First gold complex-catalysed selective hydrosilylation of organic compounds†

Hajime Ito,[a] Tatsuki Yajima,[b] Jun-ichi Tateiwa[b] and Akira Hosomi*[b]

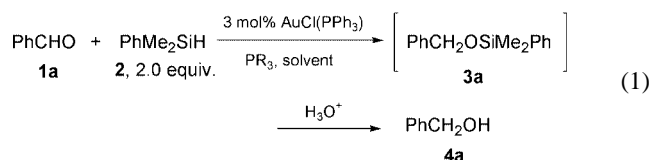[a] Institute for Molecular Science, Research Center for Molecular Materials, Myodaiji, Okazaki, 444-8585, Japan
[b] Department of Chemistry and Graduate School of Pure Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan. E-mail: hosomi@chem.tsukuba.ac.jp

The first examples of the hydrosilylation of organic compounds such as aldehydes and an aldimine using a catalytic amount of a gold complex, which accomplished versatile regio- and chemo-selective reduction of carbonyl compounds, are described.

The exploration of catalytic reactions using soluble gold complexes has been a challenging area in organic synthesis.[1,2] The design of synthetic reactions using gold complex catalysts is still considered to be a difficult subject, though some successful systems have been reported. A considerable number of transition metal complexes have been employed as catalysts for the hydrosilylation of organic compounds.[3] However, to our knowledge, no examples of hydrosilylation catalyzed by gold complexes have been reported. Recently, we found a highly reactive catalysis by a gold complex for the dehydrogenative dimerization of a hydrostannane, offering new clues to the further development of gold complex-catalyzed reactions.[4] Here we describe the first example of the hydrosilylation of organic compounds using a gold complex as a catalyst. These results reveal the novel reactivity of the gold complex as well as its versatile selectivity in the reduction of organic compounds.

We first examined the hydrosilylation of benzaldehyde **1a** using a catalytic amount of chloro(triphenylphosphine)gold(I) alone [eqn. (1), Table 1, entry 1].[5] After the addition of

$$PhCHO + PhMe_2SiH \xrightarrow[\text{PR}_3, \text{ solvent}]{\text{3 mol\% AuCl(PPh}_3)} \left[PhCH_2OSiMe_2Ph \right]$$

$$\text{1a} \qquad \text{2, 2.0 equiv.} \qquad\qquad \text{3a}$$

$$\xrightarrow{\text{H}_3\text{O}^+} PhCH_2OH$$
$$\text{4a}$$

(1)

dimethylphenylsilane **2** (2.0 mmol), the colorless mixture of chloro(triphenylphosphine)gold(I) (0.03 mmol), benzaldehyde **1a** (1.0 mmol) and dry DMF (1.0 ml) changed to a deep-purple solution and precipitation of metallic gold was observed within 10 min at 70 °C.[6] No silylated product was found under these conditions. We next examined a combination of chloro-(triphenylphosphine)gold(I) and triphenylphosphine as catalyst, which gave good results in our previous study of gold catalysis; however, here it gave a similar disappointing result (entry 2).[4] Use of tributylphosphine, which is more basic and is strongly coordinating, as an additive ligand to chloro(triphenylphosphine)gold(I) provided remarkable catalytic activity for the hydrosilylation of **1a** (entry 3). Compound **2** (2.0 mmol) was added to a mixture of chloro(triphenylphosphine)gold(I) (0.03 mmol), tributylphosphine (0.20 mmol), **1a** (1.0 mmol) and DMF (1.0 ml) under nitrogen. After stirring for 1.5 h at 70 °C, the quantitative formation of the corresponding silyl ether **3a**, the hydrosilylation product of **1a** and **2**, was observed by ^{1}H NMR spectroscopy, and alcohol **4a** was isolated in 90% yield after acidic hydrolysis.[7,8] In sharp contrast to the previous two
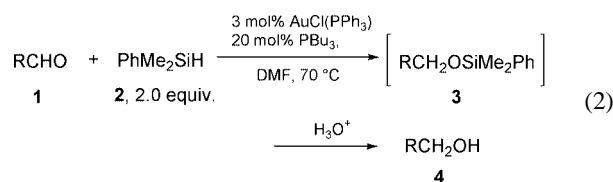
Table 1 Gold complex-catalyzed hydrosilylation of benzaldehyde **1a** under various conditions

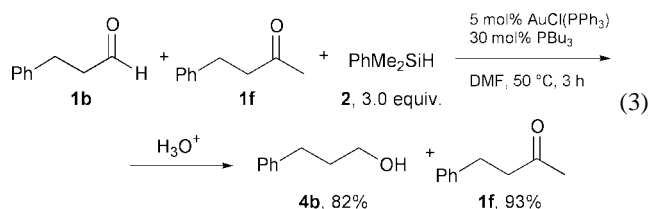| Entry[a]	Additive/equiv.	Solvent	Conditions	Yield[b] of 4a (%)
1	—	DMF	70 °C, 1.5 h	0
2	PPh$_3$, 0.2	DMF	70 °C, 1.5 h	0
3	PBu$_3$, 0.2	DMF	70 °C, 1.5 h	90
4	PBu$_3$, 0.2	Toluene	70 °C, 11 h	65
5	PBu$_3$, 0.2	THF	70 °C, 3.0 h	92
6	PBu$_3$, 0.2	MeCN	70 °C, 5.0 h	77

