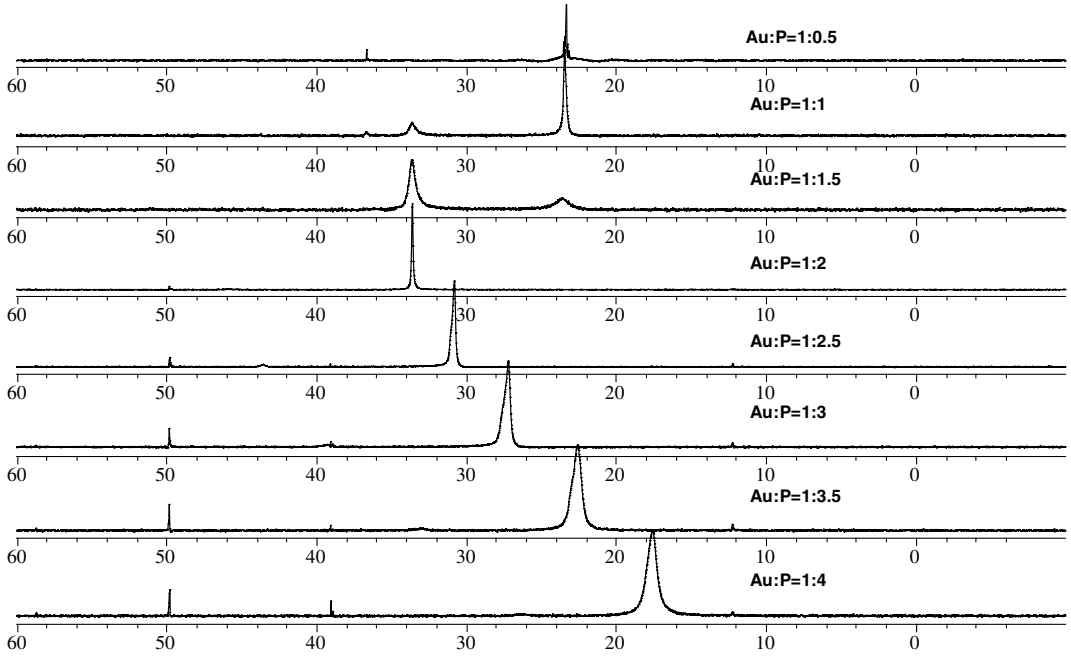
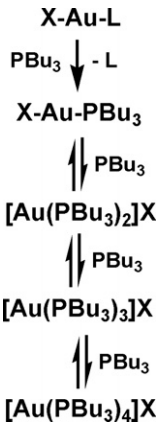


Fig. 1. ^{31}P NMR spectra of the reaction mixture of 0.08 mmol of [AuCl(tht)] with PBu_3 (at molar ratios of Au to PBu_3: 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5 and 1:4) in 350 μL of dry and degassed $CDCl_3$ under Ar at room temperature.



Scheme 2.

material). By lowering the gold concentration from 3 mol% to 1 mol%, the reaction rate decreases significantly, however not proportionally to the gold concentration. This is probably due to the changing positions of the gold–phosphine equilibria shown in Scheme 2. A similar effect could be observed by changing the concentration of PBu_3 (**4**), **1a**, and **2a**. A detailed kinetic investigation is underway to establish the kinetic model for this system.

It should be noted, that at the $Au/PBu_3 = 1:1$ or 1:2 ratios the reaction mixture became heterogeneous, evidenced by the formation of a black precipitate, and no reaction could be observed. We have therefore increased the PBu_3 concentration, in accordance to previous work [3] and our results. The hydrosilylation of 2 mmol of **1a** with 4 mmol of **2a** in the presence of 3 mol% [AuCl(PPh_3)] and 20 mol% **4** in 2 mL CH_3CN at 70 °C was monitored by in situ IR spectroscopy. To our surprise the colorless reaction mixture turned deep purple when the IR bands of **1a** disappeared (e.g. at 100% conversion of **1a**) and the formation of a black precipitate was noticed. These results have suggested that the presence of excess of PhCHO (**1a**) over $HSiMe_2Ph$ (**2a**) is an important factor, in addition to the excess of PBu_3 (**4**) over gold [3]. The reaction was also performed without added solvent. When 3.22 mmol **2a** was

