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An unprecedented catalytic reaction using gold(I) complexes

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Abstract

This paper describes an unprecedented catalytic reaction using Au(I) complexes. Au complexes efficiently catalyze dehydrogenative dimerization of trialkylstannanes. Catalytic activity of the Au(I) complex toward dehydrogenative dimerization of the trialkylstannane is extremely high (0.1 mol%, 48 h) comparable to that of Pd catalysts. The synthetic generality of this reaction was demonstrated for the reaction using tributyl-, trioctyl-, triphenylstannane. © 1999 Elsevier Science Ltd. All rights reserved.

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Extensive studies have been made, undertoken, for the synthesis and characterization of gold(I) complexes; however, utilization of these complexes as homogeneous catalysts in organic and organometallic syntheses is rare.[1–9] Although the ability of many organometallic catalysts is attributed to their redox features, Au complex catalysts were used as a Lewis acid or even as a base in some successful cases.[5–9] We describe here a new strategy for the design of a catalytic reaction using an Au complex and this catalytic reaction is comparable to Pd catalysts in efficiency.

We recently reported that the metathesis reaction of copper(I) salts and organosilicon compounds such as alkynyl-, aryl-, hydrosilanes, disilanes proceeds smoothly in an aprotic polar solvent.[10–14] Thus, we applied our findings on these reactions between Cu(I) and hydrosilane to an Au(I) complex.[10]

We first tested the reactivity of an Au(I) complex for hydrosilanes; however, the reaction between hydrosilanes and various Au(I) complexes did not occur at room temperature. We next investigated the reaction between an Au(I) complex and hydrostannane. Hydrostannanes, which readily react with various organometallic compounds, are a good probe for the survey of the catalytic reaction using an Au(I) complex.[15]

In THF solution, a stoichiometric reaction between tributylstannane **1a** and methyl(triphenylphosphine)gold(I) **2a** gave tributylmethylstannane **3** (9%) and hexabutyldistannane **4a** (54%) at room temperature for 14 h (Eq. 1).[16] The formation of a metathesis product **3** and

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Table 1
Dehydrogenative dimerization of a trialkylstannane by a gold(I) catalyst

Entry[a]	R	Catalyst	Conditions	Yield of **4** / %[b]
1	**1a**, Bu	$AuClPPh_3$ **2b**, 1 mol%	neat, r. t., 18 h	**4a**, 99
2	**1a**, Bu	$AuClPPh_3$ **2b**, 1 mol% + PPh_3, 2 mol%	neat, r. t., 4 h	**4a**, 92
3	**1a**, Bu	$AuClPPh_3$ **2b**, 0.1 mol%	neat, r. t., 72 h	**4a**, 96
4	**1a**, Bu	$AuClPPh_3$ **2b**, 0.1 mol% + PPh_3, 0.2 mol%	neat, r. t., 46 h	**4a**, 94
5	**1b**, Ph	$AuClPPh_3$ **2b**, 1 mol%	CH_2Cl_2[c], r. t., 8 h	**4b**, 91
6	**1c**, Oct	$AuClPPh_3$ **2b**, 0.1 mol% + PPh_3, 0.2 mol%	neat, r. t., 13 h	**4c**, 94

[a] A mixture of a trialkylstannnane and a gold(I) catalyst was stirred under nitrogen.
[b] Isolated yield otherwise noted.
[c] Reaction was carried out in dry dichloromethane (1.0 M).

a dehydrogenative product **4a** suggested that the Au complex mediated the reaction between the hydrostannane and the Au(I) complex. Unfortunately, we could detect no signal which should be attributed to intermediates such as an oxidative addition product of the trialkylstannane to the Au(I) complex, in the ^{31}P and ^{1}H NMR spectra during the reaction.

$$\underset{\mathbf{1a}}{Bu_3SnH} \xrightarrow[\text{THF, r. t., 14 h}]{MeAuPPh_3\ \mathbf{2a}} \underset{\mathbf{3},\ 9\%}{Bu_3Sn{-}Me} + \underset{\mathbf{4a},\ 54\%}{Bu_3Sn{-}SnBu_3} \tag{1}$$