[a] To a solution of benzaldehyde **1a** (1.0 mmol), AuCl(PPh$_3$) (3 mol%, 0.03 mmol), and phosphine (0–20 mol%, 0–0.20 mmol) in dry DMF (1.0 ml) was added dimethylphenylsilane **2** (2.0 equiv., 2.0 mmol) under nitrogen. [b] Isolated yield after hydrolysis.
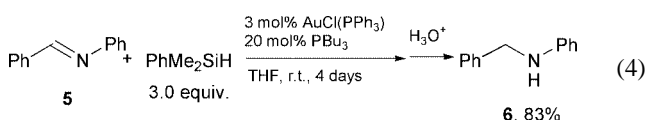
systems, the reaction mixture was colorless and a precipitate of metallic gold was not observed. Although this catalytic system was compatible with other solvents, DMF was found to be optimal (entries 4–6).[9] The generality of this gold complex-catalysed hydrosilylation was successfully demonstrated by reaction with various aldehydes [eqn. (2), Table 2]. In

$$RCHO + PhMe_2SiH \xrightarrow[\text{DMF, 70 °C}]{\begin{array}{c}\text{3 mol\% AuCl(PPh}_3)\\ \text{20 mol\% PBu}_3\end{array}} \left[RCH_2OSiMe_2Ph \right]$$

$$\text{1} \qquad \text{2, 2.0 equiv.} \qquad\qquad\qquad \text{3}$$

$$\xrightarrow{\text{H}_3\text{O}^+} RCH_2OH$$
$$\text{4}$$

(2)

particular, cinnamaldehyde, which contains a conjugated double bond, was converted to the 1,2-addition product with high selectivity, and the corresponding allyl alcohol **4c** was exclusively obtained in 94% yield after hydrolysis (entry 2).[3,10] When this catalytic system was applied to the reduction of ketone **1f**, no reduced product was obtained (entry 5). The versatile chemoselectivity of the catalyst was clearly shown by the selective reduction of the aldehyde **1b** irrespective of the presence of ketone **1f** under modified conditions [eqn. (3)].[3,10]

$$\text{1b} + \text{1f} + PhMe_2SiH \xrightarrow[\text{DMF, 50 °C, 3 h}]{\begin{array}{c}\text{5 mol\% AuCl(PPh}_3)\\ \text{30 mol\% PBu}_3\end{array}}$$

$$\text{2, 3.0 equiv.}$$

$$\xrightarrow{\text{H}_3\text{O}^+} \text{4b, 82\%} + \text{1f, 93\%}$$

(3)

Reduction of an aldimine was also carried out with hydrosilane in the presence of the gold catalyst [eqn. (4)].

$$\text{5} + PhMe_2SiH \xrightarrow[\text{THF, r.t., 4 days}]{\begin{array}{c}\text{3 mol\% AuCl(PPh}_3)\\ \text{20 mol\% PBu}_3\end{array}} \xrightarrow{\text{H}_3\text{O}^+}$$

$$\text{3.0 equiv.} \qquad\qquad\qquad \text{6, 83\%}$$

(4)

Table 2 Gold complex-catalyzed hydrosilylation of various carbonyl compounds

Entry[a]	Carbonyl compounds **1**	Conditions	Yield[b] of **4** (%)
1	3-Phenylpropanal **1b**	70 °C, 1.5 h	**4b**, 93
2	Cinnamaldehyde **1c**	70 °C, 5.0 h	**4c**, 94[c]
3	Decanal **1d**	70 °C, 1.5 h	**4d**, 51
4	Cyclohexanecarboxaldehyde **1e**	70 °C, 11 h	**4e**, 78
5	4-Phenylbutanone **1f**	70 °C, 15 h	**4f**, 0[d]

[a] To a solution of carbonyl compound **1** (1.0 mmol), AuCl(PPh₃) (3 mol%, 0.03 mmol) and tributylphosphine (20 mol%, 0.20 mmol) in dry DMF (1.0 ml) was added dimethylphenylsilane **2** (2.0 equiv., 2.0 mmol) under nitrogen. [b] Isolated yield after hydrolysis. [c] Only a 1,2-reduced product was detected. [d] The starting material was recovered in good yield (**1f**, 93%).

Although it took four days for the reaction to be complete, the corresponding reduced product **6** of aldimine **5** was obtained in good yield (83%).