Table 1
Hydrosilylation catalyzed with AuCl(tht) and PBu_3[a]

Aldehyde	Silane	Solvent	Product[b]	Yield[c] (%)
Benzaldehyde (**1a**)	Me_2PhSiH (**2a**)	CH_3CN	(Benzyloxy)dimethylphenylsilane (**3a**)	81
Benzaldehyde (**1a**)	Me_2PhSiH (**2a**)	CH_2Cl_2	(Benzyloxy)dimethylphenylsilane (**3a**)	82
Benzaldehyde (**1a**)	Et_3SiH (**2b**)	CH_3CN	(Benzyloxy)triethylsilane (**3b**)	78
Benzaldehyde (**1a**)	Et_3SiH (**2b**)	CH_2Cl_2	(Benzyloxy)triethylsilane (**3b**)	55
Propanal (**1b**)	Me_2PhSiH(**2a**)	CH_3CN	Dimethylphenylpropoxysilane (**3c**)	69
Propanal (**1b**)	Me_2PhSiH(**2a**)	CH_2Cl_2	Dimethylphenylpropoxysilane (**3c**)	56
Propanal (**1b**)	Et_3SiH (**2b**)	CH_3CN	Triethylpropoxysilane (**3d**)	30
Propanal (**1b**)	Et_3SiH (**2b**)	CH_2Cl_2	Triethylpropoxysilane (**3d**)	5
Nonanal (**1c**)	Me_2PhSiH (**2a**)	CH_3CN	Dimethylphenylsiloxynonane (**3e**)	82
Nonanal (**1c**)	Me_2PhSiH (**2a**)	CH_2Cl_2	Dimethylphenylsiloxynonane (**3e**)	95
Nonanal (**1c**)	Et_3SiH (**2b**)	CH_3CN	1-Triethylsiloxynonane (**3f**)	16
Nonanal (**1c**)	Et_3SiH (**2b**)	CH_2Cl_2	1-Triethylsiloxynonane (**3f**)	3
Benzaldehyde (**1a**)	Me_2PhSiH (**2a**)	–	(Benzyloxy)dimethylphenylsilane (**3a**)	100
Nonanal (**1c**)	Me_2PhSiH (**2a**)	–	Dimethylphenylsiloxynonane (**3f**)	100

[a] 3 mol% [AuCl(tht)] and 20 mmol% PBu_3 (**4**) in a solution of 1 mmol aldehyde and 0.9 mmol silane in 0.5 mL solvent at 70 °C for 3 h.
[b] Characterized by NMR and GC–MS.
[c] Conversion by ^1H NMR.

Table 2
The characterization of the hydrosilylation products

Product	MS data (m/z)	NMR
(Benzyloxy)dimethylphenylsilane (**3a**)	227, 197, 164, 149, 135, 91	^1H ($CDCl_3$) 7.2–7.5 (m, 3H), 7.26 (s, 5H), 4.66 (s, 2H), 0.4 (s, 6H)
(Benzyloxy)triethylsilane (**3b**)	193, 163, 135, 91	
Dimethylphenylpropoxysilane (**3c**)	194 (M^+), 179, 137, 135, 121, 105, 91, 77, 61	$^{13}C\{^1H\}$ ($CDCl_3$) 140.8, 137.5, 133.4, 129.5, 128.0, 127.8, 126.8, 126.2, 26.2, 13.9, 10.4, −1.9
Triethylpropoxysilane (**3d**)	145, 117, 103, 87, 75, 59, 47, 45, 29, 27	^1H ($CDCl_3$) 0.47–0.77 (m, 6H), 0.83–1.117 (m, 8H), 1.33–1.57 (c, 4H), 3.93 (t, 2 H)
Dimethylphenylsiloxynonane (**3e**)	263, 200, 163, 137,121, 91, 69	^1H ($CDCl_3$) 7.67 (m, 2H), 7.43 (m, 3H), 3.73 (t, 2H), 1.43 (s, 14H), 1.07 (q, 5H), 0.49 (s, 6H) $^{13}C\{^1H\}$ ($CDCl_3$) 138.0, 133.3, 129.3, 127.7, 62.7, 32.8, 32.1, 29.5, 26.0, 22.8, 14.1 (2C), 13.9, −1.8
1-Triethylsiloxynonane (**3f**)	229, 135, 103, 89, 87, 83, 75, 69, 55	
1,1,2,2-Tetramethyl-1,2-diphenyldisiloxane	286 (M^+), 271, 193, 135, 89	^1H ($CDCl_3$) δ 7.46 (m, 4H), 7.3 (m, 6H) and 0.33 (s, 12 H)
1,3-Hexaethyldisiloxane	217, 189, 161, 133, 105, 80, 66, 59	

