1594 *J. Org. Chem.* **1997,** *62,* 1594−1598

A New Gold Catalyst: Formation of Gold(I) Carbonyl, $[Au(CO)_n]^+$ ($n = 1, 2$), in Sulfuric Acid and Its Application to Carbonylation of Olefins

Qiang Xu,* Yuki Imamura, Masahiro Fujiwara, and Yoshie Souma*

Osaka National Research Institute, AIST, MITI, 1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan

Received October 28, 1996[⊗]

A new gold catalyst, $[Au(CO)_n]^+$ ($n = 1, 2$), was synthesized by using a facile method from commercial gold(III) oxide, Au_2O_3, in concentrated H_2SO_4, which exhibits high catalytic activity for carbonylation of olefins. The gold monocarbonyl $[Au(CO)]^+$ (**1**) and dicarbonyl $[Au(CO)_2]^+$ (**2**) cations coexist in H_2SO_4 solution, the former of which is much more stable than the latter. Both of the carbonyls show IR spectra of ν_{CO} (2194, 2208 cm^{-1}) higher than that of free CO (2143 cm^{-1}), indicating nonclassical (σ-only) gold−CO bonding. The gold carbonyl complexes coexisting in the concd H_2SO_4 solution exhibit a single resonance in the ^{13}C NMR spectrum at 171 ppm at ambient temperature and pressure, reflecting rapid CO exchange between **1** (164 ppm) and **2** (175 ppm). The nonclassical gold(I) carbonyl solution worked as an excellent catalyst, with which olefins reacted with CO to give *tert*-carboxylic acids in good yields at room temperature and atmospheric pressure. The gold(I) dicarbonyl cation **2** was found to function as an active species for the carbonylation. An olefin−gold(I)−carbonyl complex was proposed as a possible intermediate in the metal carbonyl-catalyzed carbonylation in the strongly acidic medium.

Introduction

A group of the noble metal carbonyl derivatives, named as *nonclassical metal carbonyls* by Strauss[1a] and Aubke,[2a] are subjected to increasing interest. The electron-rich metal carbonyls exhibit characteristic CO valence frequencies in the vibrational spectra at considerably higher wavenumbers relative to the absorption of CO gas (2143 cm^{-1}). In contrast to the "classical" metal carbonyls, in which CO acts as a σ-donor and a π-acceptor, nonclassical metal carbonyls have no significant amount of π-back bonding, resulting in weaker M−C bonds, more unstable compounds, and more reactive CO ligands, expected to be more catalytically active for carbonylation.[1a] Willner first succeeded in the synthesis of $[Au(CO)_2][Sb_2F_{11}]$ crystals by stabilizing the unstable carbonyls with the very weakly coordinating anions $[Sb_2F_{11}]^-$.[3] Thereafter, the nonclassical metal carbonyl cations were isolated successively as $[Cu(CO)_n][AsF_6]$ ($n = 1, 2, 3$),[4] $[Ag(CO)_n][B(OTeF_5)_4]$ ($n = 1, 2, 3$),[1] $[Pt(CO)_4][Pt(SO_3F)_6]$,[5] $[Pt(CO)_4][Sb_2F_{11}]_2$,[6] $[Pd(CO)_4][Sb_2F_{11}]_2$,[6] *cis*-$Pd(CO)_2(SO_3F)_2$,[2a] $[c\text{-}Pd_2(\mu\text{-}CO)_2](SO_3F)_2$,[2b] $[M(CO)_6][Sb_2F_{11}]_2$ (M = Ru or Os),[7] $[Hg(CO)_2][Sb_2F_{11}]_2$ and $[Hg_2(CO)_2][Sb_2F_{11}]_2$.[8] Now, attention is focused on the catalytic activity for carbonylation related to the high reactivity of CO caused by the diminishing M→C π-back-bonding in the nonclassical metal carbonyls.