The effect of the amount of the additional ligand on the reactivity is shown in Fig. 1. Monitoring of the reaction by ^{1}H NMR spectroscopy showed that the hydrosilylation product was formed continuously at 50 °C in the presence of 3 mol% of chloro(triphenylphosphine)gold(I) and 20 mol% of tributylphosphine with the reaction almost complete after 600 min (experiment **A**) during which the reaction mixture was colorless and transparent throughout. In experiment **B**, which was carried out with a lower amount of tributylphosphine (10 mol%) than in experiment **A**, considerable rate retardation was observed as the reaction time approached 400 min, though the initial reaction rate in experiment **B** was slightly higher than that of **A** within 200 min. A deep-purple coloration was observed immediately
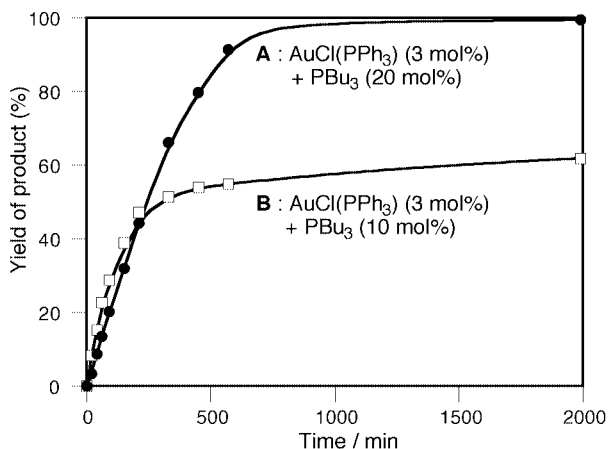
Fig. 1 Product formation *vs.* time for reactions carried out with benzaldehyde **1a** (1.0 mmol), dimethylphenylsilane **2** (2.0 mmol), 3 mol% of chloro(triphenylphosphine)gold(I) (0.03 mmol) and 20 mol% of tributylphosphine (0.2 mmol) (experiment **A**, ●) or 10 mol% of tributylphosphine (0.1 mmol) (experiment **B**, □) in DMF (1.0 ml) at 50 °C. Yields determined by ^{1}H NMR spectroscopy.

after adding the hydrosilane to reaction mixture and the slow precipitation of gold(0) was observed in experiment **B**. These results indicate that the role of the excess tributylphosphine is the prevention of catalyst decomposition rather than increasing the reaction rate.

Although the active species of this catalyst is still unclear at this stage, we propose that colorless monomeric gold complexes stabilized by the excess tributylphosphines play an important role in this reaction and that the predominant deactivation process is the formation of gold clusters and metallic gold(0) upon reduction of gold(I).

In conclusion, we have described the unprecedented hydrosilylation of organic compounds by a gold complex catalyst with high chemoselectivity. The deactivation of the gold catalyst was suppressed in the presence of an additional ligand (tributylphosphine). These results provide an important principle for the design of gold complex-catalyzed systems.

Notes and references

1 Y. Ito, M. Sawamura and T. Hayashi, *J. Am. Chem. Soc.*, 1986, **108**, 6405; Y. Fukuda and K. Utimoto, *J. Org. Chem.*, 1991, **56**, 3729; S. Komiya, T. Sone, Y. Usui, M. Hirano and A. Fukuoka, *Gold Bull.*, 1996, **29**, 131; Q. Xu, Y. Imamura, M. Fujiwara and Y. Souma, *J. Org. Chem.*, 1997, **62**, 1594; J. H. Teles, S. Brode and M. Chabanas, *Angew. Chem., Int. Ed.*, 1998, **37**, 1415.

2 For heterogeneous gold catalysts, see: J. E. Bailie and G. J. Hutchings, *Chem. Commun.*, 1999, 2151 and references therein.

3 *Comprehensive Handbook on Hydrosilylation*, ed. B. Marciniec, Pergamon Press, New York, 1992; M. Hudlicky, *Reductions in Organic Chemistry*, American Chemical Society, Washington DC, 2nd edn., 1996; M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, 2000.

4 H. Ito, T. Yajima, J. Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 1999, **40**, 7807.

5 C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1979, 1730.

6 It was reported that the reduction of a gold(I) complex with a hydride reagent gave metallic gold(0) and deeply colored gold clusters: K. P. Hall and D. M. P. Mingos, *Prog. Inorg. Chem.*, 1984, **32**, 237; G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis and J. W. A. van der Velden, *Chem. Ber.*, 1981, **114**, 3634.

7 When the isolation of the products was carried out by column chromatography (SiO₂) without acidic workup both **3a** (30%) and **4a** (58%) were obtained.

8 In the absence of a gold complex and tributylphosphine or in the presence of tributylphosphine alone as catalyst, no reaction was observed under the same conditions. See also ref. 3.

9 Although other hydrosilanes were also tested, use of phenyldimethylsilane **2** gave good results in most cases.

10 R. C. Larock, *Comprehensive Organic Transformations*, Wiley, New York, 2nd edn., 1999, pp. 1089–1096.