added to a solution of 3 mol% $AuCl(PPh_3)$ and 20 mol% **4** in 20 mmol **1a**, the hydrosilylation was completed at 90 °C within 25 min (Fig. 2 and see the reaction profile in Fig. S5 in Supplementary material) and the solution remained colorless. The addition of **2a** can be continued (e.g. 6.44 mmol and 3.86 mmol of **2a**) without the appearance of the purple color and the formation of a black precipitate until **1a** remains in slight excess.

These experiments suggest that benzaldehyde (**1a**) and PBu_3 (**4**) themselves or together play an important role in stabilizing the gold catalyst and/or forming the catalytically active species. It is also evident that the reducing power of $HSiMe_2Ph$ (**2a**) is high enough to destabilize the gold (I) catalyst giving rise to gold clusters or particles.

$$\underset{\mathbf{2a}}{2\ Me_2PhSiH} + H_2O \xrightarrow{Au/PBu_3} \underset{\mathbf{6a}}{PhMe_2Si{-}O{-}SiMe_2Ph} + 2\ H_2 \qquad (2)$$

During the investigation of the hydrosilylation of aldehydes we have identified several side reactions caused by the presence of small amounts of water and/or oxygen. Surprisingly, $HSiMe_2Ph$ (**2a**) could react with water in the presence of the PBu_3-modified [AuCl(tht)] catalyst to give H_2 and $(Me_2PhSi)_2O$ (**6a**) (Eq. 2), confirmed by GC–MS. We have also established that **2a** does not react with water at room temperature or at 70 °C. The hydrolysis of product $PhCH_2OSiMe_2Ph$ (**3a**) could have resulted in the formation of $Me_2PhSiOH$ (**7a**) and $PhCH_2OH$ (**8**), followed by the subsequent gold-catalyzed conversion of **7a** to **6a**. However, we could not detect **8** at all in the reaction mixture.

Next we have studied the possible side reactions caused by oxygen. Of course, the formation of $OPBu_3$ is a potential side reaction, which could be avoided by the careful exclusion of air during all operations. On the contrary, the oxidation of benzaldehyde (**1a**) to benzoic acid (**9b**) occurs readily opening a door for an unexpected side reaction (Scheme 3), well know for much stronger acids such as HCl (**9a**) [6].

The reaction of 3 mmol **1a**, 0.3 mmol **4**, and 0.6 mmol **9b** was monitored by NMR and the formation of **12b** could be observed. The ^{31}P NMR exhibits a broad peak at 33.5 ppm, which becomes a singlet by lowering the temperature to −20 °C. This chemical shift is similar to those displayed by ionic species containing positively charged