There have been a large number of reports dealing with the carbonylation of olefins, many of which are catalyzed by metal carbonyls.[9] In Roelen[10] and Reppe[11] reactions, the classical metal carbonyls, such as $Co_2(CO)_8$ and $Ni(CO)_4$, were used to catalyze the carbonylation of olefins to produce aldehydes and carboxylic acids, which needed high temperature and high pressure.[9] Another carbonylation, the Koch reaction, gave tertiary carboxylic acids in strong acids such as H_2SO_4, HF, H_3PO_4, or $BF_3 \cdot H_2O$, in which no metal catalysts were used and high CO pressure was necessary.[12] We previously reported that the addition of Cu(I) and Ag(I) carbonyl catalysts caused the Koch-type reaction to proceed under much milder conditions—at ambient temperature and pressure.[13] Nevertheless, the catalytic properties of the carbonyls of gold, from the same group 11, has not been known for a long period. Despite the wide utilities of Cu, Ag, and other noble metal compounds as heterogeneous or homogeneous catalysts, gold and its compounds have been generally regarded as the least useful of the noble metals as catalysts.[14]

This paper presents the gold(I) carbonyl in concentrated H_2SO_4 as a new member in the meager family[15,16] of gold catalysts, which catalyzes the carbonylation of

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

[1] (a) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003. (b) Rack, J. J.; Moasser, B.; Gargulak, J. D.; Gladfelter, W. L.; Hochheimer, H. D.; Strauss, S. H. *J. Chem. Soc., Chem. Commun.* **1994**, 685. (c) Hurlburt, P. K.; Rack, J. J.; Dec, S. F.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1993**, *32*, 373. (d) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277.

[2] (a) Wang, C.; Willner, H.; Bodenbinder, M.; Batchelor, R. J.; Einstein, F. W. B.; Aubke, F. *Inorg. Chem.* **1994**, *33*, 3521. (b) Wang, C.; Bodenbinder, M.; Willner, H.; Rettig, S.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1994**, *33*, 779.

[3] (a) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972. (b) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.

[4] Rack, J. J.; Webb, J. D.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 277.

[5] Hwang, G.; Bodenbinder, M.; Willner, H.; Aubke, F. *Inorg. Chem.* **1993**, *32*, 4667.

[6] Hwang, G.; Wang, C.; Aubke, F.; Willner, H.; Bodenbinder, M. *Can. J. Chem.* **1993**, *71*, 1532.

[7] Wang, C.; Bley, B.; Balzer-Jöllenbeck, G.; Lewis, A. R.; Siu, S. C.; Willner, H.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2071.

[8] (a) Bodenbinder, M.; Balzer-Jöllenbeck, G.; Willner, H.; Batchelor, R. J.; Einstein, F. W. B.; Wang, C.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 82. (b) Willner, H.; Bodenbinder, M.; Wang, C.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1189.

[9] For leading references, see: (a) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (b) Falbe, J., Ed. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980.

[10] Roelen, O. (to Ruhrchemie, A. G.), German Patent no. 849,548, 1938.

[11] Reppe, W. *Liebigs ann. Chem.* **1953**, *582*, 1.

[12] Koch, H. *Brennst. Chem.* **1955**, *36*, 321.

[13] (a) Souma, Y.; Sano, H. *J. Org. Chem.* **1973**, *38*, 3633. (b) Souma, Y.; Sano, H.; Iyoda, J. *J. Org. Chem.* **1973**, *38*, 2016.

[14] Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, The Netherlands, 1978.

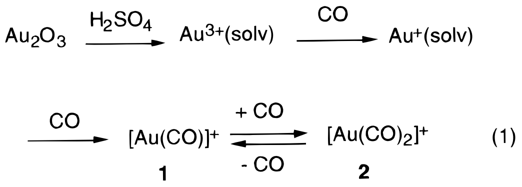
S0022-3263(96)02012-9 CCC: $14.00

olefins under atmospheric pressure and room temperature to produce *tert*-carboxylic acids in high yields. The characteristics of the gold(I) carbonyl complexes and its relation to catalytic activity in carbonylation is described. A plausible mechanism involving olefin–metal–carbonyl complexes as intermediates is proposed.