Next, we found that less than a 1 mol% amount of the gold(I) complex catalyzed dehydrogenation of hydrostannanes to give the corresponding distannanes in good yield (Eq. 2, Table 1). To a catalytic amount of chloro(triphenylphosphine)gold(I), tributylstannane was added under nitrogen at room temperature.[17] The reaction mixture turned red, and gentle evolution of hydrogen gas was observed. After being stirred for 18 h, tributylstannane disappeared at room temperature. The resultant reaction mixture was distilled directly from the reaction vessel to give analytically pure hexabutyldistannane (99%) (entry 1).

$$\underset{\mathbf{1}}{2\ R_3SnH} \xrightarrow[-\ H_2]{\text{Au catalyst } \mathbf{2}} \underset{\mathbf{4}}{R_3Sn{-}SnR_3} \tag{2}$$

Addition of 2 mol% of triphenylphosphine accelerates the reaction rate about 1.5 times faster than 1 mol% of the Au complex alone (entry 2), although the sole use of triphenylphosphine without a gold complex did not catalyze the reaction. This result shows a clear contrast to the rate retardation of reductive elimination of alkyl ligands from the Au(III) complex in the presence of an additional ligand.[3] Without an additional phosphine, insoluble materials were precipitated at the end of the reaction; nevertheless, a clear red solution was maintained during the reaction using an additional ligand. This result further shows that use of the ligand in excess is important to avoid inactivation of the active catalytic species. A smaller amount of the gold(I) complex (0.1 mol%) also worked well as a catalyst for the reaction although longer reaction time was needed. Trioctyl- and triphenylstannane also converted to the corresponding distannanes (entry 5, 6) in good yields. A typical procedure is as follows.[18] All operations were conducted under argon or nitrogen atmosphere. A gold complex **2b** (24.7 mg, 0.050 mmol) was placed in the reaction tube which was evacuated and filled with argon or nitrogen again. Freshly distilled tributylstannane **1a** (bp 80°C, 0.4 mmHg, 1.46 g, 5.0 mmol) was injected with a syringe into the reaction tube at room temperature. The mixture turned red. After stirring for 18 h, the reaction mixture was distilled directly to give analytically pure hexabutyldistannane **4a** (bath temp. 195–210°C, 0.26 mmHg, 1.44 g, 2.48 mmol, 99%) as a colorless oil. IR (neat) 2930, 1464 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ: 0.79–1.12 (m, 30H), 1.21–1.68 (m, 24H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 10.0 (J=241.2, 39.1 Hz), 13.7, 27.5 (J=52.3 Hz), 30.6; ^{119}Sn NMR (100.6 MHz, $CDCl_3$) δ: −84.5; MS *m/z*: (relative intensity), 582 (M^+, 1), 525 ($M^+-C_4H_9$, 15). Anal. calcd for $C_{24}H_{54}Sn_2$: C, 49.68; H, 9.38. Found: C, 49.81; H, 9.39.

Although utilization of a trialkylstannane as a hydride source in the Cu(I) salt-promoted reduction has been reported, the results of Au(I) complexes reveal a striking contrast to the case of the reaction between a Cu(I) salt and a trialkylstannane.[19,20] The catalytic activity of the Au(I) complex for the dehydrogenative dimerization of trialkylstannanes is comparable to that of a Pd catalyst.[21] Although some Sn–Sn bond-forming methods are known, little work on the use of transition metal catalysts has been published.[15,22] The results presented above show that the Au(I) complex is a practical catalyst for the synthesis of distannanes, which are useful reagents for organic synthesis.[22]

We have described here a strategy for the design of a catalytic reaction using Au(I) complexes. We speculate that a redox cycle between the Au(I) and Au(III) species would play an important role in the reaction; however, further studies are needed to determine the exact reaction pathway. The results shown in this paper indicate that appropriately designed Au catalysts would also be useful for various synthetic reactions.