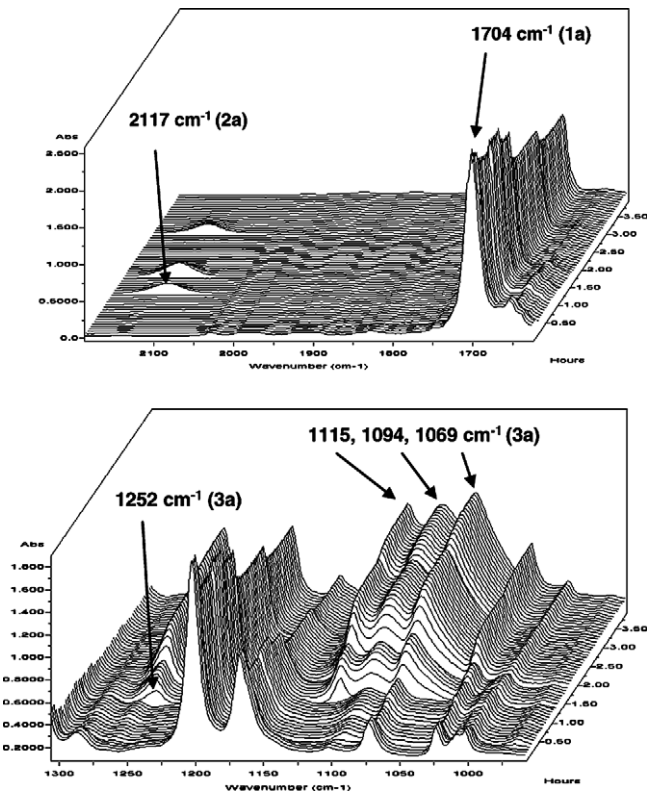
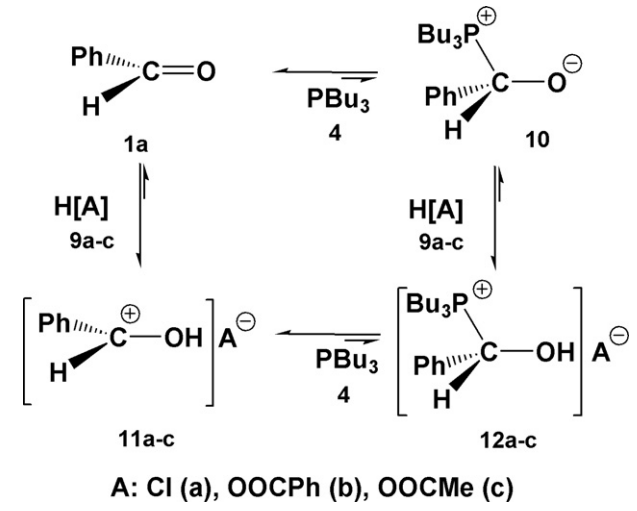


Fig. 2. In situ IR spectra of the hydrosilylation of neat (20 mmol) benzaldehyde (**1a**) in the presence of 0.6 mmol $AuCl(PPh_3)$ and 4 mmol PBu_3 (**4**) at 90 °C. Me_2PhSiH (**2a**) was added in three portions (3.22, 6.44, and 3.86 mmol) to the reaction mixture.



Scheme 3.

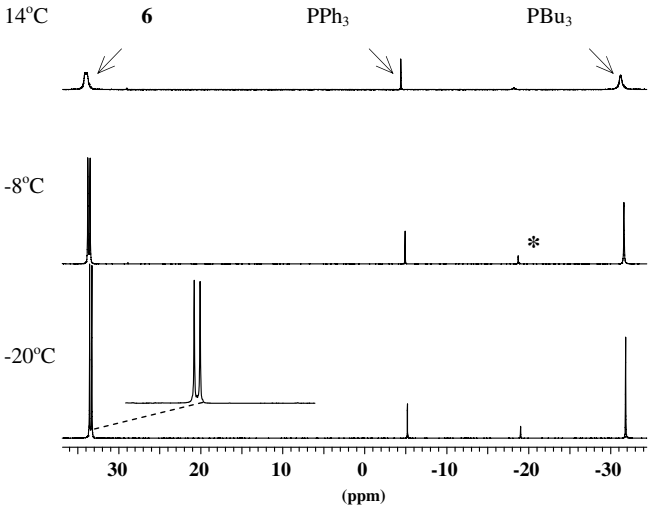


Fig. 3. ^{31}P NMR spectra of the in situ reaction of PBu_3 (**4**), ^{13}C-labelled benzaldehyde, and PhCOOH (mol ratio of 1: 10: 0.83) under Ar (with a capillary filled with PPh_3 in $CDCl_3$ as internal reference). * Unidentified impurity.