Results and Discussion

Formation and Characteristics of Gold(I) Carbonyl Complexes in H_2SO_4 Solution. Since most of the gold compounds are stabilized by coordinative anions such as CN^- or Cl^-, which are more strongly coordinating than CO, the first candidate as the starting material for preparing the gold(I) carbonyl complex is metallic gold. By oxidizing metallic gold with the strong oxidizer SO_3 in H_2SO_4, CO is absorbed to form the Au(I) carbonyls. However, it needs almost one day with vigorous stirring to dissolve the gold powder, and this procedure has a disadvantage for catalytic purposes that H_2O must be added into the resulting solution to absorb excess SO_3. Another approach is to reduce $HAuCl_4$ using H_2SO_3, and neutralize it with NaOH to form AuOH precipitates, which absorb CO to give the gold(I) carbonyls in concd H_2SO_4. The strongly coordinating Cl^- anion, which prevents CO from coordination, must be completely washed out from the AuOH precipitates in order to obtain high catalytic activity.

We have found a remarkably facile synthetic method for gold(I) carbonyls suitable for the catalytic reaction: gold(III) oxide, Au_2O_3, is reduced by CO to form $[Au(CO)_n]^+$ (n = 1, 2) in one step in concentrated H_2SO_4 solution (eq 1). The dark brown color of Au^{3+} in H_2SO_4 solution fades away during the CO uptake, and a clear solution is obtained in about 1 h. Directly exposing gold(III) oxide to CO causes it to be reduced to gold metal. The CO/Au stoichiometric ratio, the number of moles of absorbed CO per mole of Au, is 1.65 at 26.5 °C when the concentration of Au^+ in 96% H_2SO_4 is 0.1 M.



$$Au_2O_3 \xrightarrow{H_2SO_4} Au^{3+}(solv) \xrightarrow{CO} Au^{+}(solv)$$

$$\xrightarrow{CO} \underset{\mathbf{1}}{[Au(CO)]^+} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \underset{\mathbf{2}}{[Au(CO)_2]^+} \qquad (1)$$

The gold(I) monocarbonyl $[Au(CO)]^+$ (**1**) and the gold(I) dicarbonyl $[Au(CO)_2]^+$ (**2**) coexist in the above solution, exhibiting IR absorptions at 2194 and 2208 cm^{-1}, respectively (Figure 1a). Both of the CO stretching frequencies ν_{CO} are higher than that of free CO, indicating insignificant amount of π-back bonding.[1] Although the gold(I) dicarbonyl $[Au(CO)_2]^+$ was predicted to be more stable than the gold(I) monocarbonyl by an *ab initio* calculation carried out by Veldkamp and Frenking,[17] **1** was found to be more stable than **2** in concd H_2SO_4 solution, probably due to a stabilization effect from the coordination of the solvent. The unstable **2** readily releases one CO ligand to form **1** upon evacuation of the reaction flask, while the IR peak of **1** at 2194 cm^{-1} remains unchanged even after continuous evacuation over 24 h (Figure 1b).

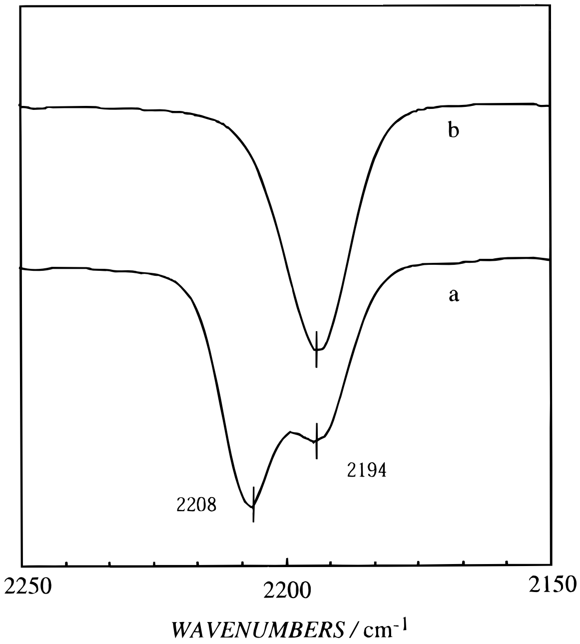


Figure 1. Infrared spectra of 0.1 M $[Au(CO)_n]^+$ (n = 1, 2) in 96% H_2SO_4 solution at room temperature. (a) At pressure of 1 atm CO. (b) After evacuating reaction flask with a rotary pump for 1 h.