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References

1. Grohmann, A.; Schmidbaur, H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Wardell, J. L., Eds.; Pergamon: New York, 1995; Vol. 3, pp. 1–56.
2. Komiya, S. *Yuki Gosei Kagaku Kyokaishi* **1988**, *46*, 1195–1204.
3. Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255–7265.
4. Komiya, S.; Shibue, A. *Organometallics* **1985**, *4*, 684–687.
5. Teles, J. H.; Brode, S.; Chabanas, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1415–1418.
6. Xu, Q.; Imamura, Y.; Fujiwara, M.; Souma, Y. *J. Org. Chem.* **1997**, *62*, 1594–1598.
7. Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405–6406.
8. Komiya, S.; Sone, T.; Usui, Y.; Hirano, M.; Fukuoka, A. *Gold Bull.* **1996**, *29*, 131–136.
9. Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729–3731.
10. Ito, H.; Ishizuka, T.; Arimoto, K.; Miura, K.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 8887–8890.
11. Ito, H.; Ishizuka, T.; Tateiwa, J.; Sonoda, M.; Hosomi, A. *J. Am. Chem. Soc.* **1998**, *120*, 11196–11197.

12. Ito, H.; Ishizuka, T.; Okumura, T.; Yamanaka, H.; Tateiwa, J.; Sonoda, M.; Hosomi, A. *J. Organomet. Chem.* **1998**, *574*, 102–106.
13. Ito, H.; Sensui, H.; Arimoto, K.; Miura, K.; Hosomi, A. *Chem. Lett.* **1997**, 639–640.
14. Ito, H.; Arimoto, K.; Sensui, H.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 3977–3980.
15. Davies, A. G. In *Organotin Chemistry*; VCH: New York, 1997; pp. 203–204 and 239–240.
16. Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140–6148.
17. McAuliffe, C. A.; Parish, R. V.; Randall, P. D. *J. Chem. Soc., Dalton Trans. 1* **1979**, 1730–1735.
18. Hexaphenyldistannane (**4b**): A mixture of a gold complex **2b** (14.8 mg, 0.03 mmol), triphenylphosphine (15.7 mg, 0.06 mmol) and triphenylstannane **1b** (1.05 g, 3.00 mmol, Tokyo Chemical Industry Co., Ltd.) was stirred for 8 h in dry dichloromethane (3.0 ml). Purification by column chromatography (silica gel, chloroform:hexane=1:1) gave hexaphenyldistannane **4b** (955 mg, 1.36 mmol, 91%) as a white solid. IR (KBr) 3060, 1429 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 7.22–7.65 (m, 25H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 128.7 (J=48.7 Hz), 137.4 (J=40.3 Hz), 139.1; ^{119}Sn NMR (100.6 MHz, $CDCl_3$) δ: –145.0. Anal. calcd for $C_{36}H_{30}Sn_2$: C, 61.77; H, 4.32. Found: C, 61.60; H, 4.46. Hexaoctyldistannane (**4c**): A mixture of a gold complex **2b** (24.7 mg, 0.05 mmol), triphenylphosphine (26.2 mg, 0.10 mmol) and trioctylstannane **1b** (2.30 g, 5.00 mmol: Tokyo Chemical Industry Co., Ltd.) was stirred for 13 h. Purification by column chromatography (silica gel, hexane) gave hexaoctyldistannane **4c** (2.15 g, 2.35 mmol, 94%) as a colorless oil. IR (neat) 2925, 1467 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.82–1.10 (m, 30H), 0.82–1.10 (m, 60H), 1.42–1.61 (m, 12H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 10.4 (J=240.0 Hz, J=39.0 Hz), 14.1, 22.7, 28.4 (J=15.8 Hz), 29.3, 29.4, 32.0, 34.6 (J=51.2 Hz); ^{119}Sn NMR (100.6 MHz, $CDCl_3$) δ: –85.3. Anal. calcd for $C_{48}H_{102}Sn_2$: C, 62.89; H, 11.21. Found: C, 62.88; H, 11.49.
19. Lipshutz, B. H.; Ung, C. S.; Sengupta, S. *Synlett* **1989**, 64–66.
20. Reaction of tributylstannane with 0.01 equivalent of both CuCl and triphenylphosphine under similar conditions as in the Au(I)-catalyzed reactions resulted in only a trace amount of hexabutyldistannane.
21. Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257–265.
22. Mitchell, T. N. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 4, pp. 2631–2633.