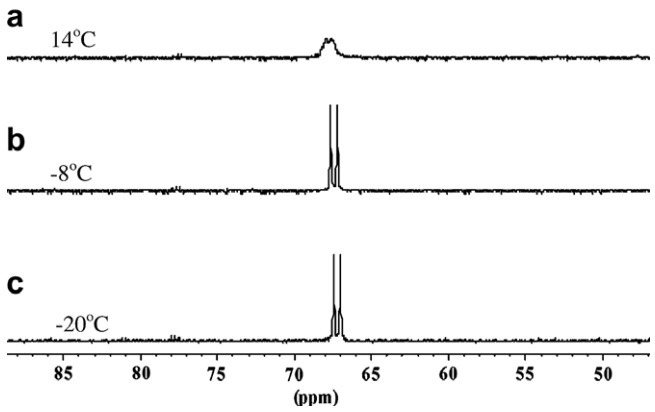
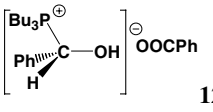
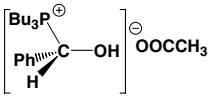
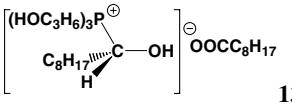
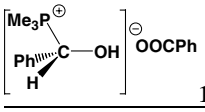


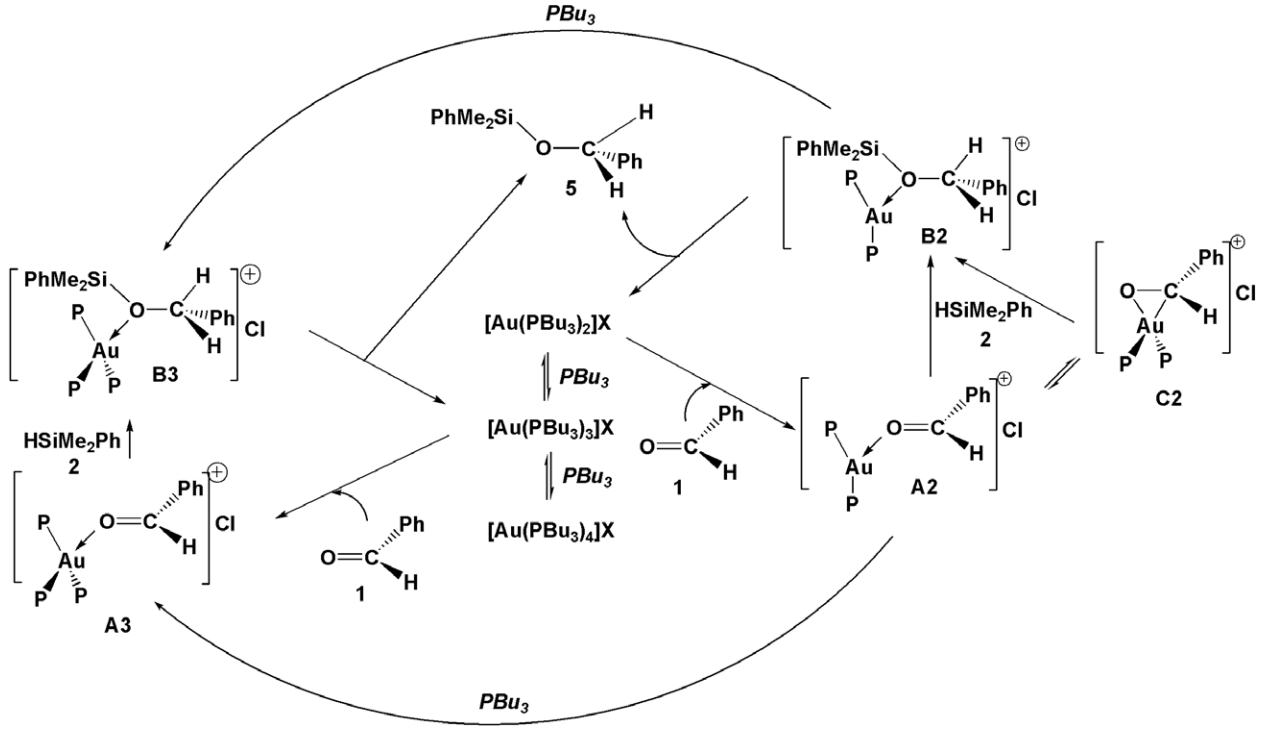
Fig. 4. $^{13}C\{^1H\}$ NMR spectra of the in situ reaction of PBu_3 (**4**), ^{13}C-labelled benzaldehyde, and PhCOOH (mol ratio: 1:10:0.83) under Ar (with a capillary filled with PPh_3 in $CDCl_3$as internal reference). Zoomed for the 45–88 ppm region to show the CH carbon directly bonded to the phosphorous atom ($\delta = 67.2$ ppm, $^1J_{PC} = 55$ Hz).