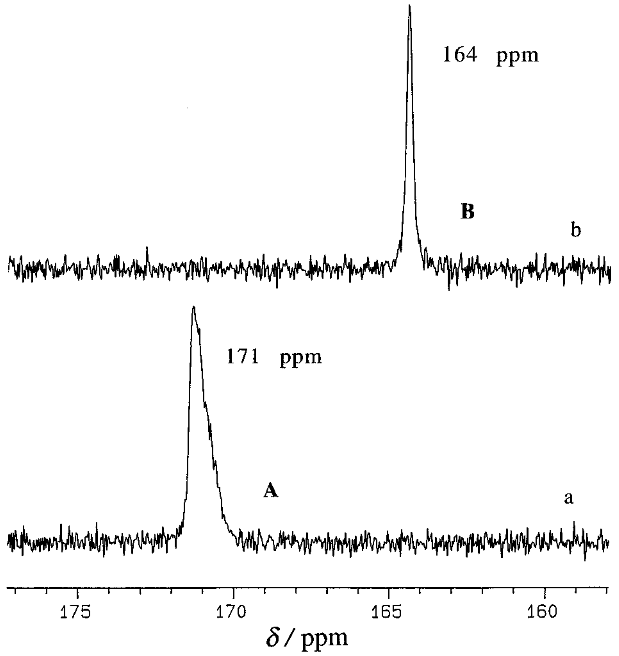


Figure 2. ^{13}C NMR spectra of 0.1 M $[Au(CO)_n]^+$ (n = 1, 2) in 96% H_2SO_4 solution at room temperature. (a) At pressure of 1 atm CO. (b) After evacuating reaction flask with a rotary pump for 1 h.

Two resonances appear in the ^{13}C NMR spectrum of the gold(I) carbonyls in concd H_2SO_4 solution at ambient temperature and pressure, a weak signal at 125 ppm due to $^{13}CO_2$, and a very intense resonance (**A**) at 171 ppm, respectively (Figure 2a). After removing the ambient CO by evacuation, the solution gives a single peak (**B**) at 164

---

(15) For example, for homogeneous gold catalysts, see: (a) Hughes, P. F.; Smith, S. H.; Olson, J. T. *J. Org. Chem.* **1994**, *59*, 5799. (b) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333. (c) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.

(16) For example, for heterogeneous gold catalysts, see: (a) Qiu, S.; Ohnishi, R.; Ichikawa, M. *J. Phys. Chem.* **1994**, *98*, 2719. (b) Fukushima, T.; Nikuta, T.; Shindo, K.; Hattori, Y. *Catal. Sci. Tecknol.* **1990**, *1*, 493. (c) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, 405. (d) Cant, N. W.; Hall, W. K. *J. Phys. Chem.* **1971**, *75*, 2914.

(17) Veldkamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613.

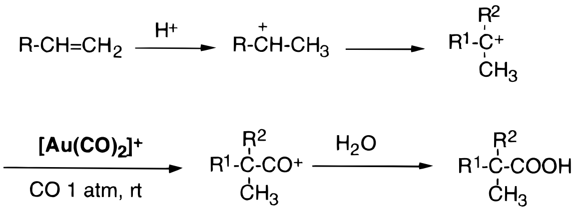
Table 1. Gold(I) Carbonyl-Catalyzed Carbonylation of Olefins in Concentrated H_2SO_4[a]

olefin	*tert*-carboxylic acid	yield/%[b]
1-hexene	2,2-dimethylpentanoic	53
	2-methy-2-ethylbutanoic	25
	others	2
1-octene	2,2-dimethylheptanoic	42
	2-methyl-2-ethylhexanoic	22
	2-methyl-2-propylpentanoic	10
	others	5
1-decene	2,2-dimethylnonanoic	33
	2-methyl-2-ethyloctanoic	16
	2-methyl-2-propylheptanoic	12
	2-methyl-2-buthylhexanoic	5
	others	4
cyclohexene	1-methycyclopentanecarboxylic	56

[a] Au_2O_3/olefin = 0.5 mmol/5 mmol, 96% H_2SO_4 10 mL, CO 1 atm, rt. [b] Based on olefin.