Table 3
$^{31}P\{^1H\}$ NMR data of the 1-hydroxy phosphonium salts

Compounds	$^{31}P\{^1H\}$ (ppm)
 **12b**	34.4
 **12c**	35.0
 **13**	37.0
 **14**	28.3

phosphorous atoms [7]. The exact structure of **12b** was delineated by using 99.9% ^{13}C-labelled benzaldehyde. The variable temperature ^{31}P NMR shows a doublet at 34.4 ppm, with a coupling constant of $^1J_{PC} = 55$ Hz, indicating the presence of a P–C bond (Fig. 3). This observation was confirmed by a doublet at 67.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum (Fig. 4). Besides the coupling constant $^1J_{PC} = 55$ Hz, the coupling constant $^1J_{CH} = 125$ Hz is also observable as expected for a methyne bonded to the phosphorous atom. Finally, the ^1H NMR spectrum shows a singlet at 12.3 ppm for the acidic proton of the hydroxyl group. It is important to emphasize, that there is no detectable reaction between **4** and freshly distilled **1a** at room temperature or at −20 °C. Similar phosphonium salts have previously been prepared by the addition of strong acids [6]. Other alkyl phosphines can also react with aldehydes in the presence of weak acids (Table 3).

Concerning the mechanism involved, our data suggest that both PBu_3 (**4**) and the aldehydes play a crucial role in stabilizing the catalytically active gold species. On the contrary, the excess of hydrosilanes is detrimental due rapid reduction of the gold catalyst. Although the formation of a tri-coordinated $AuHP_2$ intermediate was proposed for [AuCl(xantphos)]-catalyzed dehydrogenative silylation of



Scheme 4.

alcohols [8], the formation of a mononuclear species with PBu_3 seems unlikely. The increasing amount of **4** with respect to gold should increase the level of substitution [5] and thus the rate of the oxidative addition of the hydrosilane should decrease (Scheme 1) resulting in a proportionally slower catalytic reaction. Since the opposite effect was observed, an alternative mechanism must be operational. One possibility is PBu_3 (**4**) concentration dependent equilibrium positions between the $[Au(PBu_3)_n]Cl$ ($n = 2$, 3, and 4) species that may exhibit significantly different reactivity towards the aldehydes depending on the electronic density on the gold center (Scheme 4). While $[Au(PBu_3)_4]Cl$ does not have an open coordination site to activate the aldehyde, both $[Au(PBu_3)_n]Cl$ ($n = 2$ and 3) could perform the activation of the aldehyde to form oxygen-bonded **A2** and **A3** adducts, respectively, with significantly different rates. While gold(I) has little affinity for oxygen donor ligands, tertiary phosphines have shown to stabilize Au(I)–O bonds. The cation $[AuL]^+$ (L = phosphine) is isolobal with a proton and shows a great affinity for bonding to various Lewis bases [9]. The possibility for side-on coordination of the aldehyde (**C2**) cannot be ruled out, but it seems plausible for $[Au(PBu_3)_2]Cl$ only. These intermediates could readily undergo a concerted addition of the $Si^{\delta+}$–$H^{\delta-}$-bond to the $C^{\delta+}$–$O^{\delta-}$-bond resulting in the formation of a coordinated alkoxysilanes **B2** and **B3**, which readily eliminate alkoxysilane to regenerate the gold catalyst. The accelerating effect of the PBu_3 (**4**) could be also the result of converting **A2** to **A3** or **B2** to **B3**.

While the operation of a novel mechanism for gold could lead to new applications in organic chemistry, the stabilizing role of one of the substrates, e.g. the aldehydes, is unusual in homogeneous transition-metal catalysis and indeed surprising.

3. Experimental

All manipulations and NMR experiments involving air- or water-sensitive reagents were performed under an inert atmosphere of dry argon with the use of Schlenk techniques, and all solvents were dried and degassed before use. ^1H, ^{13}C and ^{31}P NMR spectra were obtained on Bruker ARX-250, Bruker Avance-400, and Bruker DRX-500 instruments in solvents like $CDCl_3$ or CD_2Cl_2 or neat reactants by using a PPh_3 insert (0.1 M PPh_3 in $CDCl_3$). Chemical shifts are quoted relative to $Si(CH_3)_4$ (external, ^1H and ^{13}C), H_3PO_4 (internal standard, ^{31}P). The in situ IR spectra were recorded on a Mettler-Toledo's ReactIR™ 1000 instrument using a SiComp probe. The spectra was recorded every 2 min. GC–MS spectra were obtained on an Agilent 6890GC instrument (with an 5973 selective mass detector) using a HP-5MS column (30 m × 0.25 mm × 0.25μm).

Commercially available $CDCl_3$ (Aldrich) and CD_2Cl_2 (Aldrich) were dried with CaH_2 (Aldrich) under N_2 or Ar. CH_2Cl_2 (Aldrich) and CH_3CN (Reanal) were distilled from CaH_2 (Aldrich) under N_2 or Ar. THF (Reanal) was freshly distilled from sodium benzophenone ketyl (Aldrich) under N_2 or Ar. [AuCl(tht)] was prepared by a method previously reported [10]. The aldehydes (Reanal and Aldrich) were freshly distilled and stored under Ar. The silanes were purchased from Aldrich and were used without further purification. At carbonyl position 99.9% ^{13}C-enriched benzaldehyde was purchased from Euriso-top and was distilled before use and stored under Ar at −18 °C.

3.1. Titration of [AuCl(tht)] with PBu_3 (4)

An NMR tube was charged with 0.08 mmol (0.0260 g) of [AuCl(tht)] and 350 μL of dry and degassed $CDCl_3$ under Ar and 10 μL PBu_3 (**4**) was added eight times at room temperature to the gold solution (molar ratios of 2:1, 1:1, 2:3, 1:2, 2:5, 1:3, 2:7 and 1:4).

3.2. General procedure for the hydrosilylation of aldehydes

[AuCl(tht)] (0.03 mmol, 0.0098 g) was placed in a Kontex tube in 0.5 mL of solvent and 0.2 mmol (50 μL) of PBu_3 (**4**), 1 mmol aldehyde (**1a**, 100 μL; **1b**, 72 μL; **1c**, 155 μL) and 0.9 mmol silane (**2a**, 140 μL; **2b**, 140 μL) were added to the reaction mixture, which was stirred at 70 °C for 3 h. The reaction vessel was then opened and the reaction mixture was analyzed by NMR or GC–MS.

3.3. Reaction of weak acids with aldehydes and phosphines

3.3.1. Reaction with ^{13}C-labelled benzaldehyde

An NMR tube was charged with 3 mmol (300 μL) ^{13}C-benzaldehyde (**1a**), 0.3 mmol (74 μL) PBu_3 (**4**), 0.25 mmol (0.030 g) benzoic acid under Argon. The NMR spectra were recorded at 300, 285, 265 and 253 K.

3.3.2. Reaction of aldehydes and phosphines in the presence of weak acids

3.3.2.1 An NMR tube was charged with 1.5 mmol (150 μL) benzaldehyde (**1a**), 1.0 mmol (250 μL) PBu_3 (**4**), and 1.35 mmol acetic acid (77 μL) under Argon and the NMR spectra were recorded at RT.

3.3.2.2 An NMR tube was charged with 1.9 mmol (325 μL) nonanal (**1c**) and 1.9 mmol (0.395 g) tris-hydroxypropylphosphine, and 0.04 mmol (0.006 g) nonanoic acid under Argon and the NMR spectra were recorded at RT.

3.3.2.3 An NMR tube was charged with 3.45 mmol (345 μL) benzaldehyde (**1a**), 0.23 mmol (24 μL) PMe_3 (**15**) and 0.51 mmol (0.063 g) benzoic acid (mol ratio 1:15:2.2) in CD_2Cl_2 under Ar and the NMR spectra were recorded at RT.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.025.

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