ppm (Figure 2b), which is attributed to **1**. An equilibrium process between **1** and **2**, which undergoes rapid CO exchange on the NMR time scale, would account for the single resonance **A** (eq 1). This observation indicates the CO exchange between **1** and **2** is much faster in H_2SO_4 than in HSO_3F. According to Willner, two signals corresponding to gold(I) monocarbonyl (162 ppm) and gold(I) dicarbonyl (174 ppm) were observed in HSO_3F at 17 °C, indicating slow exchange.[3a] This finding suggests that the weakly coordinating anion SO_3F^- produces a greater stabilization of $[Au(CO)_2]^+$. The chemical shift of **2** can be calculated to be 175 ppm by taking into consideration the CO/Au ratio. Both the high field shifts of **1** and **2** from 184 ppm (free CO) reflect insignificance of gold to carbon π-back donation, in agreement with the vibrational observations described above.[1,3]

Carbonylation of Olefins with the Gold(I) Carbonyl Catalyst in H_2SO_4 Solution. To our knowledge, very few gold catalysts have been reported so far.[14-16] This paper reveals that the nonclassical gold(I) carbonyl works as an excellent catalyst, with which olefins react readily with CO to produce *tert*-carboxylic acids in high yields at atmospheric pressure and room temperature (eq 2). The present work is the first application of gold(I) carbonyls to organic syntheses.



$$\text{R-CH=CH}_2 \xrightarrow{H^+} \text{R-}\overset{+}{\text{C}}\text{H-CH}_3 \longrightarrow \text{R}^1\text{-}\underset{\text{CH}_3}{\overset{\text{R}^2}{\text{C}^+}}$$

$$\xrightarrow[\text{CO 1 atm, rt}]{[Au(CO)_2]^+} \text{R}^1\text{-}\underset{\text{CH}_3}{\overset{\text{R}^2}{\text{C}}}\text{-CO}^+ \xrightarrow{H_2O} \text{R}^1\text{-}\underset{\text{CH}_3}{\overset{\text{R}^2}{\text{C}}}\text{-COOH} \quad (2)$$

In strong acid, the olefin is protonated to form a carbocation intermediate, which isomerizes to *tert*-carbocation prior to the carbonylation, and consequently tertiary carboxylic acids are formed.[13] Table 1 summarizes the results of the reaction of olefins with CO under atmospheric pressure and room temperature in 96% H_2SO_4, catalyzed by the gold(I) carbonyls. Without gold(I) carbonyl catalyst, olefins convert to the carboxylic acids in a lower yield than 10% under atmospheric pressure of CO, due to the oligomerization as a competing reaction. The addition of gold(I) carbonyl catalyst drastically enhances the rate of carbonylation, which is completed in 1−2 h, and *tert*-carboxylic acids are formed in high yields.

The influence of H_2SO_4 concentration on the formation of gold carbonyls and on the carbonylation of 1-hexene were studied. The results are shown in Figure 3. With the decrease of H_2SO_4 concentration, the ratio of CO/Au decreases and reaches 1.0 at 75% H_2SO_4. This indicates that the equilibrium of eq 1 shifts to the left side with the decrease in H_2SO_4 concentration. At the same time, the yield of *tert*-C_7 carboxylic acid decreases with the decrease of CO/Au. The dependence of carbonylation on the H_2SO_4 concentration is obviously parallel to that of the formation of unstable Au(I) dicarbonyl ion $[Au(CO)_2]^+$. This finding leads to a conclusion that the gold dicarbonyl **2** but not the monocarbonyl **1** is the active species for the carbonylation. No carbonylation occurs at H_2SO_4 concentration below 75%. At H_2SO_4 concentrations of 70−75%, the monocarbonyl is first formed, followed by slow reduction to gold metal. The gold(III) oxide Au_2O_3 is reduced directly to gold metal by CO in dilute H_2SO_4 solution.

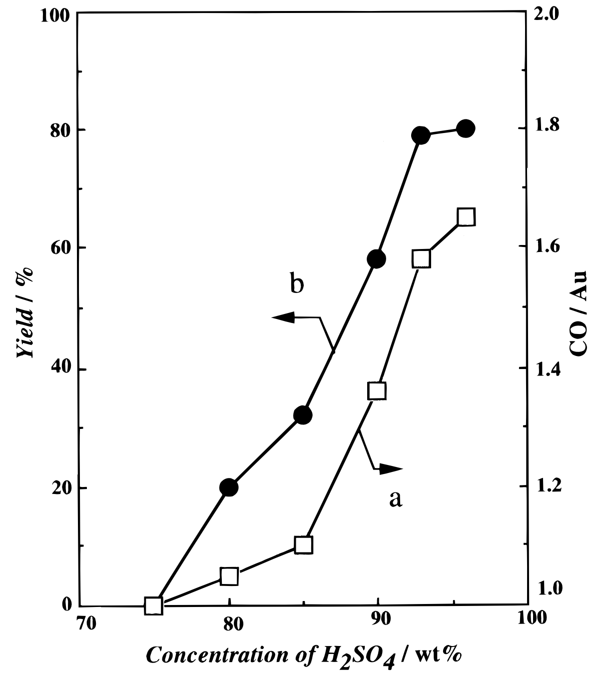


Figure 3. Dependence on H_2SO_4 concentration of (a) the ratio of CO/Au of 0.1 M $[Au(CO)_n]^+$ (n = 1, 2); (b) the yields of *tert*-carboxylic acids from 1-hexene of 5 equiv based on Au^+; at room temperature.

The discovery of gold(I) carbonyl catalyst provides us with a chance to shed light on the relationship between the property of the metal−CO bond and the catalytic activity by comparing the results of the copper(I), silver(I), and gold(I) carbonyls. The conversion of 1-hexene to *tert*-C_7 carboxylic acid ranges from 80 to 96% with the Cu(I), Ag(I), and Au(I) carbonyl catalysts.[13,18] It is worthwhile to note that the group 11 metal carbonyl catalysts have comparable catalytic activities, despite the large difference in the ratios of CO/M, which are 1.35, 0.16, and 1.65 for M = Cu, Ag, and Au, respectively, in 96% H_2SO_4.[19] The behavior can be understood by considering the properties of the metal−carbon bondings, as follows. Armentrout and co-workers[20] estimated metal−carbonyl bond energies for the gas phase complex ions $[Cu(CO)_n]^+$ and $[Ag(CO)_n]^+$ (n = 1−4): $(CO)_xCu^+CO$ bond

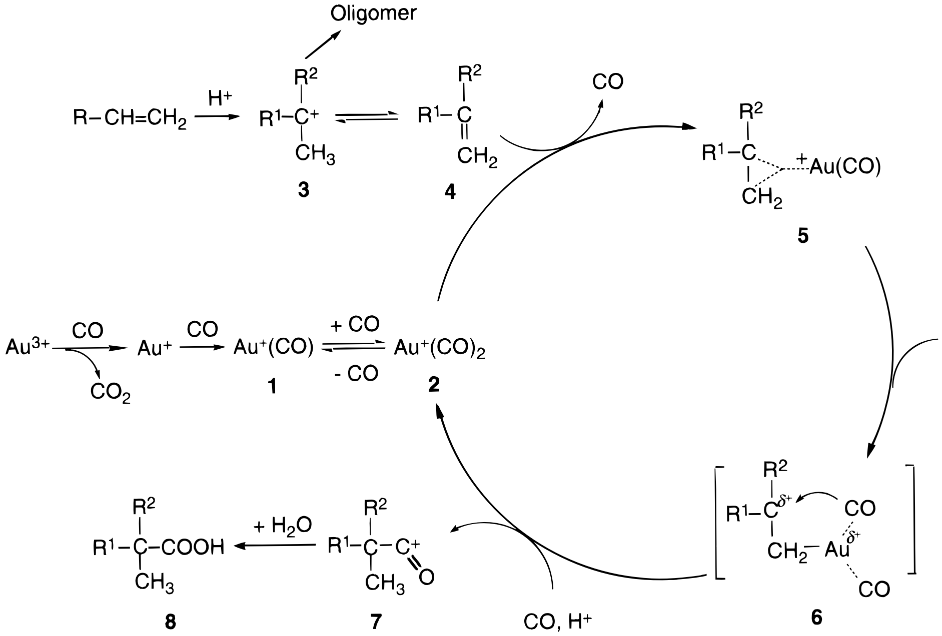
---

(18) Souma, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1717.

(19) (a) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* **1976**, *15*, 968. (b) Souma, Y.; Sano, H. *Chem. Lett.* **1973**, 1059.

(20) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 4071.

Scheme 1



energies at 0 K of 36, 41, 18, and 13 kcal/mol for $x = 0$, 1, 2, and 3, respectively; $(CO)_xAg^+CO$ bond energies at 0 K of 21, 26, 13, and 11 kcal/mol for $x = 0$, 1, 2, and 3, respectively. Veldkamp and Frenking[17] calculated (MP2 level of theory) $(CO)_xAg^+CO$ bond energies of 21, 27, and 12 kcal/mol for $x = 0$, 1, and 2, respectively; $(CO)_xAu^+$-CO bond energies of 45, 50, and 9 kcal/mol for $x = 0$, 1, and 2, respectively. The calculations predicted the stability of the metal carbonyls to be in the order of Ag < Cu < Au. In the present work, we found that both of the Cu(I) and Au(I) monocarbonyls remain unchanged after continuous evacuation for one day, whereas no Ag(I) carbonyls survive even after brief evacuation for several seconds. These observations indicate the existence of the stable species, which corresponds to the ratio of $CO/M > 1$ for M = Cu or Au, and reflect the absence of the stable Ag(I) monocarbonyl, which accounts for the ratio of $CO/Ag < 1$ in concd H_2SO_4 at room temperature. The disadvantage of the low CO absorption by Ag^+ is compensated for by the high activity arising from the weak Ag–CO bond. The relationship between the property of the metal–CO bond and the catalytic activity, as discussed above, may also aid our understanding of heterogeneous reactions in which nonclassical metal carbonyls may play important roles, such as NO reduction by CO with zeolites ion-exchanged by group 11 metal ions.[16a] Furthermore, the nonclassical carbonyls may also provide new insight into the carbonylation reactions that are catalyzed by classical metal carbonyls.

The mechanism of the carbonylation is of great interest. The aspect of reaction in acidic media should be much different from that of the usual metal–carbonyl-catalyzed carbonylation in mild media, such as Roelen or Reppe reaction.[9] We propose a plausible mechanism of the metal–carbonyl-catalyzed carbonylation of olefin in strongly acidic media, as shown in Scheme 1. When olefin is added to the strong acid H_2SO_4, it forms a carbocation, which isomerizes to the carbocation **3**. An equilibrium process exists between the carbocation **3** and the isomerized olefin **4**, a part of which oligomerizes to give higher weight molecules in a competitive reaction. One of the two CO ligands of the gold dicarbonyl **2** is replaced by **4**, which coordinates to Au to form π complex **5**. Similar organometallic ions like ethylene-, norbornylene-, and cyclohexylenemercurium ions, which were prepared from Hg^{2+}, the isoelectronic ion of Au^+, have been observed by Olah et al. in superacidic media.[21] Indeed, at the starting point of reaction where olefin is added into the concd H_2SO_4 solution containing the gold(I) carbonyl catalyst, CO evolution was first observed, which is followed by CO consumption, reflecting the onset of carbonylation. In the complex **5**, since the tertiary and primary carbons are unsymmetrically bridged, the relatively positive charge should be located at the tertiary carbon. The coordination of the next CO to Au assists the migration of CO to the partly positively charged tertiary carbon via the intermediate **6**, which transforms to the acyl cation **7**. The acyl cation **7** consequently reacts with water to give the carboxylic acid.

As described above, the solution containing only the gold monocarbonyl **1** has no catalytic activity, and the catalytic carbonylation of olefin proceeds only under conditions when the gold dicarbonyl **2** exists in the H_2SO_4 solution (Figure 3). The findings can be interpreted by the proposed reaction mechanism. At lower concentration of H_2SO_4, the solvent has more strongly coordinating ability. In a H_2SO_4 solution of low concentration, the coordinating solvent molecule bonding to the gold(I) monocarbonyl inhibits the second CO ligand from bonding to gold to form the gold(I) dicarbonyl complex. The tightly bound solvent molecule and CO ligand result in the lack of the formation of the olefin–gold complex. On the other hand, in the concd H_2SO_4 solution having lower coordinating ability, the gold dicarbonyl complex is formed, and the second ligand of the unstable complex is so weakly bound that is easily replaced by olefin to form the olefin–gold(I)–carbonyl complex, via which carbonylation proceeds.

In summary, we have found a remarkably facile one-step procedure to form the gold(I) carbonyls, $[Au(CO)_n]^+$ ($n = 1$, 2) from gold(III) oxide and CO in concentrated H_2SO_4. IR and ^{13}C NMR spectra indicate an insignificant

---

[21] (a) Olah, G. A.; Yu, S. H. *J. Org. Chem.* **1975**, *40*, 3638. (b) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1973**, *95*, 6067. (c) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1971**, *93*, 2320. (d) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1971**, *93*, 1261.

amount of π-back bonding in the gold(I) carbonyls. ^{13}C NMR spectra also exhibit an equilibrium process between the mono- and dicarbonyl cations, which undergo rapid CO exchange in the concd H_2SO_4 solution at room temperature. The nonclassical gold(I) carbonyl was applied for the first time to an organic reaction as a catalyst, in which olefins react with CO to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure. It has been found that the catalytic carbonylation of olefin proceeds only under such conditions that the unstable gold dicarbonyl exists in the H_2SO_4 solution.

Experimental Section

Reagents. Commercial reagents Au_2O_3 (Rare Metallic Co.), H_2SO_4 (96%, Kanto Chemical Co.), CO (Nippon Sanso), D_2SO_4 (96% in D_2O, ISOTEC Inc.), and ^{13}CO (^{13}C enrichment 99%, ICON) were used for the preparation and characterization of gold(I) carbonyls.

Reagents (special grade, Wako Pure Chemical) 1-hexene, 1-octene, 1-decene, and cyclohexene were used for the carbonylation without further purification.

Preparation of Au(I) carbonyls was performed with a 200 mL three-necked flask connected to a carbon monoxide gas buret, similar to the equipment used in the previous works.[13,19] The apparatus containing 221 mg (0.5 mmol) of Au_2O_3 and 10 mL of 96% H_2SO_4 was evacuated by a rotary pump to remove air, and then carbon monoxide was introduced from the gas buret. The mixture of Au_2O_3 and H_2SO_4 was stirred vigorously. Carbon monoxide was absorbed by gold(I) ion in about 60 min.

Characterization of Au(I) Carbonyls. The infrared spectra were obtained on thin films between two silicon discs on a JASCO FT/IR-230 spectrometer. ^{13}C NMR spectra were obtained on a JEOL JNM-A500 spectrometer operating at 125.65 MHz. Liquid samples were contained in sample tubes of 5 mm o.d., in which coaxial inserts of external reference $^{13}CH_3OH$ were placed. The solvent, D_2SO_4, was used as a lock. ^{13}C-Enriched CO was used for ^{13}C NMR measurements. Chemical shifts are given in δ units (parts per million) downfield from tetramethylsilane.

Carbonylation of olefins was carried out with a similar method to that described in the previous papers.[13] From a syringe, 5 mmol of olefin was added dropwise during 60 min to the gold(I) carbonyl solution. Reaction was finished in 1−2 h, and the reaction mixture was poured over ice−water. The products were extracted by hexane and analyzed by GC, NMR, and IR.

Identification of 2,2-dimethylpentanoic, 2-methy-2-ethylbutanoic, 2,2-dimethylheptanoic, 2-methyl-2-ethylhexanoic, 2-methyl-2-propylpentanoic, 2,2-Dimethylnonanoic, 2-methyl-2-ethyloctanoic, 2-methyl-2-propylheptanoic, 2-methyl-2-buthylhexanoic, and 1-methycyclopentanecarboxylic acids was carried out by comparison of retention times and “spiking” with authentic samples. The authentic samples were prepared by the carbonylation of olefins catalyzed by the Cu(I) carbonyl catalyst.[13]

JO9620122